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INTRAMOLECULAR EFFECTS OF METAL COORDINATION
ON THE PHOTOCHEMISTRY OF KETONES

By

Rosemary Bartoszek

A DISSERTATION

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ABSTRACT

INTRAMOLECULAR EFFECTS OF METAL COORDINATION ON THE PHOTOCHEMISTRY OF KETONES

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The photoprocesses of pyridyl ketones coordinated to rhenium(I) and ruthenium(II) metal complexes were investigated. The triplet photoreduction reaction of the pyridyl ketone was used to monitor the reaction from the upper excited state. Irradiation into the ketone chromophore did not always lead to photoreduction from the ligand excited state. In addition to decay from the ground state, additional decay pathways to lower lying metal-metal (LF) and metal to ligand charge transfer (MLCT) excited states are also present. When pyridyl ketone photoreduction was observed, it was possible to determine the rate of this internal conversion.

Type II fragmentation was not observed for the bromotricarbonyl-rhenium(I) pyridyl ketone complexes. There is a decreased ability for light absorption by the pyridyl ketone carbonyl chromophore. This is evidenced by intense metal derived transitions overlapping the pyridyl ketone n, π^* transition in the absorption spectra. Complex decomposition occurs before a measurable amount of product formation.

Type II fragmentation was observed for the pyridyl ketone pentaammineruthenium(II) complexes. A decreased ability to absorb

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1. *Journal of the American Medical Association*, 1997; 277: 103-107.
 2. *Journal of the American Medical Association*, 1997; 277: 108-112.
 3. *Journal of the American Medical Association*, 1997; 277: 113-117.

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light directly into the carbonyl chromophore lowers the Type II fragmentation efficiency. The ϕ_{II} for the pyridyl ketone hydrochloride salts are comparable to the ϕ_{II} for the ruthenium(II) complexes when corrections for light absorption are made. This suggests that with coordination of the lone electron pair of the pyridyl nitrogen, the same effects operate on the 1,4-biradical. Ligand photosubstitution occurs only with the meta pyridyl ketone pentaammineruthenium(II) complexes from the LF excited state. Side reactions, among them complex decomposition, compete with the intermolecular photoreduction and the rate of decay from the upper excited state cannot be quantitatively determined. The lifetime data for the complexes and corresponding hydrochloride salts were used to determine a rate of less than 10^8 sec^{-1} for internal conversion to the lower energy excited states.

To my parents, Aloisius and Frances
Bartoszek
and my husband, Roman.

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INTRODUCTION

Electronic Transitions in Organometallic Complexes

The origin of excited state behavior exhibited by a transition metal complex containing organic ligands lies in the interaction of the three types of electronic transitions illustrated¹ in Figure 1. The highest energy transitions are the internal ligand (IL) or intra-ligand (LL) transitions involving only ligand orbitals and in general are almost unaffected by metal coordination. As a result, the emission and other excited state behavior are often very similar to that of the uncoordinated ligand.¹ The lowest energy ligand field (LF) or d-d transitions are derived from the metal d orbitals and are mainly localized on the central metal. These energy levels are relatively insensitive to solvent polarity and ligand substituents.^{2,3} Intermediate in energy are the metal-to-ligand or ligand-to-metal charge transfer (MLCT or LMCT) transitions whose occurrence depends upon relative energies of filled orbitals. MLCT transitions can be expected only when the ligands possess low-lying empty orbitals and the metal ion has filled orbitals lying higher than the highest filled ligand orbitals. The best examples are complexes containing CO, CN or aromatic amines as ligands.⁴ In contrast to the LF transitions, these transitions are extremely sensitive to solvent polarity and the nature of the organic ligand. The transition metal and the nature of the ligands together determine the relative energies of these three transitions.

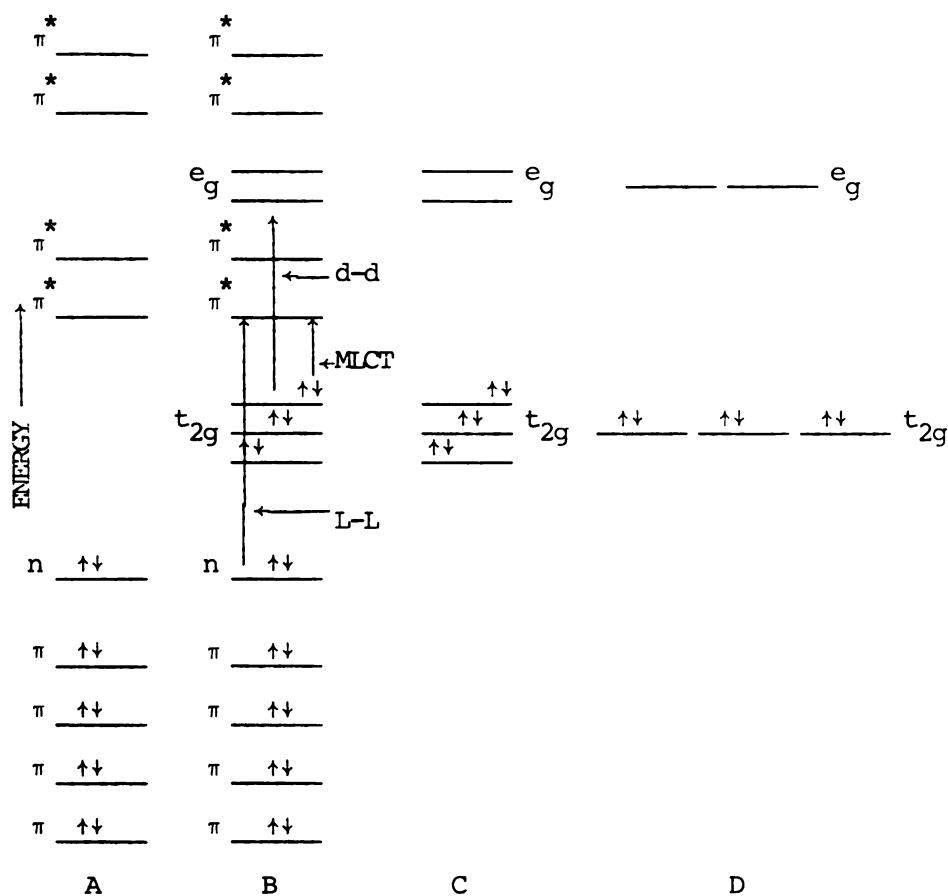


Figure 1. Simplified molecular orbital diagram of a pentaammineruthenium(II) pyridyl ketone complex: A. Pyridyl ketone orbitals. B. Orbitals resulting from the mixing of metal and antibonding ligand orbitals. C. Metal orbitals in the presence of an octahedral field. D. Crystal field approximation of ruthenium(II) 4d orbitals.

Organometallic Photochemistry

Prior to 1955, organometallic photochemical studies consisted mainly of investigations of isolated cases and little attempt was made to explain the quantitative observations in terms of specific excited state behavior.⁵ In 1968, Crosby⁶ carried out fundamental

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spectroscopic studies on Ru^{2+} , Co^{3+} , Os^{2+} , Ir^{3+} , Rh^{3+} and Pt^{4+} complexes having π -conjugated ligands. Many of these d^6 metal ion complexes were found to be highly luminescent, photochemically stable materials with potential applications in electrooptical and laser devices. Knowledge and understanding of organometallic complexes at that time was limited and summarized in reviews by Endicott,⁷ Adamson et. al.,⁸ Fleischauer et. al.,⁹ and the comprehensive book by Balzani and Cassini.¹⁰ Today the field of organometallic photochemistry of d^3 and d^6 metal ion complexes has become large and diverse.^{11,12} Chromium(III) is the model for the d^3 metal ion system as a result of intensive photophysical and photochemical studies.⁵ Studies in the d^6 metal ion system are numerous. Flash studies^{13,14} on cobalt(III) ammine complexes show that redox reactions are the main pathways in aqueous solution and these complexes are most often used as quenchers for $[\text{Ru}(\text{bipy})_3]^{2+}$,¹⁶ and $[\text{Os}(\text{bipy})_3]^{2+}$.¹⁷ Like cobalt(III), iron(II),¹⁸ osmium(II)¹⁹ and iridium(III)²⁰ have also been used as redox quenchers. In addition, flash photolysis of $\text{Fe}^{\text{II}}(\text{TIM})\text{L}_2$ complexes (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; L = NCS, imidazole, CH_3CN or CO)²⁰ results in photosubstitution and linkage isomerization. Ligand labilization results upon irradiation of the LF and CT bands of pentaammineiridium(II) complexes in aqueous solution.²¹ To date, the photochemical substitution reactions of osmium(II)²² and platinum(IV)²³ have received little attention.

Exclusive photoaquation of py-X ($\phi \sim 0.47$) results upon irradiation of the pyridine-substituted pentaammineiridium(III) complexes.²⁴ The combination of measured lifetimes of halopentaammineiridium(III) complexes in aqueous solution^{25,26} with the previous conclusion that

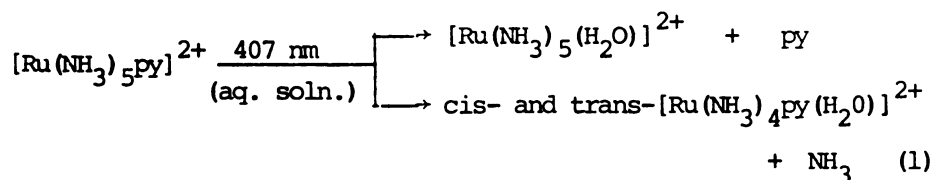
intersystem crossing and internal conversion to the lowest energy LF excited state occurs with unit efficiency,²⁷ allowed calculation of the individual rate constants for the radiative, nonradiative and reactive pathways.²⁶ It was determined that photoaquation occurs 14-15 times faster than the analogous ground state reaction. Ruthenium(III) amines have been used for electron transfer quenching of nonemitting excited states²⁸ and the reduction of copper in biological systems.²⁹ However, the majority of the research has been involved with the ruthenium(II) complexes described below.

Photochemistry of Ruthenium(II) Complexes

The photochemistry of various ruthenium(II) complexes with nitrogen ligands, (e. g. $[\text{Ru}(\text{bipy})_2\text{L}_2]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ where bipy = 2,2'-bipyridine and L = N-heteroaromatic ligands) has been investigated by both spectroscopic techniques and photochemical studies. In 1960, Brandt³⁰ reported the narrow band emission at 667 nm of $[\text{Ru}(\text{bipy})_3][\text{Cl}]_3$ and assigned it to a π^* (mostly ligand) $\rightarrow (t_{2g})$ transition. The free ligand emits at 426 nm.³¹ Extensive investigation carried out on the complex allowed assignment of the 667 nm emission as phosphorescence from the lowest MLCT triplet of the complex.^{32,33} Complexes such as $[\text{Ru}(\text{bipy})_3]^{2+}$ and its derivatives have been subjected to a large number of studies³⁴ and were found to be light stable,³⁵ inert toward substitution at ambient temperature in fluid solution,³⁶ and luminescent in solution at room temperature as well as in a glass at low temperature.³² In general, there is little wavelength dependence for emission³⁵ and the complexes are exceptionally useful triplet sensitizers.³⁷ The excited state model by Crosby and coworkers treats

the luminescent complex as a $4d^5 Ru^{3+}$ core with three bipyridyl ligands, with the electron transferred into the lowest antibonding orbital of one of the ligands.^{32,35,36} Recent experimental evidence^{38,39} however points to the fact that the $[Ru(bipy)_3]^{2+}$ once thought to be substitutionally inert, does undergo permanent substitution photochemistry.

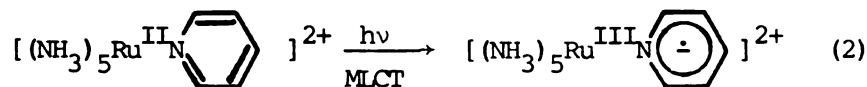
In contrast to the bipyridine ruthenium(II) complexes, pentaammineruthenium(II) complexes with N-heteroaromatic ligands such as pyridine are nonluminescent but exhibit wavelength dependent photochemistry. Sigwart and Spence⁴⁰ reported that the oxidation of ruthenium(II) to ruthenium(III) was the principal photochemical reaction pathway for the pentaammineruthenium(II) molecular nitrogen complex, $[Ru(NH_3)_5N_2]^{2+}$. In 1969, Ford and coworkers⁴¹ found that the photochemical reactions of several pentaammineruthenium(II) complexes in aqueous solution included ligand aquation as well as oxidation of the ruthenium(II) to ruthenium(III). For example, irradiation at the MLCT absorption bands of pentaamminepyridineruthenium(II) tetrafluoroborate in aqueous solution resulted only in photoaquation (1). This conclu-



sion was based on the following observations: 1) the MLCT band was regenerated after excess pyridine was added after irradiation. 2) ion-exchange elution of the photoproducts confirmed the spectroscopic quantum yields. 3) ruthenium(III) was not detected.

Metal-to-ligand charge transfer excitation has been postulated

to lead to an excited state (MLCT)* having an oxidized metal ion and a radical ligand in the coordination complex (2).⁴² Two possible con-



sequences of the (MLCT)* state are photooxidation of ruthenium(II) to ruthenium(III) and an enhanced reactivity of the pyridine ligand with electrophiles. However, it was found that photooxidation does not occur and studies with deuterium labelled complex showed that H-D exchange on the pyridine ring was low ($\phi_{\text{D}} \sim 0.001$). Further work⁴³ has shown that the low quantum yield for pyridine aquation ($\phi \sim 0.04$) from aqueous $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ is essentially wavelength independent over the 254-436 nm range, suggesting conversion of the initially populated states to a common state.

The quantum yield for pyridine displacement on irradiation into the MLCT band was found to be a function of pH in solution.⁴⁴ The quantum yield range of 0.04-0.075 was attributed to competitive acid-dependent and acid-independent reactions of a short lived intermediate or excited state. Flash studies by Natarajan and Endicott³⁷ on this complex demonstrated the presence of an intermediate with an acid - dependent lifetime. They proposed an intermediate formed by rehybridization and protonation of the pyridine nitrogen to give a ruthenium (II) coordinated free radical species.

To explain the mechanism of photoaquation, Ford ruled out the (MLCT)* state as the lowest energy excited state since low spin d^5 ruthenium(III) ammine complexes are relatively substitution inert.⁴⁵ Radiationless deactivation to a "hot" ground state would explain the

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competition between pyridine and ammonia aquation since the competition occurs in the corresponding thermal reaction.⁴⁶ However, vibrational relaxation is expected to occur at a faster rate in aqueous solution and no wavelength dependence on the quantum yield is seen.⁴³ Ford concludes that a ligand field excited state (LF)^{*} populated from the (MLCT)^{*} is responsible for ligand labilization, since octahedral ruthenium(II) has an electron in the σ^* - orbital making it more reactive than the ground state. Charge transfer and ligand $\pi\pi^*$ absorptions dominate the absorption spectrum so the presence of a LF state can only be inferred. For ruthenium(II) ammine complexes not dominated by MLCT absorptions, LF bands are identifiable at wavelengths comparable to that of the $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ MLCT band. $[\text{Ru}(\text{NH}_3)_6]^{2+}$ ($\lambda_{\text{max}} = 390 \text{ nm}$, $\epsilon = 39 \text{ M}^{-1}\text{cm}^{-1}$) and $[\text{Ru}(\text{NH}_3)_5\text{CH}_3\text{CN}]^{2+}$ ($\lambda_{\text{max}} = 350 \text{ nm}$, $\epsilon = 163 \text{ M}^{-1}\text{cm}^{-1}$) undergo substitution ($\phi \sim 0.2$) in aqueous solution,⁴⁷ consistent with the general observation that LF excitation of low spin d^6 complexes lead to substitution processes for the heavier transition metals.⁴⁸ Direct excitation into the LF state for $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ plays a minor role due to the very large extinction coefficient of the MLCT band ($\epsilon = 7700 \text{ M}^{-1}\text{cm}^{-1}$).⁴²

The energy of the MLCT band ($\lambda_{\text{max}}(\text{CT})$) of $[\text{Ru}(\text{NH}_3)_5(\text{py-X})]^{2+}$ is very sensitive to the nature of the substituent X.⁴⁹ The substituent X (CH_3 , H, Cl, CONH_2 , phenyl, CF_3 , CO_2^- , CO_2CH_3 , CHO) cannot undergo its own chemical reaction. In aqueous solution, Ford observed that where $\lambda_{\text{max}}(\text{CT})$ exceeds 460 nm, $\phi_{\text{py-X}}$ was dramatically lower than for complexes having $\lambda_{\text{max}}(\text{CT})$ of higher energy. A partial listing of the data in Table 1 shows that the range of $\phi_{\text{py-X}}$ spans more than three orders of magnitude.⁵⁰ Direct comparison of the $\phi_{\text{py-X}}$ values suffers

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from the fact that λ_{irr} is also a variable; however, additional studies showed that varying λ_{irr} did not change the relative order of $\phi_{\text{py-X}}$. From the data it is seen that the appropriate electron withdrawing substituent leads to a reversal in the relative energies of the lower excited states to make a substitutionally unreactive charge transfer excited state lowest in energy. On the basis of these results, the following model was postulated. There are "reactive" complexes with $\lambda_{\text{max}}(\text{CT}) < 460 \text{ nm}$ presumably having a lowest energy (LF)^{*} excited

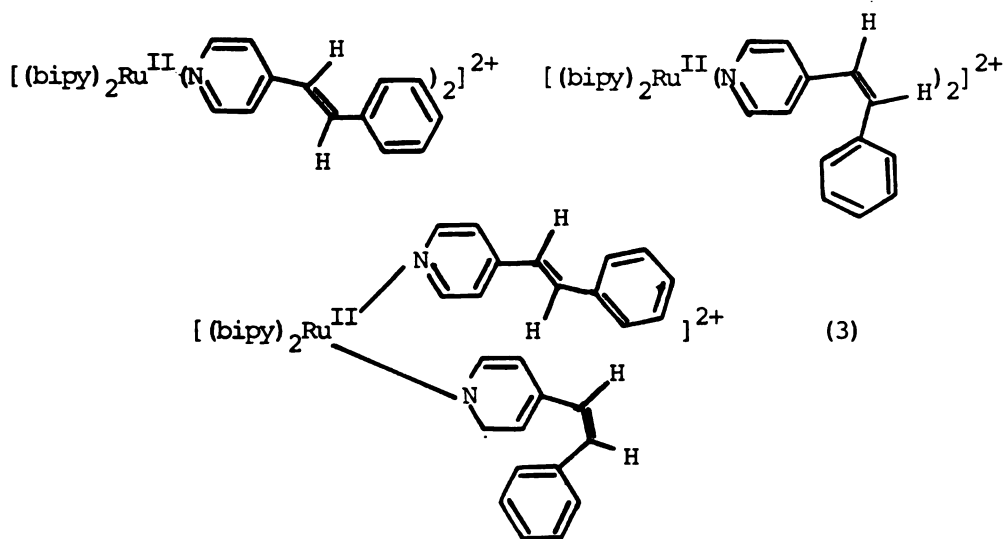
Table 1. Spectroscopic quantum yields⁴⁹ for some $[\text{Ru}(\text{NH}_3)_5(\text{py-X})]^{2+}$ in aqueous solution.

X	$\lambda_{\text{max}}(\text{CT}), \text{ nm}$	$\lambda_{\text{irr}}, \text{ nm}$	$\phi_{\text{py-X}}(\text{spec}), \text{ mol/einstein}$
CH ₃	398	405	0.037
H	407	405	0.045
CF ₃	454	455	0.022
COCH ₃	523	520	0.00025
CHO	545	546	0.00005

state and "unreactive" complexes with $\lambda_{\text{max}} > 460 \text{ nm}$ presumably having a lowest energy (MLCT)^{*} excited state. The energy of the MLCT band is very sensitive to solvent and in cases where the (MLCT)^{*} and (LF)^{*} excited states have similar energies, changes in the solvent alone may be sufficient to reverse the order of these states and thus change the reactivity of the complex.

Whitten and Zarnegar⁵¹ investigated ruthenium(II) complexes of the type $[\text{Ru}(\text{bipy})_2\text{L}_n][\text{X}]_{2-n}^{2+}$ where L = 4-stilbazole and X = BF_4^- or PF_6^- .

Here the substituent on the pyridine ring was an isomerizable double bond which may undergo its own photochemical reaction. These complexes do not photodissociate. They exhibit wavelength dependent luminescence and undergo wavelength dependent isomerization of the stilbazole double bond under direct or sensitized isomerization in butyronitrile (3).



Isomerization from the triplet state in the ruthenium(II) complexes is less efficient in comparison to that observed for the free ligand (Table 2).⁵² Inefficiency is also evident when triplet sensitizers are used and $\phi_{t \rightarrow c}$ values range from 0.001 to 0.04. Whitten postulated that low energy irradiation produces a (MLCT)* excited state which behaves like the radical anion of the olefinic ligand and results in preferential cis to trans isomerization with the highest efficiency. High energy irradiation produces excited states with nearly an equal probability of decay to the cis and trans ground states, appearing very similar in behavior to the free ligand.⁵³ The authors concluded that the wavelength effects are due to a rapid reaction of the upper excited

Table 2. Photokinetic data⁵² for the isomerization of the bipyridyl-ruthenium(II) 4-stilbazole complexes in butyronitrile.

λ_{irr} , nm	$\phi_{trans \rightarrow cis}$	$\phi_{cis \rightarrow trans}$	% trans, pss
313	0.15	0.156	35
366	0.05	0.15	88
436	0.05	0.60	85
570	----	----	88
366 ^a	0.37	0.35	50

^a4-stilbazole in benzene.⁵³

state and are not due to slow radiationless processes.

Photochemistry of the Rhenium(I) Complexes

Metal carbonyl complexes are among the most photoreactive transition metal complexes known.⁵⁴ The excited state decay processes in fluid solution are dominated by ligand exchange and substitution.⁵⁵ Prior to 1972, the only metal carbonyl complexes known to luminesce were the low spin d^6 tungsten, molybdenum and chromium complexes, which exhibited emission only at low temperature.⁵⁴ $W(CO)_5py$ exhibited ligand field(LF) absorption bands⁵⁶ and LF emission in a glass with a lifetime of 3×10^6 sec.⁵⁷ Wrighton, Hammond and Gray^{58,59} found that the derivatives of $ClRe(CO)_3X$, where $X = 1,10$ -phenanthroline and related ligands exhibited emission both at 77°K in glassy media and at 298°K in fluid solution. The variation in both emission band maxima and lowest absorption maxima with X and solvent polarity was consistent with a metal to ligand charge transfer (MLCT) rather than a ligand field (LF) transition. Substantial triplet character was attributed to the

(MLCT)* emitting state from energy transfer experiments and the emission lifetimes (10^{-5} sec at 77°K , 10^{-6} sec at 298°K).⁵⁹

Wrighton and coworkers⁶⁰ found that complexes of $\text{XRe}(\text{CO})_3\text{L}_2$, where $\text{X} = \text{Cl}, \text{Br}$ and $\text{L} = \text{trans-3- and trans-4-styrylpyridine}$, have lowest energy absorption bands of intraligand nature. Irradiation of the styrylpyridine complexes into the lowest energy absorption band (313 or 366 nm) resulted in cis to trans isomerization of the coordinated ligands with a quantum efficiency in the range 0.49–0.64 and stationary states that are no less than 84% cis. Triplet sensitization gave stationary states and quantum yields for the coordinated styrylpyridines which were near those found for the free ligand.⁵³ Little photosubstitution ($\phi \sim 0.01$) of the coordinated stilbene occurred

The absorption spectra of $\text{XRe}(\text{CO})_3\text{L}_2$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and $\text{L} = 4\text{-phenylpyridine}, 4,4'\text{-bipyridine}$ ⁶¹ also have high energy absorption bands which are assigned to intraligand(IL) $\pi\pi^*$ transitions and in addition have low energy bands assigned to MLCT transitions. The emission at 298°K is attributed to a (MLCT)* excited state having considerable triplet character. The emission at 77°K intensifies, shifts to the blue and becomes longer lived. MLCT character dominates the featureless emission spectrum for the 4,4'-bipyridine complexes. The appearance of structure in the emission of the 4-phenylpyridine complex shows that some IL $\pi\pi^*$ character is present.

The 3- and 4-benzoylpyridine derivatives of $\text{XRe}(\text{CO})_3\text{L}_2$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$,⁶² are also emissive at 77°K and 298°K . The broad structureless emission observed at 298°K with a lifetime of 10^{-6} sec is associated with the MLCT transition in the absorption spectrum. At low temperatures, the 4-benzoylpyridine complexes exhibited the usual effects: the

emission undergoes a blue shift, intensifies, becomes longer lived (4×10^{-5} sec) and remains featureless. The 3-benzoylpyridine complexes on the other hand, exhibited multiple emission. The total emission spectrum exhibited some structure with a lifetime of 5×10^{-7} sec. Another long-lived, very structured component of emission was observed using a phosphoroscope attachment which allows observation of only long-lived emission (> 1 ms). The short lived emission at low temperature was assigned to the same (MLCT)^{*} transition as that observed at 298°K. The long-lived structured emission was assigned to a slightly perturbed $n\pi^*$ triplet state of the 3-benzoylpyridine and attributed to the fact that the lowest (MLCT)^{*} and $n\pi^*$ excited states are not thermally equilibrated at 77°K.

Wrighton and coworkers⁶³ have used $\text{fac-}[\text{SRe}(\text{CO})_3\text{L}]^+[\text{CF}_3\text{SO}_3]^-$ where S = CH_3CN , PhCN, pyridine, piperidine and L = 2,2'-biquinoline, 1,10-phenanthroline) to show that a variation in the charge density on rhenium(I) results in a variation in the energy of the (MLCT)^{*} emissive state. For the 2,2'-biquinoline complexes, no long-lived component of emission was seen at 77°K and the energy of the MLCT state shift to higher energy. An increase in the percent of long-lived emission correlates with the MLCT band shift and is attributed to the increased importance of the $\pi\pi^*$ triplet state.

Photochemistry of Aromatic Aliphatic Ketones

The photochemical reduction of aromatic alkyl ketones, both intramolecular and intermolecular, involves the transfer of hydrogen to the carbonyl oxygen. The intramolecular photoreduction process is the Norrish Type II reaction.⁶⁴ The intermolecular photoreduction

process involves the abstraction of hydrogen from a suitable substrate to produce semipinacol and hydrogen donor radicals which proceed on to specific products dependent upon the reaction conditions.

The energy diagram in Figure 2 represents the energies of the excited states with respect to the ground state of a phenyl alkyl ketone. In solution, when a ketone absorbs light, it is excited to an

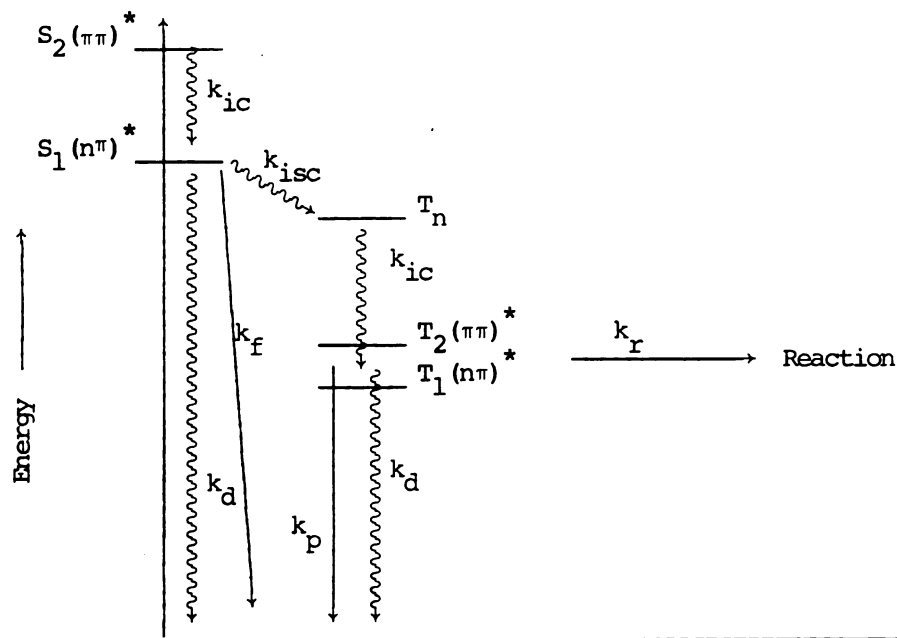


Figure 2. Jablonski diagram for a phenyl alkyl ketone.

upper singlet state and then decays rapidly to the lowest singlet excited state ($k_{ic} \sim 10^{11} - 10^{13} \text{ sec}^{-1}$)⁶⁵. The normal decay processes of the excited singlet state such as radiationless decay (k_d) and fluorescence ($k_f \sim 10^6 \text{ sec}^{-1}$) are slow and rapid intersystem crossing occurs to the triplet manifold ($k_{isc} = 10^{11} \text{ sec}^{-1}$), often with unit efficiency.⁶⁶ Emission from the lowest triplet state to the ground

state (k_p) is known as phosphorescence.

The Norrish Type II Reaction

Aromatic alkyl ketones possessing gamma hydrogens on the alkyl side chain have been found to undergo cleavage to acetophenone and an alkene upon irradiation with ultraviolet light. This process, referred to as the Norrish Type II reaction,⁶⁴ is an excellent monitor of the triplet state reactivity of ketones.⁶⁷ The accepted mechanism for the Norrish Type II reaction, proceeding through the hydroxy 1,4-biradical intermediate is shown in Figure 3.

Low quantum yields of acetophenone formation are often observed despite fast rates of gamma hydrogen abstraction.⁶⁷ By deuterium

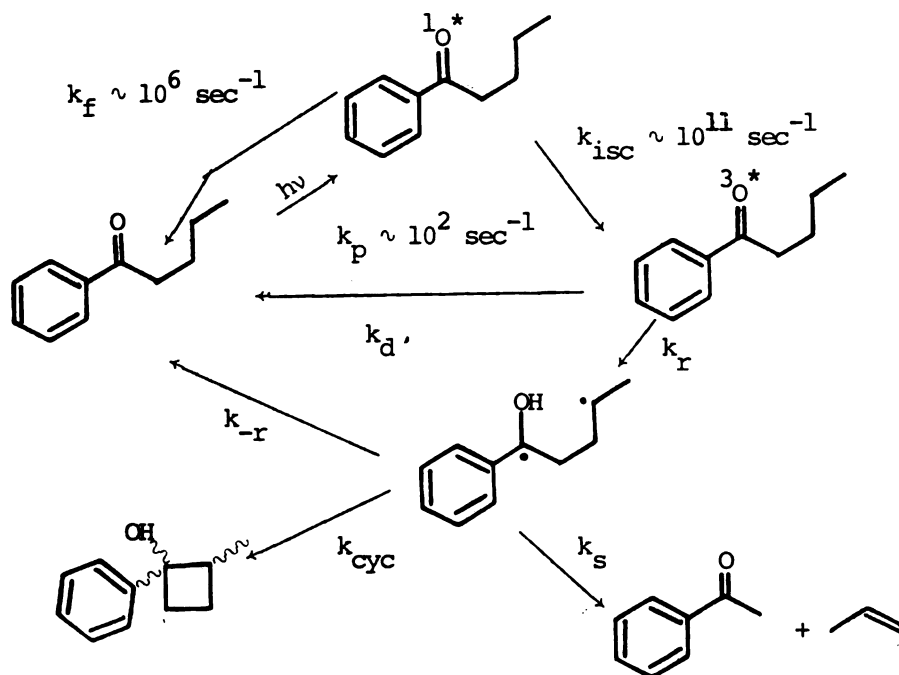


Figure 3. The mechanism of the Norrish Type II reaction.

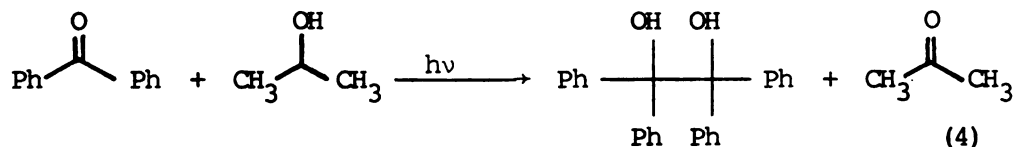
labeling, Coulson and Yang⁶⁸ found that the gamma hydrogen atoms were involved in whatever decay processes were responsible for the low quantum yields. Wagner and Hammond^{69,70} were the first to postulate that reverse gamma hydrogen transfer was occurring. As evidence, Wagner found that polar solvents and Lewis bases raised the total quantum yield to unity by solvating the 1,4-biradical intermediate and preventing reverse hydrogen transfer.⁷¹ Yang⁷² was the first to identify the cyclobutanols formed in this reaction. Cyclobutanols have been found to generally account for 10-15% of the cleavage yields and thus allow for a reasonable estimate of their yield when direct measurement is not possible.⁷³ The above polar solvent effects and observation of both acetophenone and cyclobutanols are consistent with the hypothesis that gamma hydrogen abstraction led to the formation of a 1,4-biradical intermediate.^{72,74} Lewis⁷⁵ and others⁷⁶ have been among those to provide evidence for the intermediacy of the 1,4-biradical. Wagner and Zepp⁷⁷ trapped the 1,4-biradical intermediate of γ -methoxybutyrophenone using alkyl mercaptans.

Solvents and substituents influence the reactivity of aromatic alkyl ketones by altering the energy levels of the n, π^* and π, π^* triplet excited states (Figure 2)^{67,78} The n, π^* excited state involves the promotion of an electron from the nonbonding orbital on oxygen to a π antibonding orbital. As a result, the excited state is electron deficient and radical-like in the proximity of the oxygen atom.⁷⁹ The n, π^* triplet excited state is said to be responsible for gamma hydrogen abstraction and has reactivity similar to that of a tert-butoxy radical.⁸⁰ The π, π^* excited state on the other hand involves promotion of a π electron to a π^* antibonding orbital. While the exact nature of

the π, π^* excited state is not clear,⁸¹ the electron spin is most likely localized on the aromatic ring⁸² and the carbonyl oxygen remains electron rich. In many cases, the two triplet states are close enough to equilibrate and the decreased reactivity when the π, π^* triplet is lowest results from low equilibrium concentration of the reactive n, π^* triplet state.⁸³ Solvents affect the energy of the triplet state such that polar solvents stabilize the π, π^* triplet state relative to the n, π^* triplet excited state. Substituents on the phenyl ring alter the energy of the triplet states and affect the reactivity of the triplet carbonyl toward gamma hydrogen abstraction.⁸³ Electron withdrawing groups raise the energy of the π, π^* triplet excited state relative to the n, π^* triplet excited state. Electron donating groups stabilize the π, π^* triplet excited state with respect to the n, π^* triplet excited state.^{84,85} Substituents on the alkyl side chain affect the rate of gamma hydrogen atom abstraction in parallel with their effects on C-H bond strength.^{86,87}

Intermolecular Photoreduction

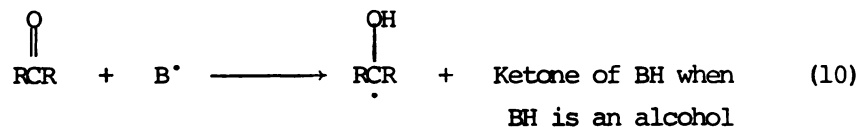
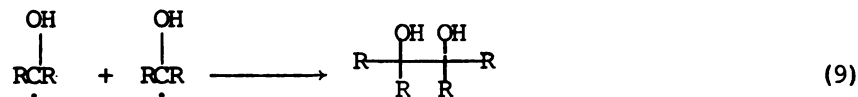
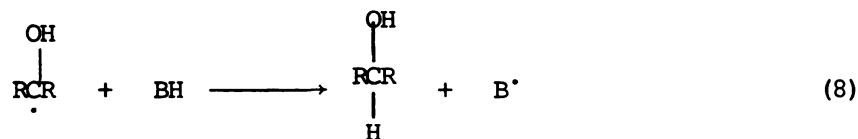
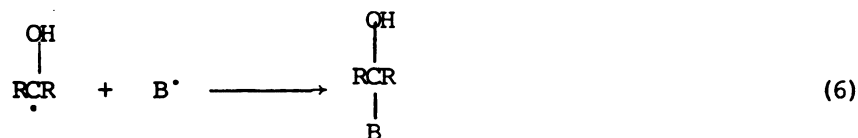
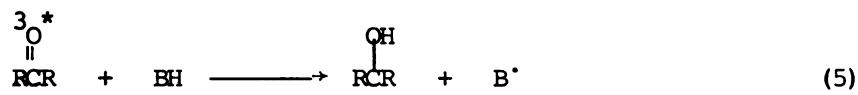
Ciamician and Silber⁸⁸ first observed intermolecular photoreduction by isolating benzopinacol after irradiation of benzophenone in isopropyl alcohol (4). The early emphasis in photoreduction studies



was on synthetic application since the pinacol products were prepared more readily and in higher chemical yields than by nonphotochemical methods.⁸⁹ The mechanistic studies conducted with photoreduction have included hydrogen donors other than alcohols⁹⁰ such as

hydrocarbons,⁹¹ amines,⁹² tributylstannane,⁹³ ethers,⁹⁴ sulphides,⁹⁵ mercaptans⁹⁶ and phenols.⁹⁷ Alcohols and alkylbenzenes are often the hydrogen donors of choice since the photoproducts are relatively easy to analyze.

The intermolecular photoreduction mechanism involves initial bimolecular interaction of the triplet ketone excited states with hydrogen donor (5) and the products which are isolated are dependent upon the reaction conditions. The photoreduction of benzophenone with toluene gives the hydroxy radical and benzyl radical coupling products in (6), (7) and (9).⁹⁸ The irradiation of acetone with tributylstannane results in the formation of isopropyl alcohol,⁹³ according to



reaction (8). The irradiation of acetophenone with 1-phenylethanol produced ketone, pinacol (9) and oxidized the 1-phenylethanol to acetophenone (10).⁹⁹ At first it was thought that the oxidation of alcohol resulted from the disproportionation of the carbinol radicals. However Pitts^{100,101} and later Cohen,⁹⁹ found that optically active alcohols were not racemized when photolyzed with aryl ketones. The carbinol radicals are instead oxidized by ground state ketone as in (10), consistent with the fact that ketone disappearance quantum yields approach a value of two dependent upon the reaction conditions.¹⁰²

The reactive state in intermolecular photoreduction was identified as triplet¹⁰³ from emission and quenching studies on compounds such as benzophenone.¹⁰¹⁻¹⁰⁴⁻¹¹⁰ Experimental evidence has accumulated that the accepted mechanism is an oversimplification.¹¹¹ In 1959, Pitts¹⁰¹ reported a colored, oxygen-sensitive intermediate for (4) which Backstrom¹¹³ later assigned to a charge transfer complex of the hydroxy benzophenone radical and hydroxy isopropyl radical. Recent work with compounds such as trifluoroacetophenone has shown that the first step in the photoreduction mechanism does not always involve hydrogen abstraction from the donor and is influenced not only by the substituent on the ketone as observed for the Type II fragmentation but is also influenced by the donor itself.^{114,115} Trifluoroacetophenone exhibits π, π^* emission and reacts in one half the quantum yield observed for acetophenone, yet its triplet reacts one hundred times faster than triplet acetone with toluene. The results suggest the following scheme involving a primary charge transfer interaction (Figure 4). This mechanism still allows for direct hydrogen abstraction and the new

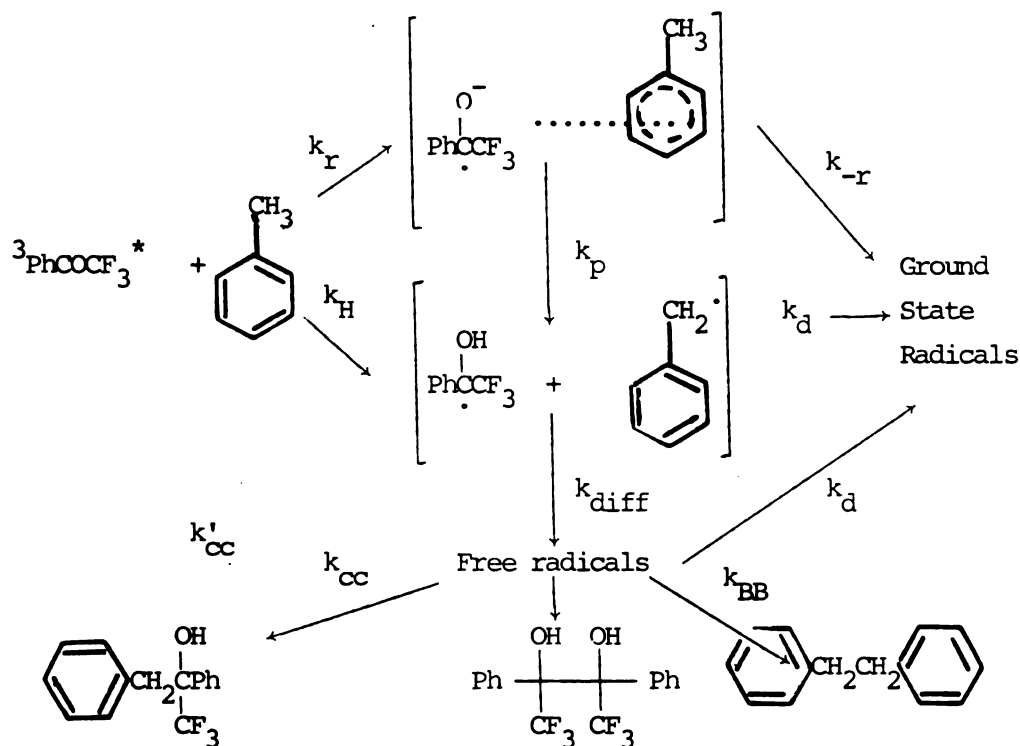


Figure 4. The mechanism for the reaction of trifluoroacetophenone with toluene in benzene,

source of inefficiency (k_{-r}) may lower ϕ_{BB} . The involvement of charge transfer in the photoreduction of trifluoroacetophenone with alkyl benzenes is well supported. The triplet state reactivities show a marked sensitivity toward substituents on the aromatic ring with a negative ρ value.¹¹⁷ Donors without abstractable hydrogen interact with the triplets as efficiently as donors with abstractable hydrogen. The rate constants of triplet-donor interaction are not reduced by deuterium substitution.¹¹⁷ The triplet reactivities are not sensitive to C-H bond strength.^{116,117}

Photochemistry of Pyridyl Alkyl Ketones

Wagner and Capen¹¹⁹ studied the Norrish Type II Fragmentation processes for the n-propyl and n-butyl pyridyl ketones in benzene and tert-butyl alcohol solutions and found that the aza ring substituent had a definite effect on the excited state chemistry. The quantum yields of acetylpyridine formation for the pyridyl alkyl ketones were lower than those observed for the analogous phenyl alkyl ketones. Accompanying this decrease in efficiency of the pyridyl alkyl ketones was an increase in the triplet excited state reactivity (k_T) in comparison to the phenyl alkyl ketones. The energy changes of the n, π^* and π, π^* triplet excited states implied by the spectroscopic data could not explain the increases seen in excited state reactivity. A further discussion of the results and their implications is postponed until the discussion section of this thesis.

Very limited studies have been carried out on the intermolecular photoreduction reactions of the pyridyl ketones. Early mechanistic studies focused on the migratory aptitudes of the alkyl and pyridyl groups in the pinacol-pinacolone rearrangement of the acetyl and benzoyl pyridines.¹²⁰ The decay kinetics of benzoylpyridine ketyl radicals were investigated by Nelson and Hayon using pulse radiolysis.¹²¹ Finally, the photochemistry of di-(4-pyridyl)ketone in 2-propanol was studied in consecutive recording of absorption, emission, nmr and esr spectra during photolysis and the dark period. Derivatives of di(4-pyridyl)ketone and the isolated photoproduct di(4-pyridyl)methanol were synthesized and used to characterize the spectroscopically detected intermediates.¹²²

Kinetics

In order to understand the excited state processes, it is necessary to make quantitative measurements of the quantum yields, lifetimes and rate constants. The quantum yield for any photochemical process is the product of probabilities (11) where ϕ_{ES} represents the probability that the absorption of light produces the requisite excited state, ϕ_R represents the probability that the excited state will undergo the primary photoreaction required for process i and ϕ_p represents the probability that any metastable intermediate proceeds on to ground state product.

$$\phi_i = \phi_{ES}\phi_R\phi_p \quad (11)$$

For the intramolecular hydrogen abstraction, the Norrish Type II process is described as follows:

$$\phi_{II} = \phi_{isc}\phi_{BR}\phi_p = \phi_{isc}k_r\tau\phi_p \quad (12)$$

where ϕ_{BR} is the probability of 1,4-biradical formation and ϕ_p is the probability that the 1,4-biradical will cleave to form enol and olefin. The experimentally determined quantities are ϕ_{isc} , the quantum yield of intersystem crossing; k_r , the rate of gamma hydrogen abstraction and τ , the lifetime of the triplet ketone excited state.

By definition:

$$\frac{1}{\tau} = k_r + k_d + k_p \quad (13)$$

where k_p is usually negligibly small at room temperature and k_d is the sum of all pseudounimolecular forms of triplet decay which produce nothing measureable. In the presence of an external quencher, Q, (13)

becomes:

$$\frac{1}{\tau} = k_r + k_d + k_q [Q] \quad (14)$$

where k_q is the rate constant for quenching of the ketone triplet excited state. Using the value of ϕ from (13) and (14) in (12) gives the Stern Volmer Equation (15)¹²³ where ϕ_0 is the quantum yield in the absence of quencher. A plot of ϕ_0/ϕ versus $[Q]$ gives a straight line

$$\frac{\phi_0}{\phi} = k_q \tau [Q] + 1 \quad (15)$$

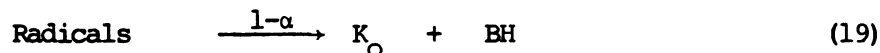
with the slope of $k_q \tau$. The value of k_q is known for triplet quenchers in various solvents,¹²⁴ and the value of τ is easily determined.

Intersystem crossing yields were measured by ketone sensitization of known triplet isomerization reactions.¹²⁵ The efficiency of intersystem crossing (ϕ_{isc}) can be determined from the following:

$$\frac{\alpha}{\phi_{c \rightarrow t}} = \phi_{isc} \left(1 + \frac{1}{k_q \tau [Q]} \right) \quad (16)$$

where α is the photostationary state cis-trans ratio of the olefin quencher and $\phi_{c \rightarrow t}$ is the measured quantum yield for isomerization at that concentration.

For intermolecular hydrogen abstraction, the excited state mechanism is similar to the Norrish Type II mechanism, except that product formation occurs after diffusion apart of the radical intermediates:



Based on (11), the quantum yield of product in the absence of quencher is:

$$\phi_{\text{Product}} = \frac{\phi_{\text{isc}} \alpha k_r [\text{BH}]}{k_r [\text{BH}] + k_d} \quad (20)$$

and the product yield in the presence of external quencher is:

$$\phi_{\text{Product}} = \frac{\phi_{\text{isc}} \alpha k_r [\text{BH}]}{k_r [\text{BH}] + k_d + k_q [\text{Q}]} \quad (21)$$

One obtains (22) by dividing (20) by (21) which in final form is identical to (15), except for a different definition of τ :

$$\frac{\phi_o}{\phi} = \frac{k_r [\text{BH}] + k_d + k_q [\text{Q}]}{k_r [\text{BH}] + k_d} = 1 + k_q \tau [\text{Q}] \quad (22)$$

$$\frac{1}{\tau} = k_r [\text{BH}] + k_d \quad (23)$$

Inversion of (20) indicates a linear relationship (24) between $(\phi)^{-1}$ and $[\text{BH}]^{-1}$. The slope of the line produced by the data plotted according to (24) is $k_d(\alpha\phi_{\text{isc}}k_r)^{-1}$ and the intercept is $(\alpha\phi_{\text{isc}})^{-1}$. Dividing the slope by the intercept gives k_d/k_r which can be substituted into (23) along with the value of τ determined from Stern Volmer quenching studies (15) to obtain the values for k_d and k_r .

$$\frac{1}{\phi} = \frac{1}{\alpha\phi_{\text{isc}}} \left(1 + \frac{k_d}{k_r [\text{BH}]} \right) \quad (24)$$

Research Goals

The work to be discussed in this thesis is concerned with the intramolecular effects of metal coordination on the photochemistry of

ketones. From the foregoing description, it is clear that excited state behavior in organometallic complexes is influenced by the interactions of the ligands and their substituents with the central metal atom. The substituents on the ruthenium and rhenium complexes previously studied are either nonreactive photochemically or undergo simple double bond isomerization. The results suggest that reaction from an upper excited state is occurring. This is in contrast to the excited state processes in organic molecules, where reaction proceeds with few exceptions from the lowest excited state.¹²⁶ It is evident that the elaboration of the excited state mechanism in these and other organometallic complexes rests in the selective quenching of the upper excited state in the excited state manifold. We reasoned that the use of pyridyl ketones as ligands would probe the mechanism of excited state behavior, the alkyl pyridyl ketone substituent acting as a monitor of triplet state reactivity.

The main goal of this work was to find reactions from an upper excited state competitive with decay to the lower excited states. With the large number of photochemically active complexes to choose from,¹²⁷ the study was narrowed to those systems which already showed promise of observable excited state behavior. The relative ease of preparation and photosubstitution inertness of the pentaammineruthenium(II) system suggested that this system would be best suited for a study using alkyl pyridyl ketones as ligands. The alkyl pyridyl ketone complexes of tricarbonylrhenium(I) were also investigated after the observation by Wrighton⁶² in 1978 of n, π^* emission from the tricarbonylbromorhenium(I) benzoylpyridine systems.

Initially, pyridyl alkyl ketones with gamma hydrogens on the alkyl

side chain were used as ligands for both metal systems and triplet state reactivity was monitored through the Norrish Type II reaction. Pyridyl ketone hydrochloride salts were studied as model complexes for the metal complexed ketones. The intermolecular photoreduction of the pyridyl ketone hydrochloride salts and pentaammineruthenium(II) pyridyl ketone complexes was examined to complement the intramolecular Norrish Type II photoreduction. The overall goal of these studies was to estimate the rate of internal conversion in the organometallic systems.

RESULTS

Pyridyl Ketones and Hydrochloride Salts

Compound Preparation

All pyridyl ketones were prepared by a Grignard reaction using the appropriate cyanopyridine and haloalkane. The reaction gave high crude yields (80-95%), but purification often was difficult since undesired reaction side products had boiling points within a degree or two of the desired pyridyl ketone. Meta-substituted compounds proved the most difficult, 2-methyl-1-(3-pyridyl)butanone requiring both spinning band distillation and hydrochloride salt recrystallization to obtain a sample pure enough for photolysis (<0.5% impurity). The hydrochloride salts were prepared by bubbling hydrogen chloride gas through an ether solution of the appropriate pyridyl ketone. The salts were prone to decomposition and were often isolated in an inert atmosphere before storage in a vacuum dessicator at 0°C. The ketones were stored under refrigeration; trace impurities (<0.5%) caused the initially colorless solutions to turn yellow. The compounds and their corresponding abbreviations are listed in Tables 3 and 4. For example, 1-(4-pyridyl)pentanone is denoted as 4VP and 1-(4-pyridyl)pentanone hydrochloride as 4VPHCl.

Intramolecular Photoreduction

Photoproduct Identification

All compounds produced acetylpyridene and an alkene upon

irradiation at 313 nm. A base impregnated gc column was used to convert the hydrochloride salts to the free pyridyl ketone for analysis. The results were identical to those obtained by regenerating the free pyridyl ketone using anhydrous potassium carbonate prior to analysis.¹²⁸ The pyridyl ketone was identified by comparison of the gas chromatograph(gc) retention time with an authentic sample. The small peaks observed before and after the unfragmented ketone were assumed to be the expected cyclobutanones⁷³ and account for 10-15% of the cleavage yields. Attempts to isolate these compounds by preparative gc were unsuccessful. A yellow color¹¹⁹ appeared only when 2BP, 2VP and 3BP were irradiated. The color was most intense upon prolonged irradiation especially in polar solvents, and least intense in the presence of high quencher concentration. The color disappeared when the solution was exposed to the atmosphere. For 2BP, competitive gamma hydrogen abstraction by the pyridine nitrogen is possible, as observed for pyrimidyl ketones.^{129,130} An additional product peak appeared upon irradiation of the meta-substituted compounds, but attempts to isolate the compound by preparative gc were unsuccessful.

Quantum Yields

Quantum yields for photoproduct formation were obtained by irradiation at 313 nm in a "merry-go-round" apparatus¹³¹ at 25°C. Solutions containing various concentrations of ketone, often in the presence of various concentrations of additive, were irradiated in parallel with 0.1 M solutions of valerophenone actinometer in benzene. The ϕ_{II} for 0.1 M valerophenone has been measured as 0.33 in benzene

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solution¹³² and all quantum yields are reported relative to that value. Quantum yields were measured at less than 5% conversion for fragmentation studies and 20% conversion for ketone disappearance studies. All quantum yields are listed in Tables 3 and 4.

Quantum yields ($\phi_{\max}$) were measured in benzene solution containing 1.0-8.0M tert-butyl alcohol. Increasing the concentration of tert-butyl alcohol caused the quantum yield to rise until it reached a maximum value, at which point it leveled off or slowly decreased.¹³² Representative plots of quantum yield versus tert-butyl alcohol concentration are shown in Figures 5 and 6. The free pyridyl ketones show a greater variation in quantum yield than the pyridyl ketone hydrochloride salts over the alcohol concentration range. The maximum quantum yields for the pyridyl ketones approach unity while the quantum yields for the pyridyl ketone hydrochloride salts are much lower (0.12-0.42).

Figures 7 and 8 demonstrate the effect of varying ketone concentrations on quantum yields. Plots of quantum yield versus ketone concentration were linear. The positive slope of the line varies both with aza position¹¹⁹ and alkyl side chain. The free pyridyl ketones show a greater concentration effect than the pyridyl ketone hydrochloride salts. The values extrapolated to zero ketone concentration are contained in Tables 3 and 4 under the heading ϕ_0^∞ .

The ϕ_{II} value is enhanced by the addition of 2% water to the acetonitrile (Table 5). Various additives (zinc chloride, rhenium(I) and ruthenium(II) complexes) decreased ϕ_{II} as illustrated for 4VP

Table 3. Photokinetic data for the pyridyl ketones.^a

Compound	Solvent	ϕ^b	ϕ_{-K}	$\phi_{\max}^c$	ϕ_o^∞	ϕ_{isc}^d	$k_q \tau, M^{-1} e$
(2BP)	Benzene Acetonitrile	0.16 0.25	0.23 0.83	0.39 -	0.12 0.21	- -	537. $\pm$ 1 583. $\pm$ 31
(3BP)	Benzene Acetonitrile	0.44 (0.28) ^f 0.70	0.45 0.85	0.87 -	0.22 0.52	- -	(190) ^f 542. $\pm$ 23
(4BP)	Benzene Acetonitrile	0.20 0.63	0.33 0.86	0.62 -	0.13 0.55	- -	(80) ^f 204. $\pm$ 3
(2VP)	Benzene Acetonitrile	0.20 (0.18) ^f 0.70	0.26 (0.20) ^f 0.75	0.87 (0.79) ^f -	0.13 (0.14) ^f 0.68	1.04 -	23.3 (27) ^f 56. $\pm$ 3
(3VP)	Benzene Acetonitrile	0.35 (0.29) ^f 0.84	0.36 (0.42) ^f 0.87	0.88 -	0.30 (0.16) ^f 0.79	1.1 -	17. (16) ^f 31. $\pm$ 2

Table 3. Table 3 (cont'd.)

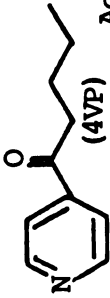
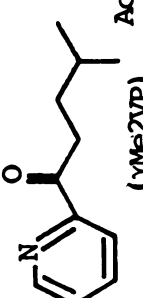
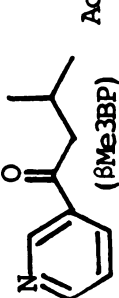
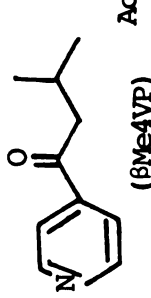
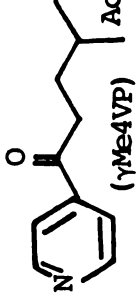
Compound	Solvent	ϕ^b	ϕ_{-K}	$\phi_{\max}^C$	ϕ_O^∞	ϕ_{isc}	$k_{q,\tau,M}^{-1} e$
 (4VP)	Benzene	0.23 (0.26) ^f	0.38 (0.31) ^f	0.60(0.57) ^f	0.19(0.22) ^f	0.98	7.3 (7.3) ^f
	Acetonitrile	0.60	0.71	-	0.55	-	10.±1
 (γMe2VP)	Benzene	0.19	0.23	0.75	0.15	-	6.7±0.1
	Acetonitrile	0.73	0.79	-	0.65	-	7.9±0.3
 (βMe3BP)	Benzene	0.31	0.44	0.74	0.24	-	90.
	Acetonitrile	0.76	0.81	-	0.54	-	107.±8
 (βMe4VP)	Benzene	0.16	0.21	0.51	-	-	-
	Acetonitrile	0.60	0.67	-	-	-	41.1±0.1
 (γMe4VP)	Benzene	0.18	0.27	0.51	0.16	-	1.73±0.3
	Acetonitrile	0.58	0.67	-	0.54	-	2.5±0.1

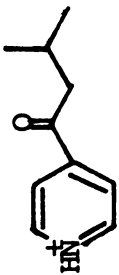
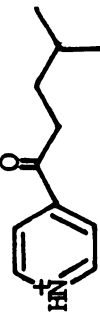
Table 3. (cont'd.)

^a0.05 M ketone, irradiated at 313 nm. ^bQuantum yield for the formation of acetylpyridine. ^cMaximum quantum yield of acetylpyridine in the presence of tert-butyl alcohol. ^dcis→trans 1,3-Pentadiene isomerization. ^ecis- and trans-1,3-Pentadiene quencher. ^fRef. 119.

Table 4. Photokinetic data for the pyridyl ketone hydrochloride salts.^a

Compound	ϕ^b	ϕ_{-K}	$\phi_{\max}^c$	ϕ_O^∞	$k_q^\tau,^d \text{ M}^{-1}$	$k_q^\tau,^e \text{ M}^{-1}$
 (2BPHCl)	0.11	0.21	0.14	0.11	$11. \pm 2$	-
 (3BPHCl)	0.23	0.35	0.42	0.18	$42. \pm 2$	-
 (4BPHCl)	0.092	0.19	0.14	0.09	23.3 ± 0.4	-

Table 4. (cont'd.)

Compound	ϕ^b	ϕ_{-K}	$\phi_{\max}^c$	ϕ_O^∞	$k_{q\tau}^d, M^{-1}$	$k_{q\tau}^e, e^{-1}$
 (8Me4BPHCl)	0.16	0.22	0.15	0.13	-	7.4
 (γMe4VPHCl)	0.13	0.22	0.12	0.13	2.18	2.0

^a0.05 M ketone in acetonitrile, irradiated at 313 nm. ^bQuantum yield for the formation of acetylpyridine. ^cMaximum quantum yield of acetylpyridine in the presence of tert-butyl alcohol. ^dcis-trans mixture of 1,3-Pentadiene quencher. ^eEthyl sorbate quencher.

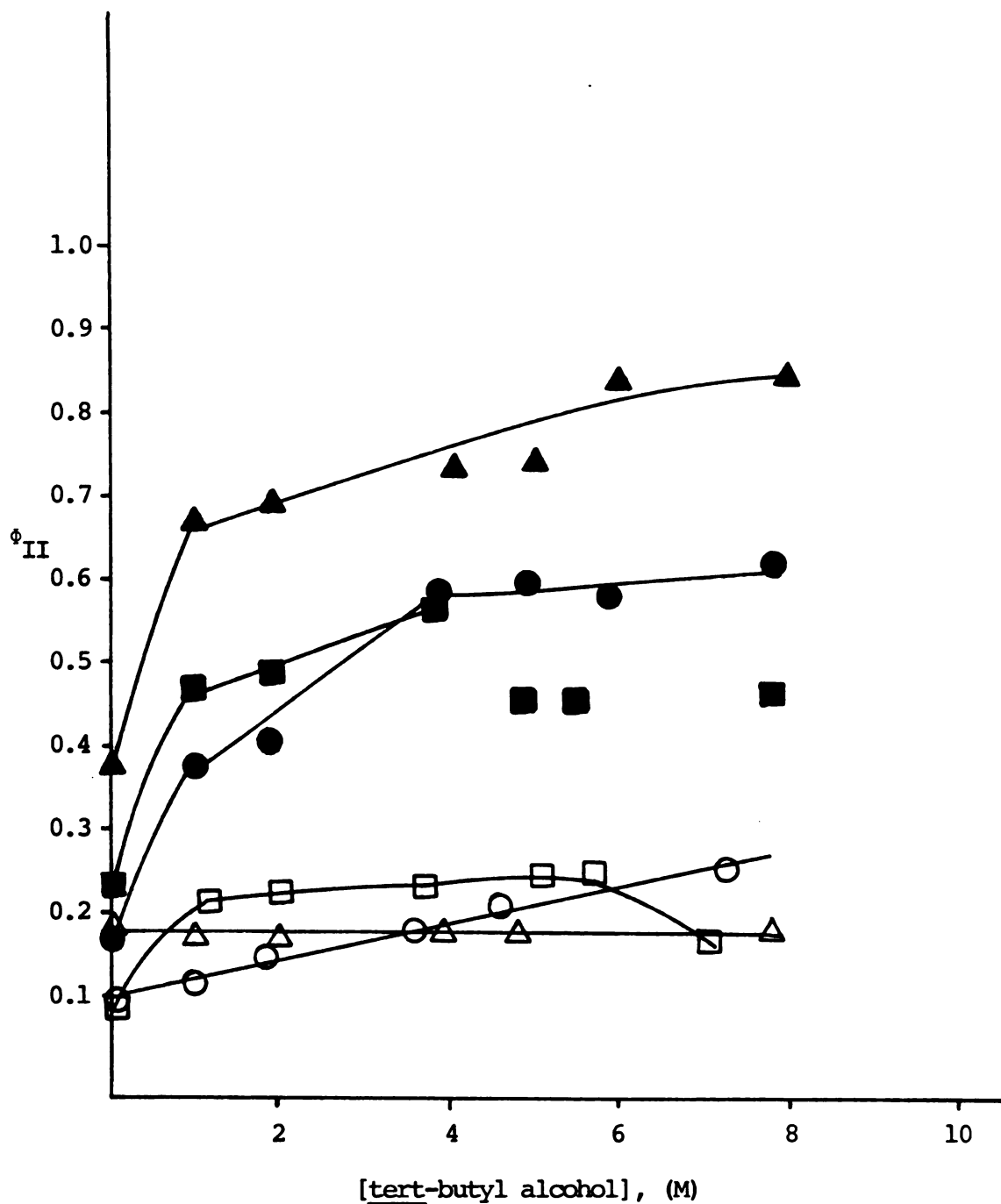


Figure 5. Effect of concentration of *tert*-butyl alcohol on quantum yield of acetylpyridine formation for 2VP (●), 3VP (▲), 4VP (■), 2VPHCl (○), 3VPHCl (△) and 4VPHCl (□). Formation of acetylpyridine monitored.

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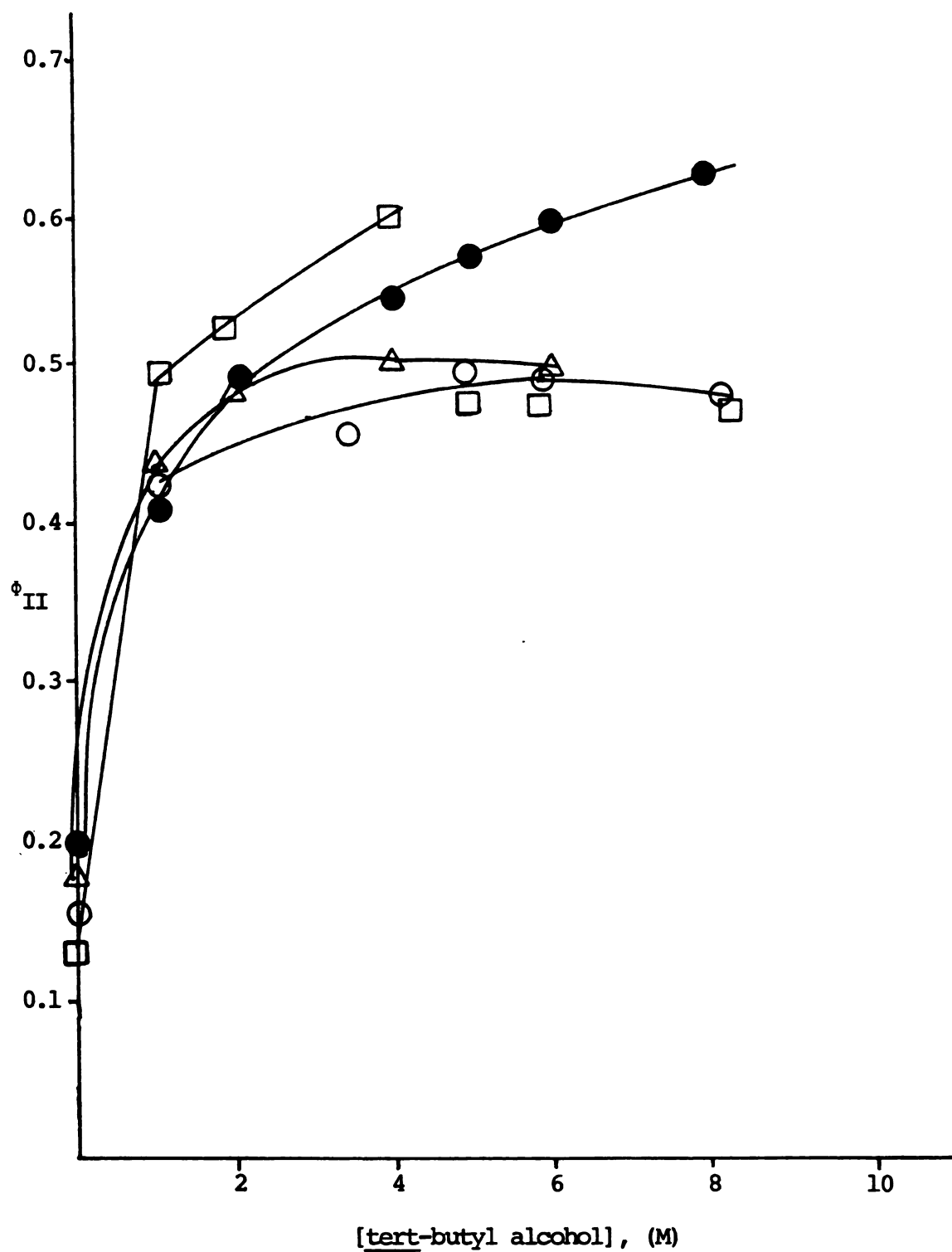


Figure 6. Effect of concentration of *tert*-butyl alcohol on quantum yield of 4-acetylpyridine formation for 4BP (●), γ Me4VP (Δ), 4VP ($\square$) and β Me4BP (○). Formation of 4-acetylpyridine monitored.

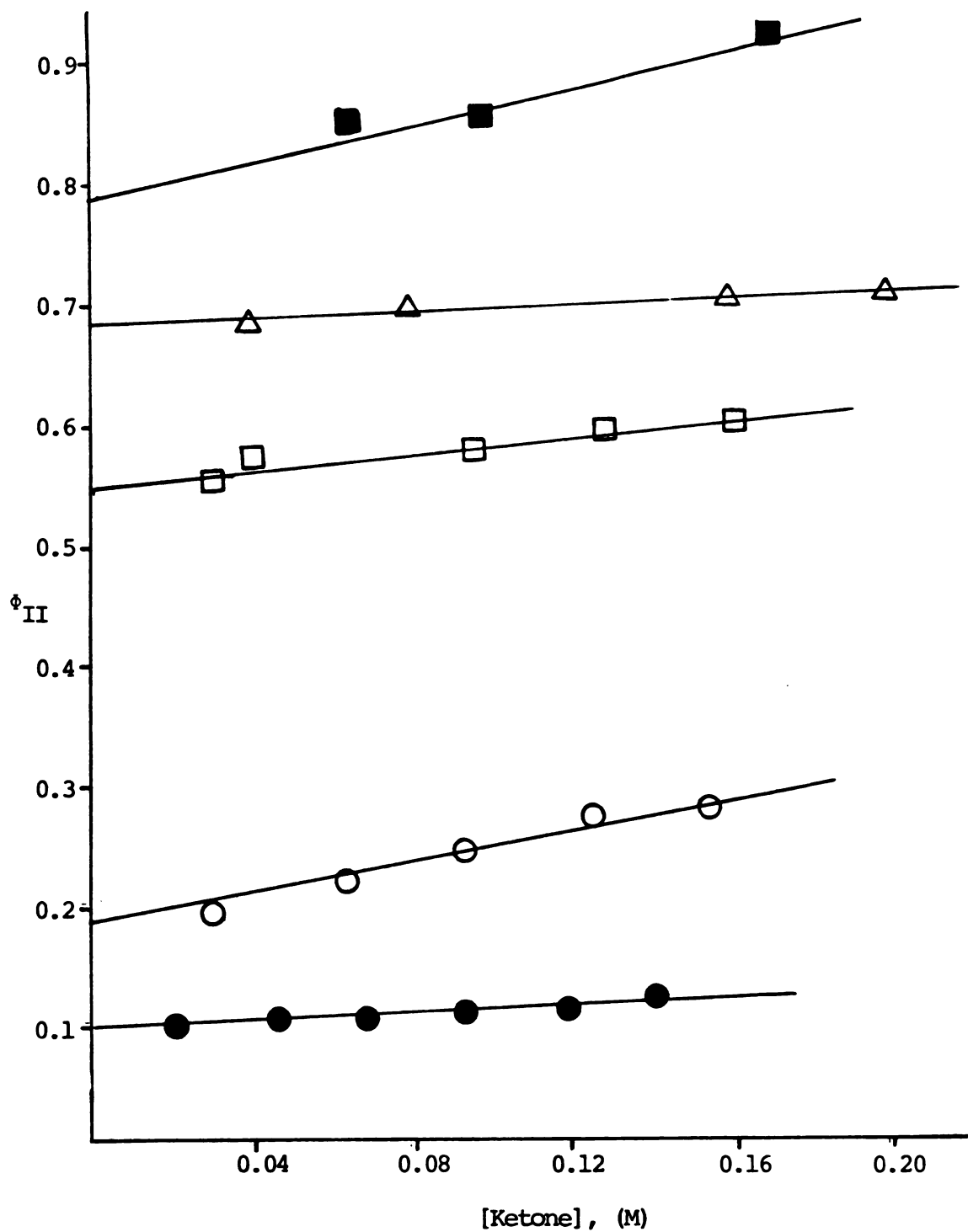


Figure 7. Effect of concentration of ketone on quantum yield for 2VP(△), 3VP(■) and 4VP(□) in acetonitrile; 4VP(○) in benzene and 4VPHCl(●) in acetonitrile. Formation of acetylpyridine monitored.

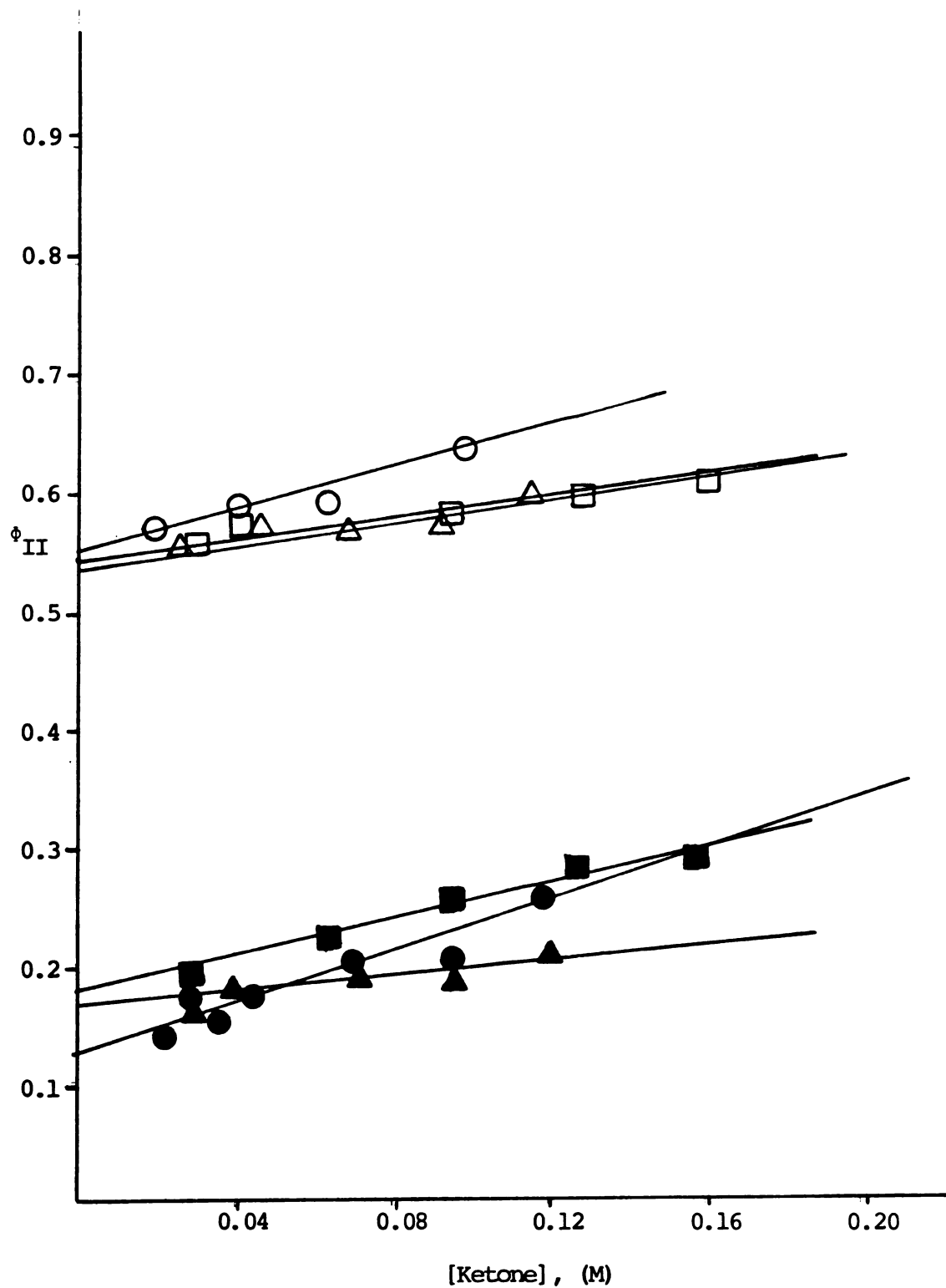


Figure 8. Effect of concentration of ketone on quantum yield for 4BP (○), 4VP (□) and γ Me4VP (△) in acetonitrile; 4BP (●), 4VP (■) and γ Me4VP (▲) in benzene. Formation of acetylpyridine monitored.

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in Table 6.

The error associated with the quantum yields was determined by carrying out at least one duplicate runs per compound and was found to be $\pm 5\%$ for acetylpyridine quantum yields and $\pm 10\%$ for ketone disappearance quantum yields (ϕ_{-K}).

Table 5. Effect of water on the quantum yield of 4-acetylpyridine for 1-(4-pyridyl)pentanone in acetonitrile.

<u>% water</u>	<u>ϕ_{4AP}</u>
1	0.57
2	0.58
3	0.54
4	0.50
5	0.47

Table 6. Effect of various additives on the quantum yield of 4-acetylpyridine for 1-(4-pyridyl)pentanone.

<u>Additive</u>	<u>[4VP] : [ZnCl₂]</u>	<u>ϕ_{4AP}</u>
ZnCl ₂ ^a	4 : 1	0.16
ZnCl ₂ ^a	2 : 1	0.15
ZnCl ₂ ^a	1 : 1	0.14
none		0.23

<u>Additive</u>	<u>Absorbance 4VP : Absorbance Additive</u>	<u>ϕ_{4AP}</u>
[Ru(NH ₃) ₅ py] [BF ₄] ₂ ^a	2 : 1	0.11
[Ru(NH ₃) ₅ 4VP] [BF ₄] ₂ ^a	2 : 1	0.12
BrRe(CO) ₅ ^b	2 : 1	0.042
BrRe(CO) ₃ (4VP) ₂ ^b	2 : 1	0.061

^a acetonitrile solvent. ^b benzene solvent.

Quenching Studies

Stern Volmer quenching studies were performed by the 313 nm irradiation of 0.05 M ketone solutions containing varying amounts of quencher. The concentration of photoproduct, normally an acetylpyridine, was determined using the area ratio of product : internal standard described in the Experimental Section. A cis, trans mixture of 1,3-pentadiene was used for the studies in benzene. Ethyl sorbate and 1,3-pentadiene gave identical results in acetonitrile. Ethyl sorbate was used in acetonitrile solution when high quencher concentration was required because of its greater solubility. Conversions were usually kept below 7% for the tubes without quencher and slopes were linear out to ϕ_0/ϕ values of 6. Duplicate quenching runs indicate a $\pm 5\%$ error in $k_q\tau$ determinations. Values of $k_q\tau$ are listed in Tables 3 and 4. Representative Stern Volmer plots are presented in Figures 9 and 10.

Intersystem Crossing Studies

Intersystem crossing yields were determined by parallel irradiation at 313 nm of 0.05 M ketone solutions containing varying amounts of cis-1,3-pentadiene and 0.1 M acetophenone solutions containing 1.0 M cis-1,3-pentadiene.¹²⁵ The concentrations of cis- and trans-1,3-pentadiene isomers were determined by gc analysis. Plots of $0.55(\phi_{c \rightarrow t})^{-1}$ versus quencher concentration were linear as shown in Figure 11. Irradiation of the pyridyl ketone hydrochloride salts with cis-1,3-pentadiene was accompanied by a competing reaction producing a white precipitate and a product obscuring the cis- and trans-1,3-pentadiene gc peaks.



Figure

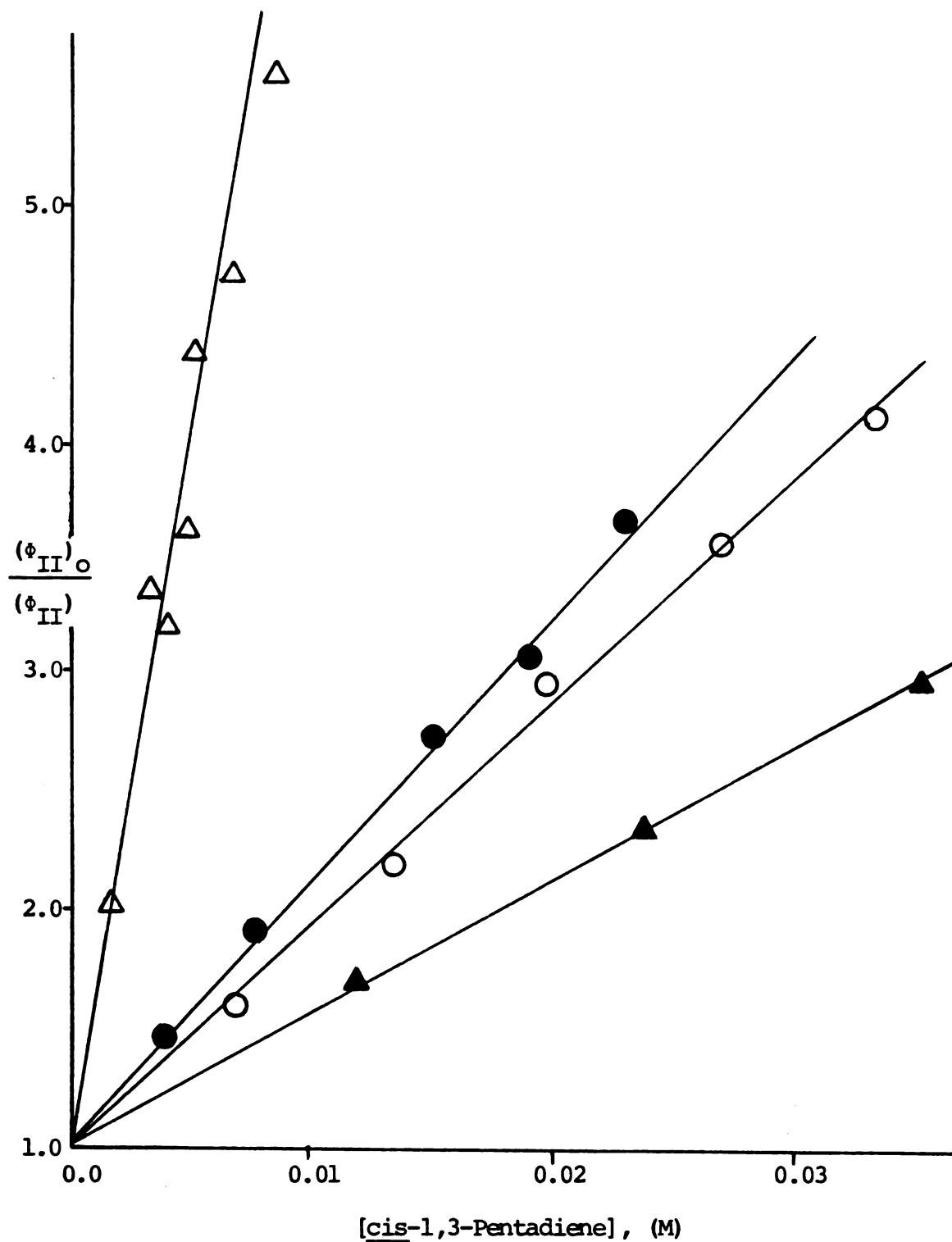


Figure 9. Stern Volmer plot for β Me3BP in benzene($\circ$); β Me3BP($\bullet$), 3BP(Δ) and 2VP($\blacktriangle$) in acetonitrile. Formation of acetylpyridine monitored.

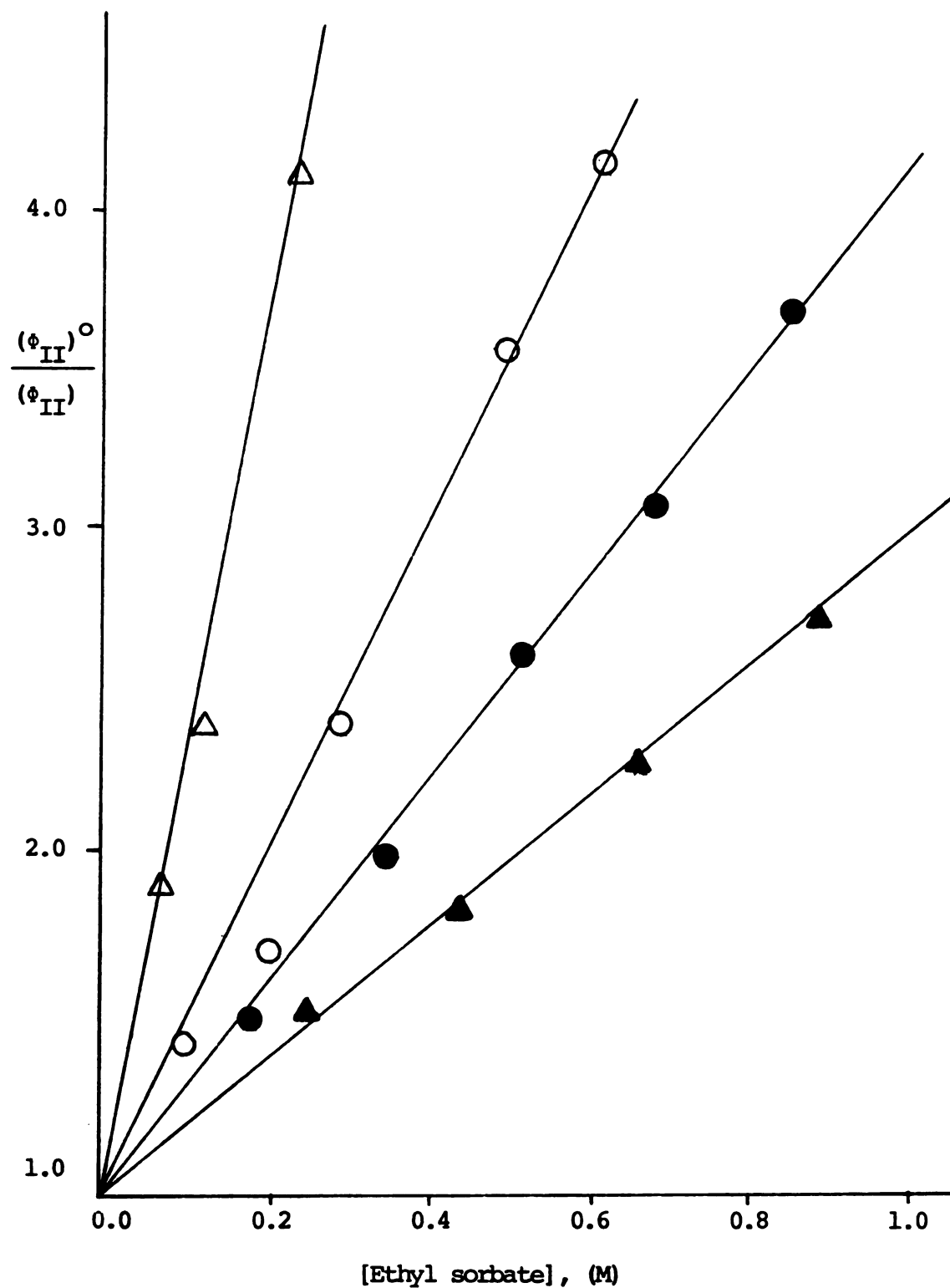


Figure 10. Stern Volmer plots for 3VPyCl ($\circ$), 4VPyCl ($\bullet$), 6Me3BPyCl (Δ) and γ -Me4VPyCl ($\blacktriangle$) in acetonitrile. Formation of acetylpyridine monitored.

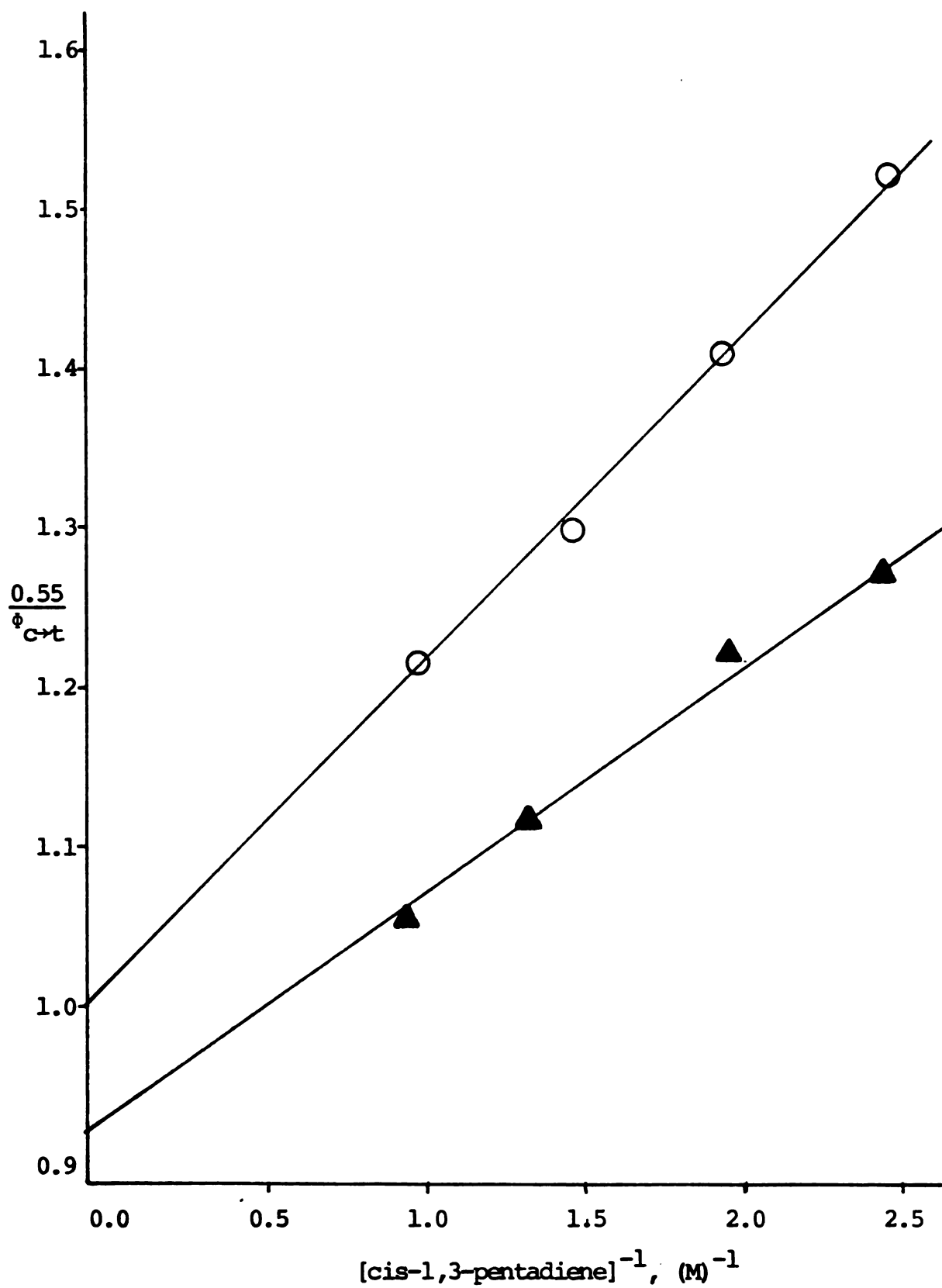


Figure 11. The sensitized isomerization of *cis*-1,3-pentadiene by 4VP ($\circ$) and 3VP ($\blacktriangle$) in benzene.

Intermolecular Photoreduction

Photoproduct Identification

In all cases the photoproduct resulting from the hydrogen atom donating substrate was analyzed for the kinetic studies. Formation of acetone, 2,3-diphenyl-2,3-butanediol, bibenzyl and 1,2-di-*p*-tolylethane was detected by comparison with the gc retention time of authentic samples. Irradiation of the acetylpyridine hydrochloride salts with toluene produced bibenzyl. Irradiation of 3APHCl and 4APHCl with *p*-xylene in acetonitrile produced 1,2-di-*p*-tolylethane and a white precipitate identified as the pyridyl ketone hydrochloride salt pinacol. Irradiation of 3APHCl with 1-phenylethanol in acetonitrile produced a yellow colored solution containing acetophenone and a yellow oil assumed to be the pyridyl ketone hydrochloride salt pinacol. Irradiation of 4APHCl with 1-phenylethanol in acetonitrile produced acetophenone and a white precipitate identified as the pyridyl ketone hydrochloride salt pinacols. Acetophenone pinacol was not detected in the 1-phenylethanol studies. Irradiation of 3APHCl and 4APHCl with 2-propanol in acetonitrile produced acetone and the pyridyl ketone hydrochloride salt pinacols.

Quantum Yields

Quantum yields for acetone, acetophenone and 1,2-di-*p*-tolylethane formation were obtained by the parallel irradiation of degassed samples in acetonitrile and 0.1 M solutions of valerophenone in benzene at 313 nm in the "merry-go-round" apparatus at 25°C.^{131,132} The samples contained 0.01 M pyridyl ketone hydrochloride salt and either 0.0125-1.0 M 2-propanol, 0.1-0.5 M 1-phenylethanol or 0.5-2.5 M *p*-xylene. All quantum yields are corrected for total absorbance of

light by the pyridyl ketone hydrochloride salt. Percent conversion was 5% or less and product/standard area ratios were obtained by gc analysis. Plots of ϕ^{-1} versus $[\text{hydrogen donor}]^{-1}$ were linear (Figures 12-14) and values for the slope and intercept are listed in Table 7. The plot of quantum yield of photoproduct formation versus [4APHC1] was linear.

Quenching Studies

Stern Volmer quenching studies were performed by the 366 nm irradiation of a 0.01 M ketone solution containing a constant amount of hydrogen donor and 0.0015-0.015 M naphthalene in acetonitrile. Conversions were kept below 7% for the tube without quencher and slopes were linear out to ϕ_0/ϕ values of 2. Duplicate quenching runs indicate a $\pm 5\%$ error in $k_q\tau$ determination. Values for $k_q\tau$ are listed in Table 7 and the Stern Volmer plots are presented in Figure 15.

Table 7. Photokinetic data for the intermolecular photoreduction of the pyridyl ketone hydrochloride salts in acetonitrile.^a

<u>Ketone</u>	<u>Donor</u>	<u>Slope</u>	<u>Intercept</u>	<u>$k_q\tau, \text{M}^{-1}$ b</u>
4APHC1	p-xylene	170.	2.5	-
4APHC1	1-phenylethanol	5.9	1.8	6.3-18.5 ^c
4APHC1	2-propanol	1.2	1.8	34 $\pm$ 1 ^d
3APHC1	1-phenylethanol	6.0	2.3	-
3APHC1	2-propanol	6.4	1.2	56 $\pm$ 2 ^e

^a0.01 M ketone, irradiated at 313 nm, all slopes and intercepts analyzed by least squares. ^b366 nm, naphthalene quencher. ^c[1-phenylethanol] = 0.4 M. ^d[2-propanol] = 0.376 M. ^e[2-propanol] = 0.67 M.

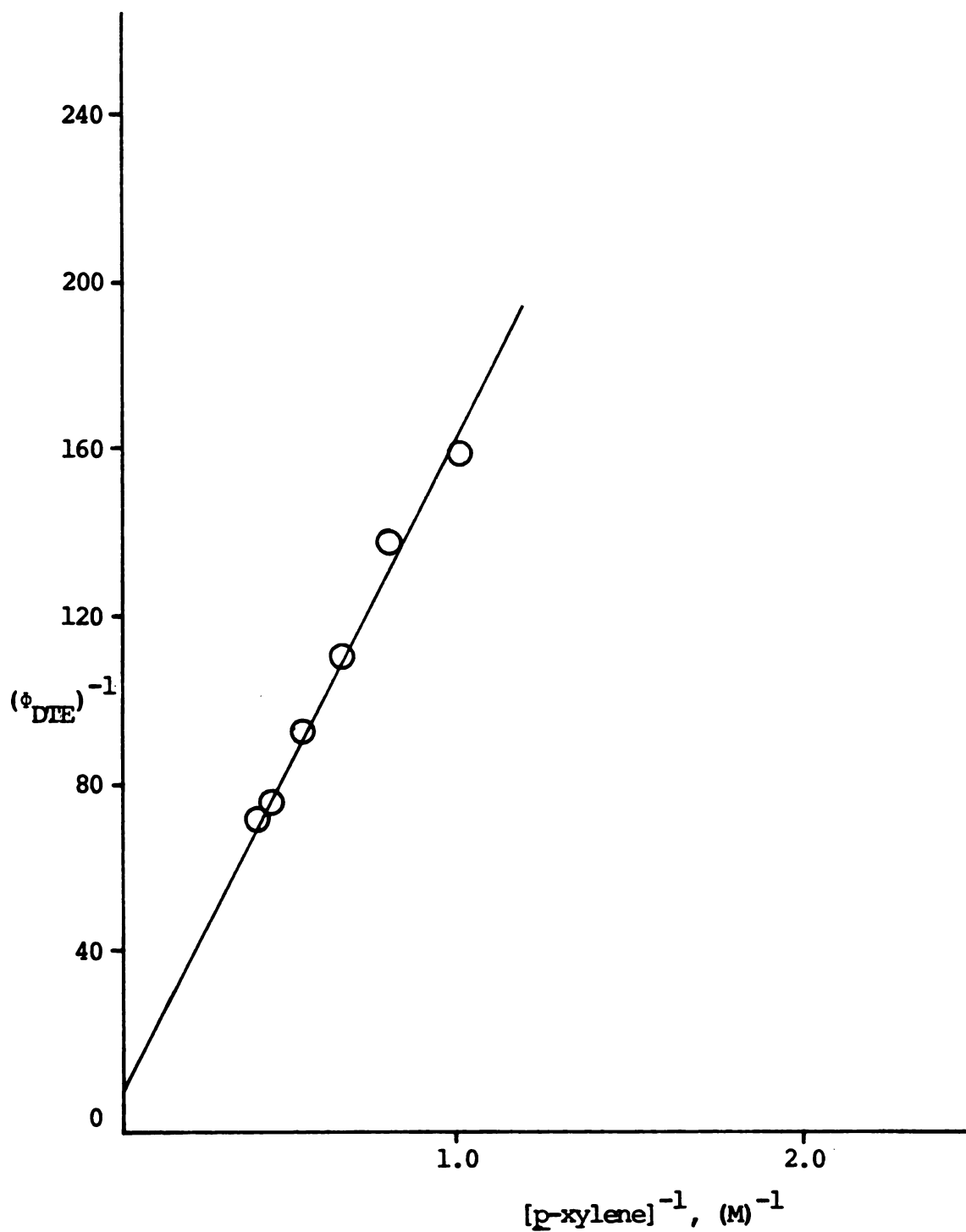


Figure 12. Dependence of quantum yield of 1,2-di-p-tolyethane (DTE) on p-xylene concentration, 4-acetylpyridine hydrochloride in acetonitrile. Formation of DTE monitored.

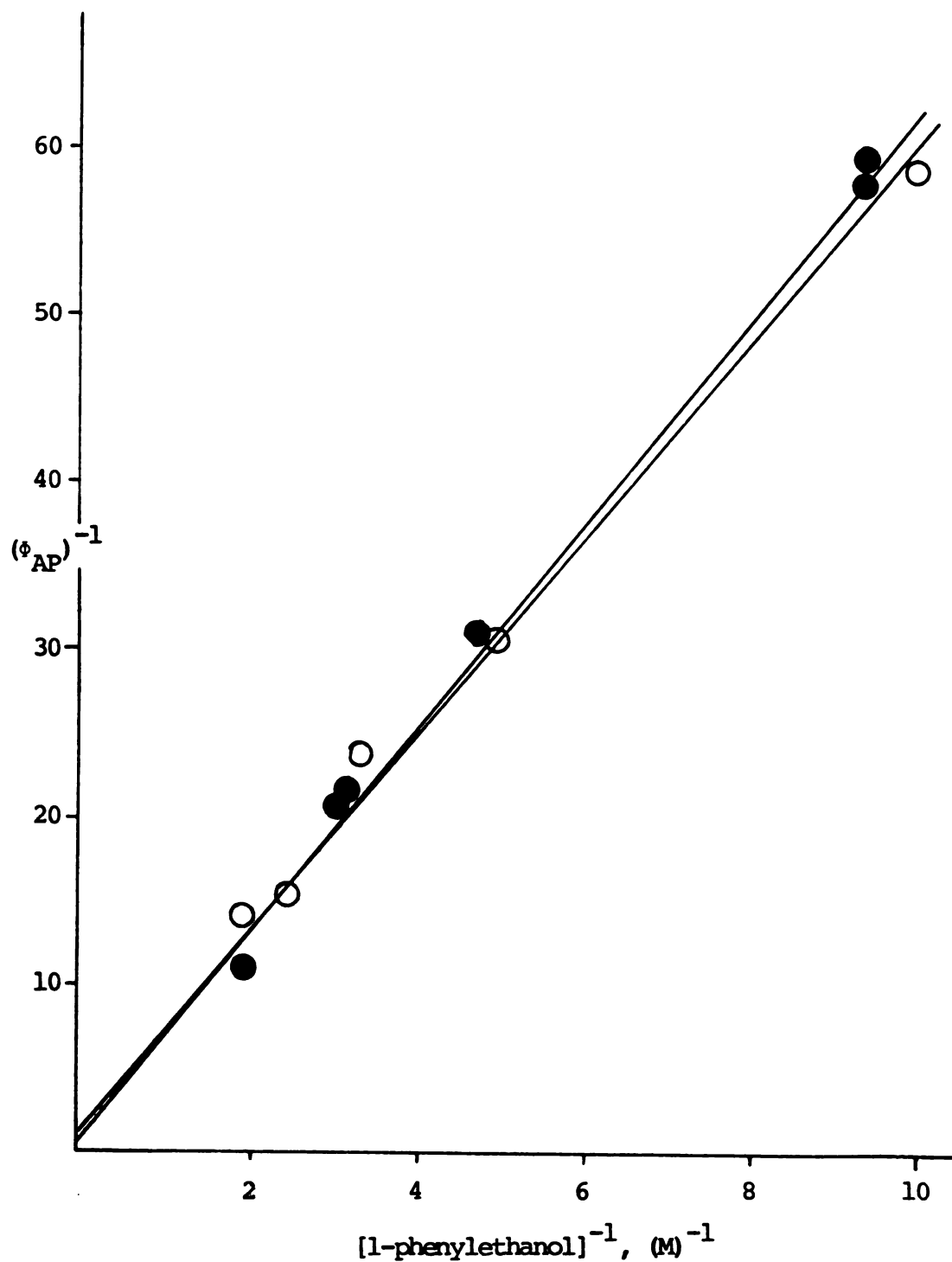


Figure 13. Dependence of quantum yield of acetophenone formation on 1-phenylethanol concentration in acetonitrile, 4-acetylpyridine hydrochloride (○) and 3-acetylpyridine hydrochloride (●). Formation of acetophenone monitored.

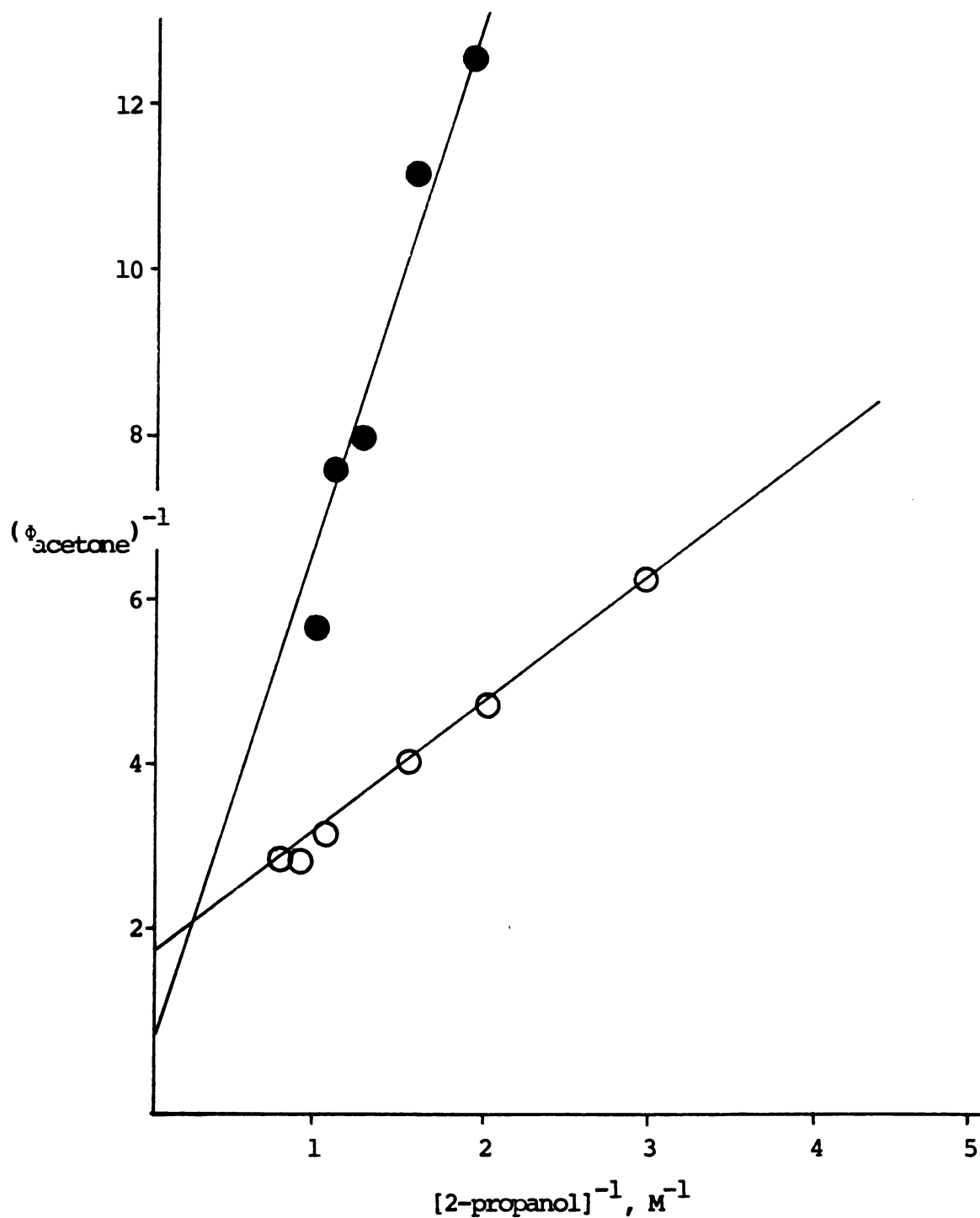


Figure 14. Dependence of the quantum yield of acetone formation on 2-propanol concentration in acetonitrile, 4-acetylpyridine hydrochloride(○) and 3-acetylpyridine hydrochloride(●). Formation of acetone monitored.

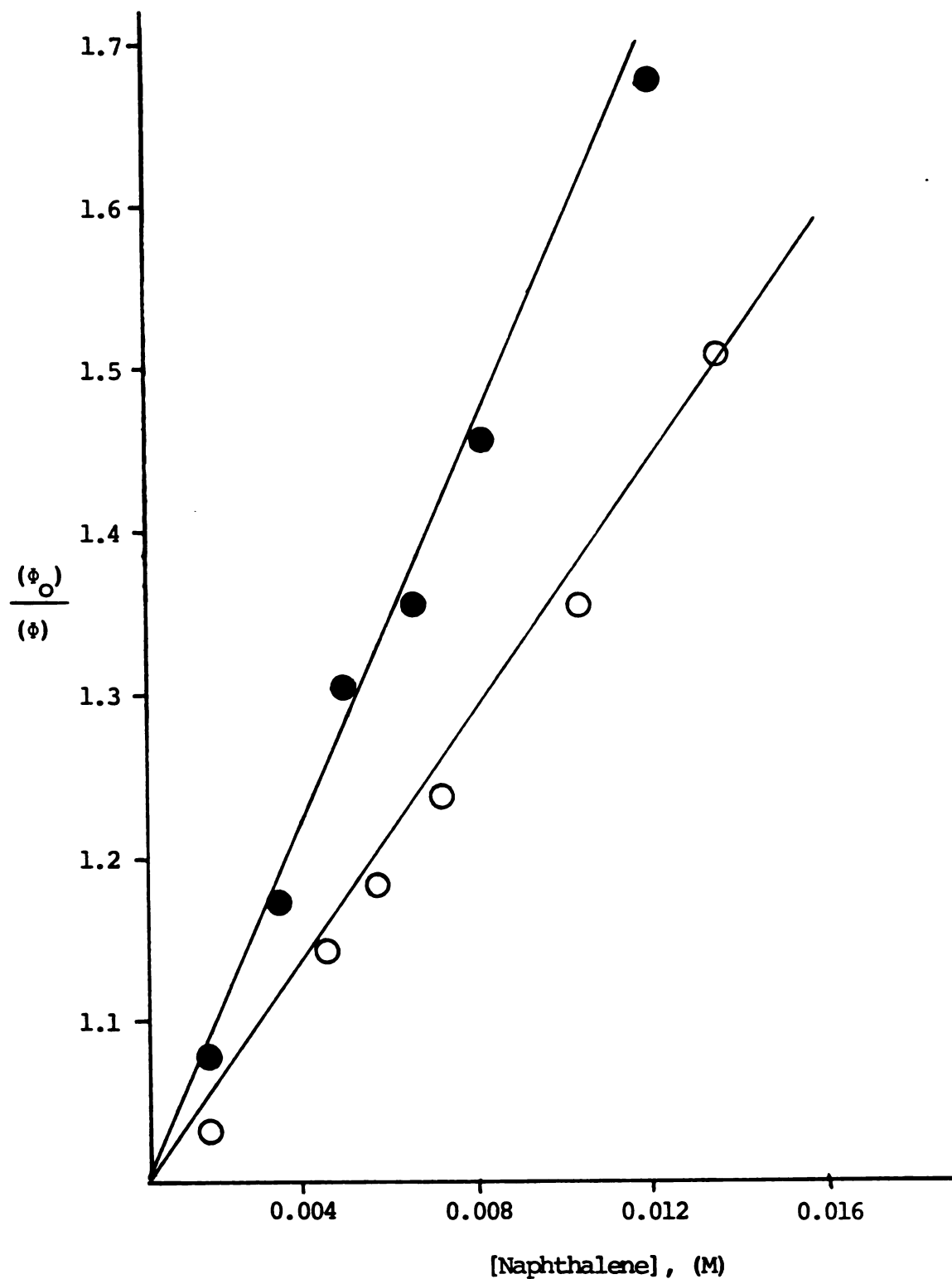


Figure 15. Stern Volmer plots for 4APhCl in the presence of 0.4 M 2-propanol (○) and 3APhCl in the presence of 0.66 M 2-propanol (●) in acetonitrile solution. Formation of acetone monitored.

Product formation is not quenched by 0.04 M naphthalene upon irradiation of 0.01 M 3APHCl with 0.1-0.5 M 1-phenylethanol and 0.01 M 3APHCl and 0.01 M 4APHCl with 0.3-2.5 M *p*-xylene. Formation of 4APHCl from 0.01 M 4VPHCl is quenched by 0.03-1.1 M *p*-xylene with a $k_q\tau$ value of 1.69. The formation of 4APHCl from 0.011 M 4VPHCl is not quenched by 0.01-1.4 M benzene. Formation of 4AP from 0.012 M 4VP is not quenched by 0.0-0.4 M *p*-xylene.

Spectroscopic Studies

The absorption maxima are found in the Experimental Section, while the molar absorptivities (ϵ) and triplet energies (E_T) are listed in Table 8. Corrected phosphorescence spectra (see Experimental Section) were obtained at 77°K in ethanol and a 5:1 mixture of methylcyclohexane 2-methylbutane. Emission spectra for the pyridyl ketone hydrochloride salts were obtained at 77°K in ethanol. The compounds do not emit at room temperature. Concentrations of pyridyl ketone were approximately 1×10^{-4} M. The triplet energies of the butyryl pyridyl ketones lie 3 kcal higher in energy than the valeryl pyridyl ketones. This situation also exists with the phenyl alkyl ketones where E_T (butyrophenone) = 74.5 kcal and E_T (valerophenone) = 71.8 kcal.¹³⁴ The lack of change of triplet energy with solvent polarity for 3VP and 4VP was previously observed with valerophenone.¹³⁴ Representative emission spectra of the pyridyl ketones and corresponding hydrochloride salts are seen in Figures 16-18. The spectra obtained in ethanol are less structured than in the hydrocarbon solvents. The triplet energies of a given pyridyl ketone and its corresponding hydrochloride salt are very similar.

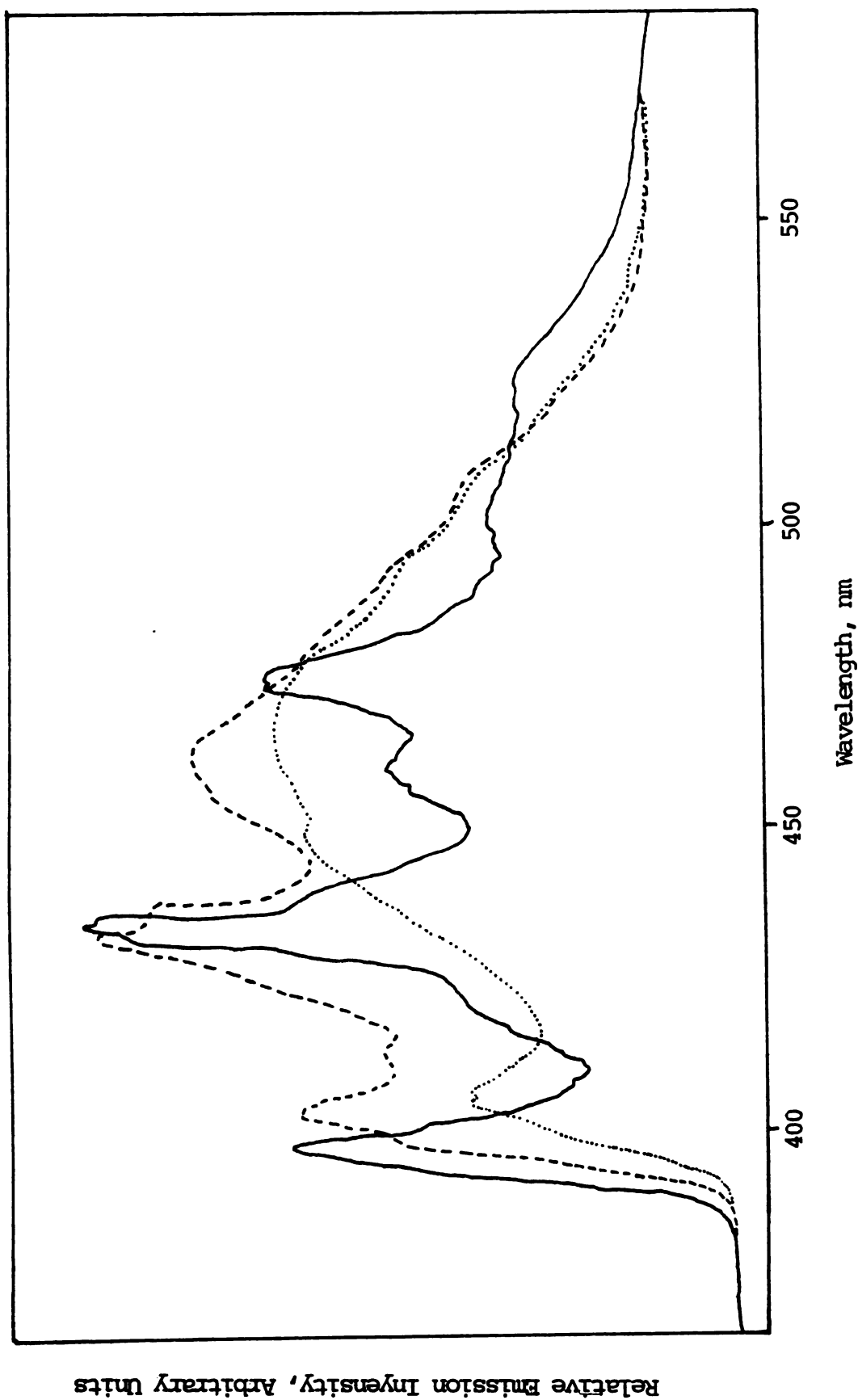


Figure 16. Phosphorescence spectra of 1-(4-pyridyl)pentanone in 5:1 methylcyclohexane:2-methylbutane (—) and ethanol (---); 1-(4-pyridyl)pentanone hydrochloride in ethanol (.....); 77K.

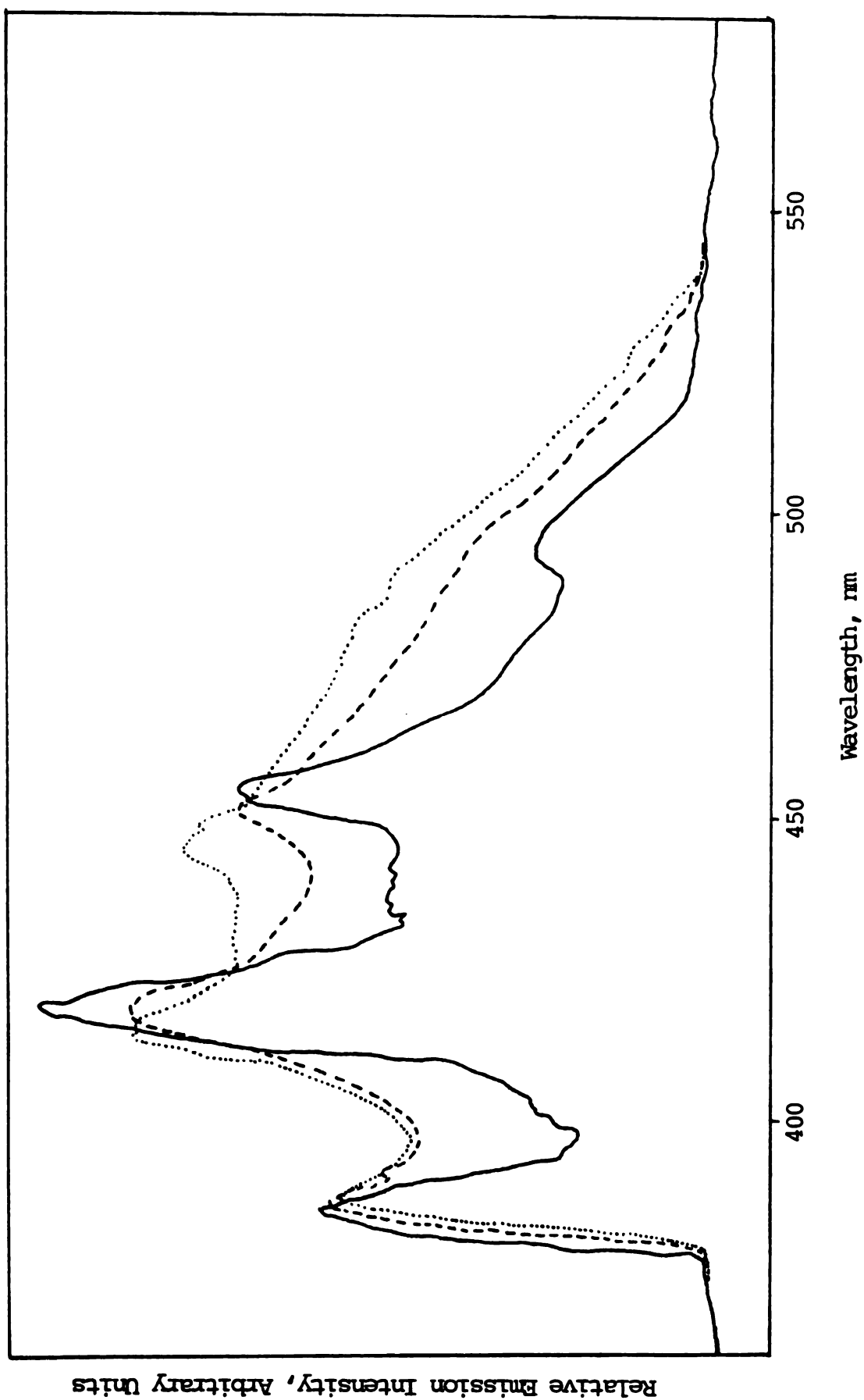


Figure 17. Phosphorescence spectra of 1-(3-pyridyl)pentanone in 5:1 methylcyclohexane:2-methylbutane (—) and ethanol (---); 1-(3-pyridyl)pentanone hydrochloride in ethanol (.....); 77K.

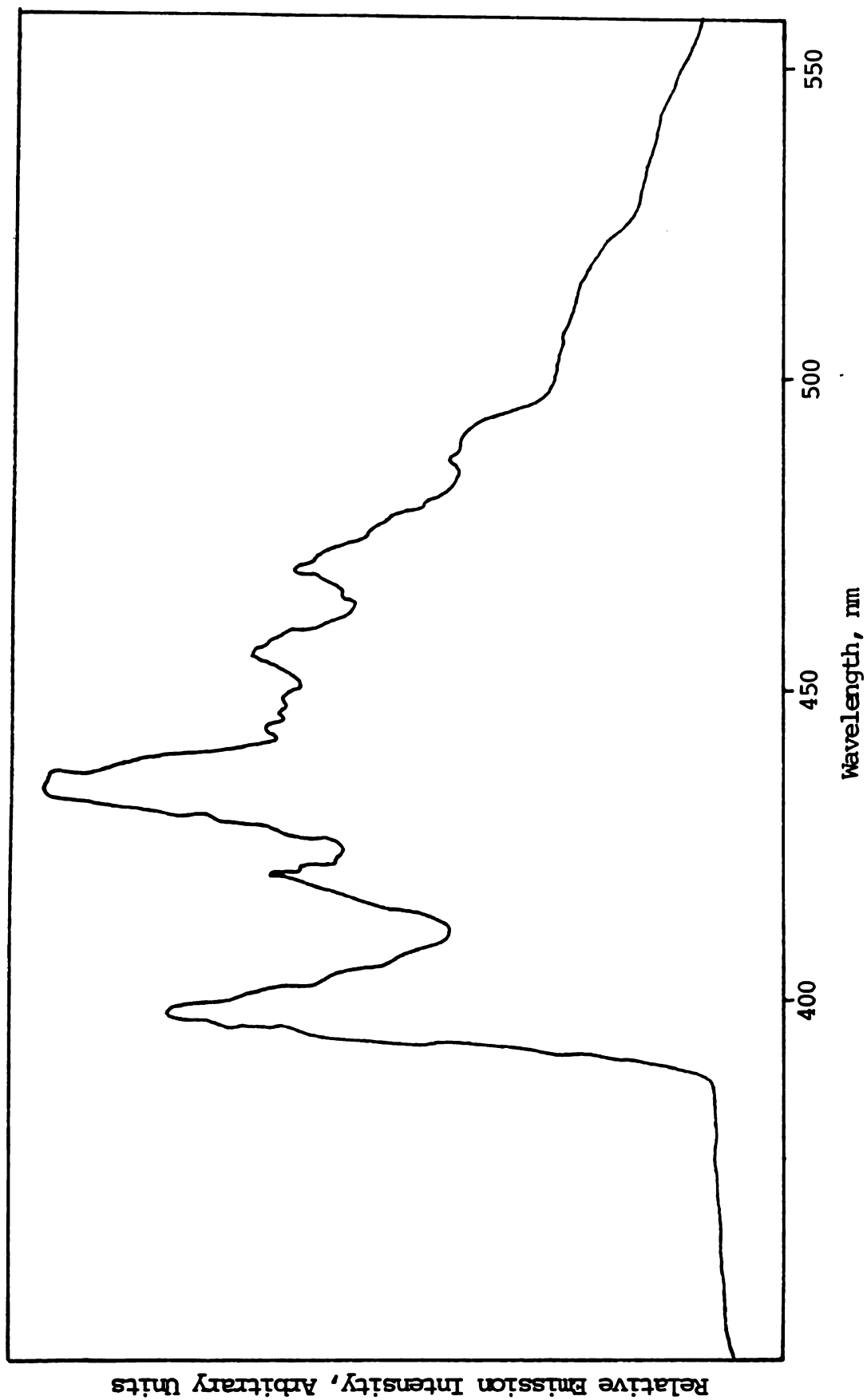


Figure 18. Phosphorescence spectrum of 1-(2-pyridyl)pentanone in 5:1 methylcyclohexane: 2-methylbutane at 77K.

Table 8. Spectroscopic data for the pyridyl ketones and corresponding hydrochloride salts.

<u>Ketone</u>	<u>Absorption</u>		<u>Emission</u>
	<u>Acetonitrile</u>	<u>Benzene</u>	E_T , kcal/mol
	$\epsilon_{313nm},^a M^{-1}cm^{-1}$	$\epsilon_{313nm}, M^{-1}cm^{-1}$	
2AP	77 (85)	74	70.9 ^d 70.9 ^{c,d}
2BP	54 (78)	51	75.2
2VP	62 (93)	41	71.9
γ Me2VP	76 (53)	58	71.8
3AP	51 (38)	49	71.1 ^d 73.1 ^{d,e}
3BP	47 (70)	40	74.5
β Me3BP	57 (97)	42	72.2
3VP	57 (44)	47	73.6 73.6 ^c
4AP	90 (58)	147	69.5 ^d 70.3 ^{d,e}
4BP	88 (61)	88	-
β Me4BP	88 (57)	125	-
4VP	92 (65)	125	71.9 71.0 ^c
γ Me4VP	102 (70)	207	72.4
3VPHCl	(44)	-	73.4 ^c
4VPHCl	(65)	-	70.8 ^c

^aNumbers in parenthesis refer to the corresponding pyridyl ketone hydrochloride salts. ^b5:1 methylcyclohexane:2-methylbutane unless otherwise noted. ^cEthanol. ^dReference 133. ^eReference 133, 1:1 ethanol:methanol.

Ruthenium Complexes

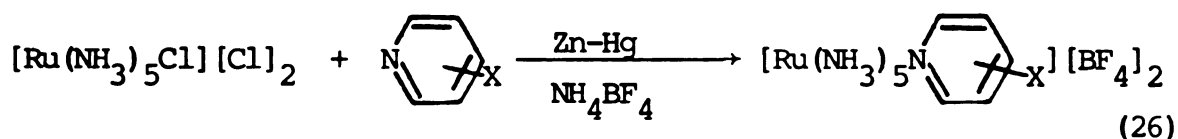
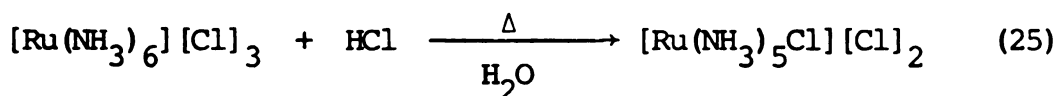
Preparation and Identification

The method of choice for the synthesis of chloropentaammine-ruthenium(III) dichloride is shown in (25). The substituted pyridine pentaammineruthenium(II) complexes were synthesized by dripping an aqueous solution of $[Ru(NH_3)_5Cl][Cl]_2$ through a zinc mercury amalgam

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column into an aqueous solution of excess ligand. The ruthenium(II) complex was then precipitated as the tetrafluoroborate salt (26) as detailed in the Experimental Section. High crude yields were obtained



but great losses in complex resulted on recrystallization. The complexes are stable when stored under argon at 0°C.

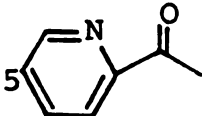
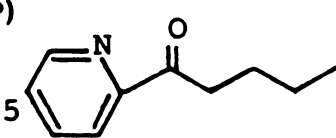
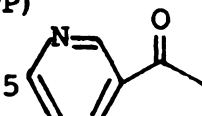
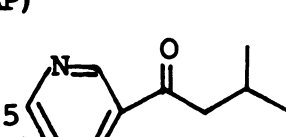
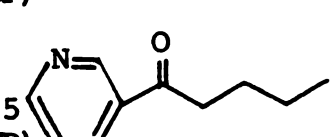
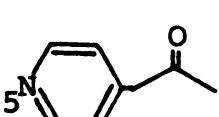
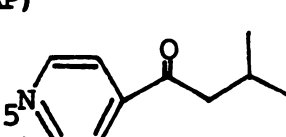
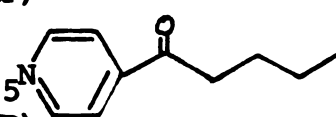
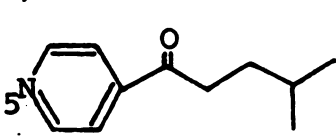
Synthesis using granular mercuric chloride for the zinc mercury amalgam gave pyridine and pyridyl ketone pentaammineruthenium(II) complexes with λ_{max} of the MLCT band matching the literature values ($\epsilon_{\text{MLCT}} = 7700 \text{ M}^{-1}\text{cm}^{-1}$).¹³⁵ $[\text{Ru}(\text{NH}_3)_5\text{py}][\text{BF}_4]_2$ gave the correct elemental analysis while unsatisfactory analysis were obtained for the valerylpyridine pentaammineruthenium(II) complexes. The pentaamine-pyridine ruthenium(II) tetrafluoroborate complex was easily recrystallizable while great product loss accompanied the increase in extinction coefficient of the MLCT λ_{max} (ex. Ru4VP: $\epsilon_{503 \text{ nm}}$ increased from 7700 to 9680 $\text{M}^{-1}\text{cm}^{-1}$) on recrystallization of the pentaamine-ruthenium(II) valerylpyridyl ketone complexes. Only the para-valerylpyridyl ketone complex gave microfine crystals and the best elemental analysis of the isomers.

Synthesis using powdered mercuric chloride for the zinc-mercury amalgam gave pyridyl ketone pentaammineruthenium(II) complexes immediately having high extinction coefficients for the λ_{max} MLCT band (i.e. Ru4VP: $\epsilon_{503 \text{ nm}} = 11400 \text{ M}^{-1}\text{cm}^{-1}$) and recrystallization had

no effect on the λ_{max} MLCT extinction coefficient. Elemental analyses gave the correct percentage of carbon but were somewhat low in hydrogen and nitrogen. The nonreproduceability in duplicate analysis of the same sample and $\pm 0.4\%$ range are indicative of the problems in combustion of the pyridyl ketone pentaammineruthenium(II) complexes. Other workers experienced similar problems, eg. $[\text{Ru}(\text{NH}_3)_5\text{NCR}]^{2+}$ where R = CH_3 , C_6H_5 , $(\text{CH}_2)_4\text{COO}^-$ and $\text{CH}=\text{CHCH}_3$; ¹³⁶ $[\text{Ru}(\text{NH}_3)_5\text{C}_5\text{H}_4\text{NCHO}]^{2+}$, ¹³⁷ and $[\text{Ru}(\text{NH}_3)_5\text{S}(\text{CH}_3)_2]^{2+}$. ¹³⁸

The absorption spectra of the ruthenium(II) pyridyl ketone complexes show intense metal to ligand charge transfer bands (MLCT) in the visible region and intraligand bands (IL) in the ultraviolet region. The absorption spectra for the complexes which were synthesized using powdered mercuric chloride to prepare the zinc-mercury amalgam are listed in Table 9, along with the abbreviations for the complexes. For example, pentaammine[1-(4-pyridyl)pentanone]ruthenium(II) tetrafluoroborate is Ru4VP. The MLCT maximum (λ_{max}) band position depends on both solvent polarity ¹³⁵ and the position of the nitrogen in the ring. Increasing the solvent polarity shifts the MLCT λ_{max} to lower energy. In solvents of similar polarity, meta pyridyl ketone complexes, like the pentaaminepyridineruthenium(II) complex, ⁵¹ show essentially no MLCT band shift. The MLCT band red shifts 15 nm for the para-pyridylketone pentaammineruthenium(II) complexes when the solvent is changed from acetonitrile to water. The position of the nitrogen and its effect on the energy of the MLCT band is reflected in the color of the complex. The yellow pyridyl complex is of highest energy, followed by the blue meta, purple para and orange-red ortho complexes. Representative absorption spectra are shown in Figures 19-22. Finally, the

Table 9. Absorption spectral data for the pentaammineruthenium(II) pyridyl ketone tetrafluoroborate complexes.

Complex	$\lambda_{\max}$, nm (ϵ , $M^{-1}cm^{-1}$)	ϵ_{313nm} , $M^{-1}cm^{-1}$
$[Ru(NH_3)_5]$  (RuPy)	408 (6160) 407 (6270) 244 (4190) ^b	460 _b 830 _b
$[Ru(NH_3)_5]$  (Ru2AP)	624 (4550) 387 (3545) 273 (7385)	1110
$[Ru(NH_3)_5]$  (Ru2VP)	625 (3010) 382 (2565) 272 (6200)	1200
$[Ru(NH_3)_5]$  (Ru3AP)	412 (3350) 258 (3750) 223 (6740)	260
$[Ru(NH_3)_5]$  (Ru β Me3BP)	415 (4700) 259 (6020) 412 (4705) 259 (5330) 277 (7715) ^b	555 _b 650 _b
$[Ru(NH_3)_5]$  (Ru3VP)	412 (4460) 257 (4780) 223 (9995)	330
$[Ru(NH_3)_5]$  (Ru4AP)	510 (11450) 266 (4035)	260
$[Ru(NH_3)_5]$  (Ru β Me4BP)	506 (9820) 266 (3350) 218 (7000)	250
$[Ru(NH_3)_5]$  (Ru4VP)	503 (11400) 268 (2980) 519 (10220) 266 (3095) 223 (6020) ^b	325 _b 310 _b
$[Ru(NH_3)_5]$  (Ru γ Me4VP)	505 (9220) 265 (3690) 519 (9970) 267 (3020) 222 (5560)	400 _b 390 _b

^a Acetonitrile solvent unless otherwise noted. ^b Aqueous solution.

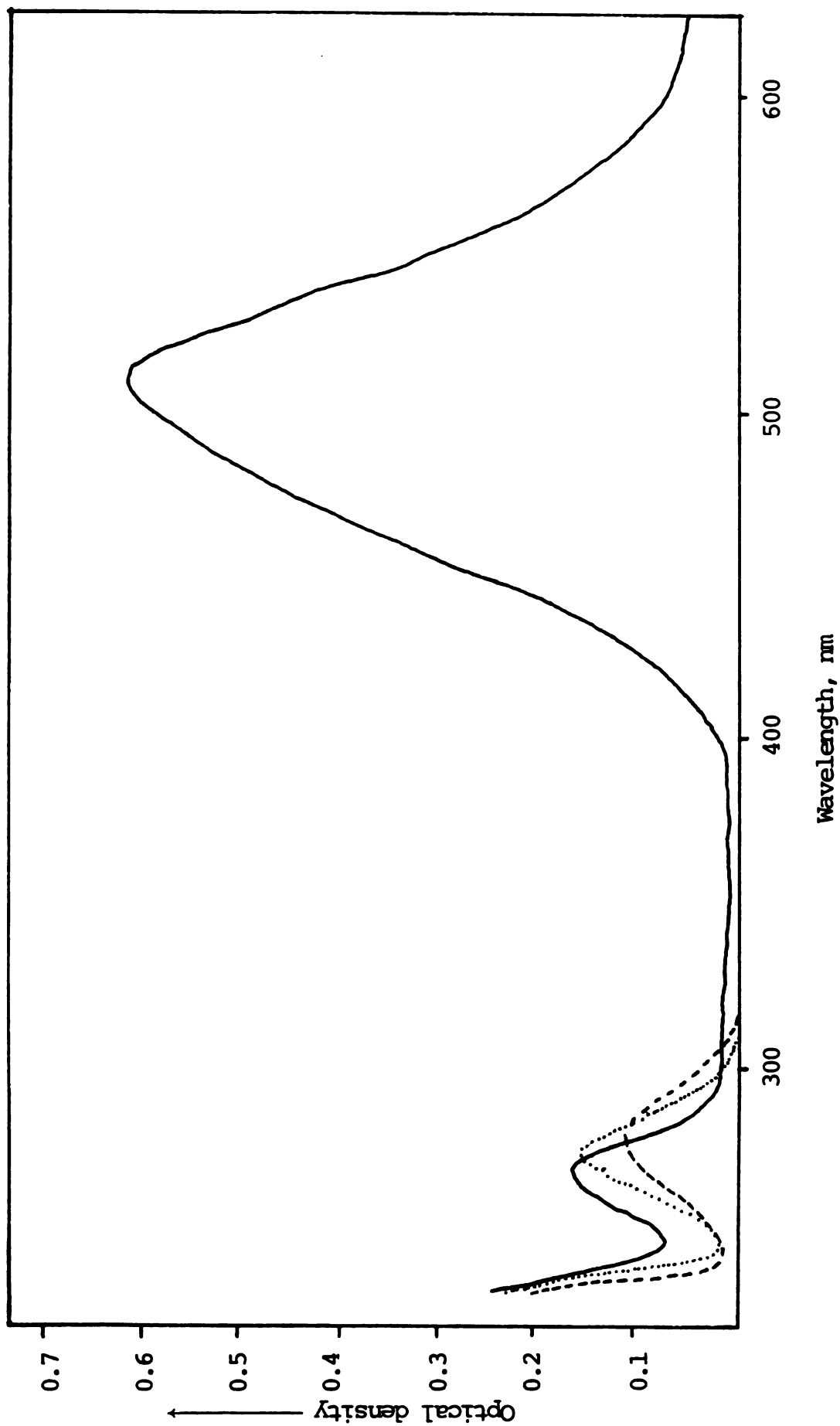


Figure 19. Absorption spectra of 5.4×10^{-4} M $[\text{Ru}(\text{NH}_3)_5(1-(4\text{-pyridyl})\text{pentanone})][\text{BF}_4]_2$ (—), 5.4×10^{-4} M $1-(4\text{-pyridyl})\text{pentanone}$ (---) and 5.1×10^{-4} M $1-(4\text{-pyridyl})\text{pentanone hydrochloride}$ (.....) in acetonitrile.

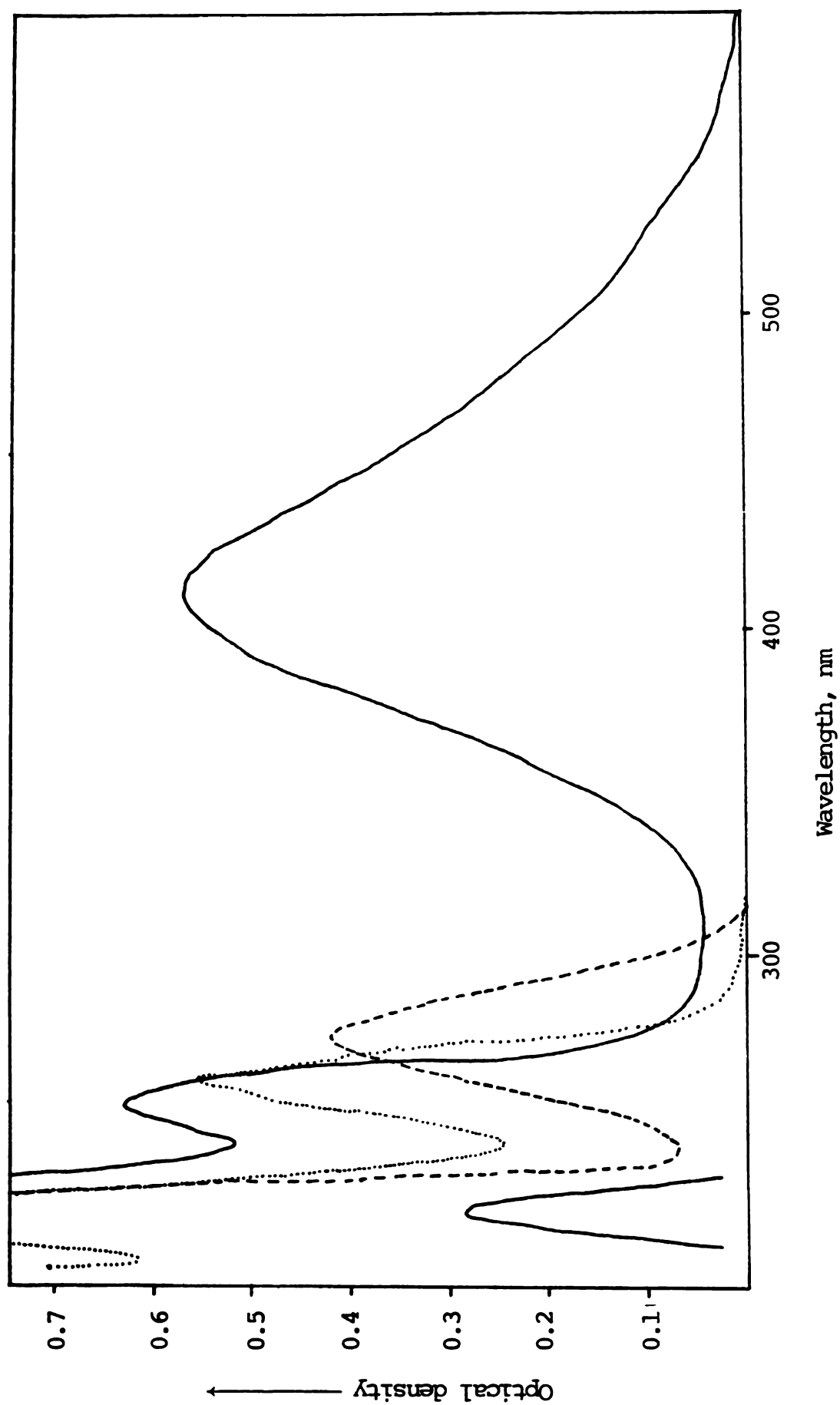


Figure 20. Absorption spectra of $1.3 \times 10^{-4} \text{ M}$ $[\text{Ru}(\text{NH}_3)_5(1-(3\text{-pyridyl})\text{pentanone})][\text{BF}_4]_2$ (—), $1.3 \times 10^{-4} \text{ M}$ $1-(3\text{-pyridyl})\text{pentanone}$ (---) and $1.3 \times 10^{-4} \text{ M}$ $1-(3\text{-pyridyl})\text{pentanone hydrochloride}$ (----) in acetonitrile.

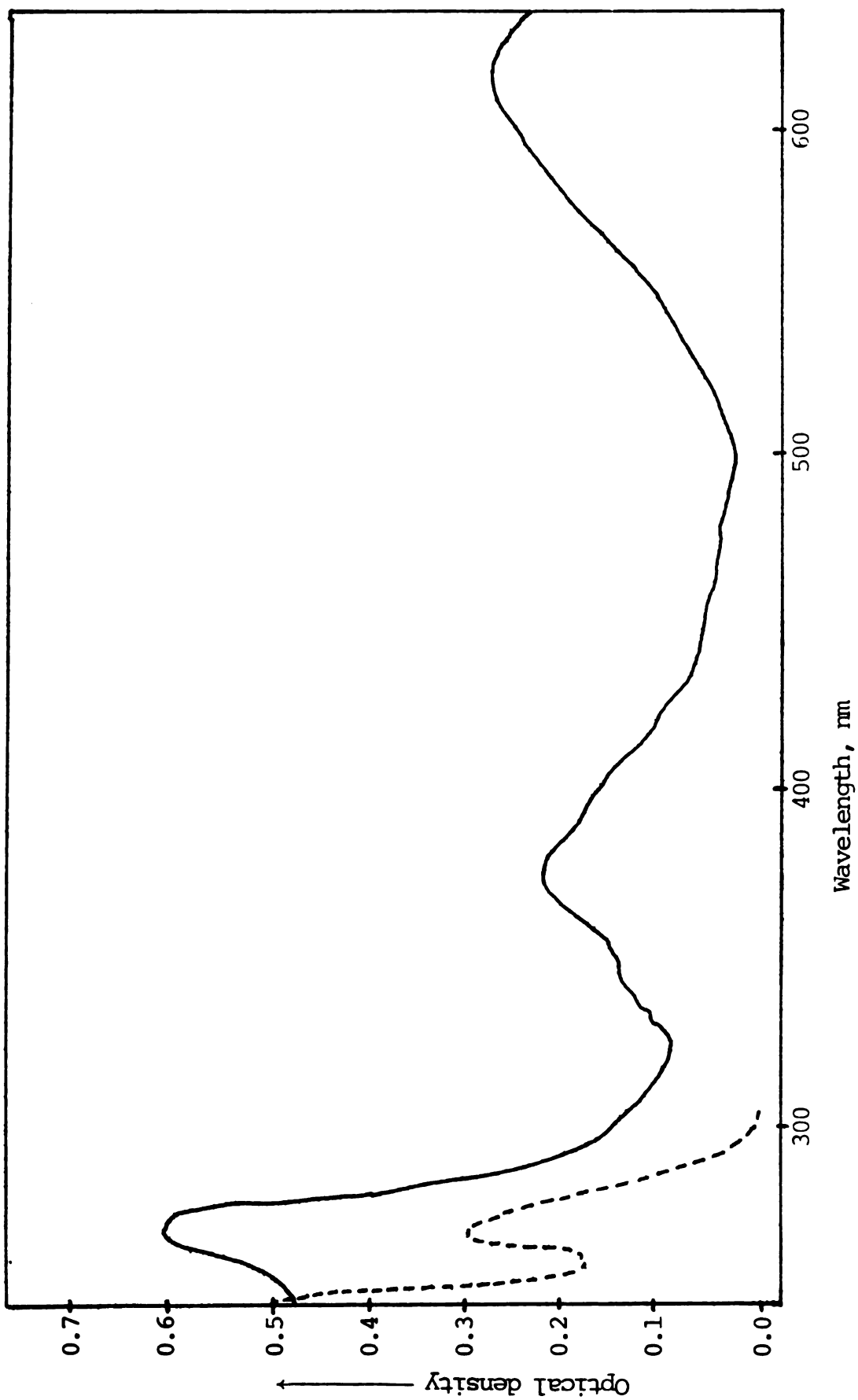


Figure 21. Absorption spectra of 1×10^{-5} M $[\text{Ru}(\text{NH}_3)_5(1-(2\text{-pyridyl})\text{pentanone})] [\text{BF}_4]_2$ (—) and 1×10^{-5} M $1-(2\text{-pyridyl})\text{pentanone}$ (---) in acetonitrile.

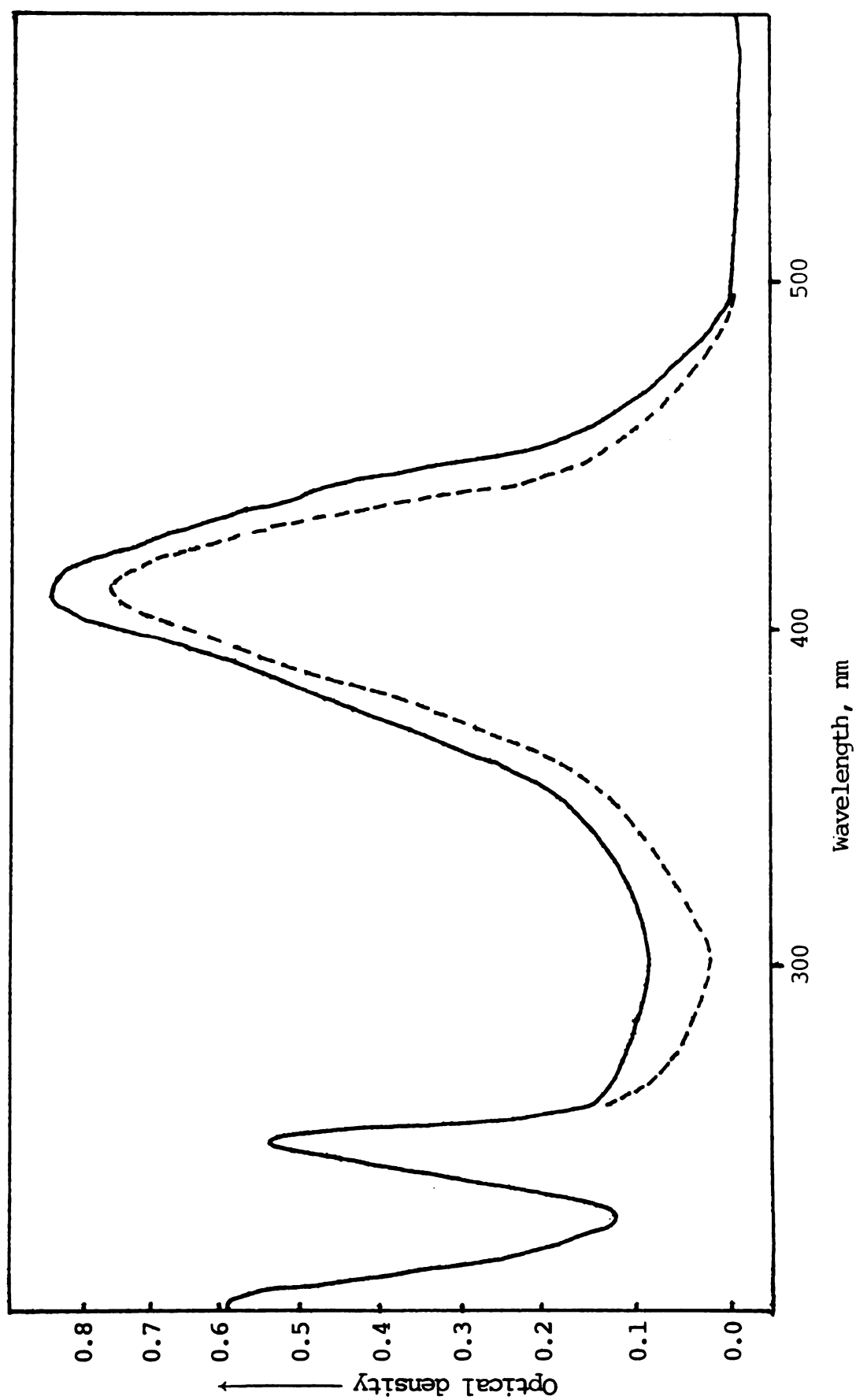


Figure 22. Absorption spectra of $[\text{Ru}(\text{NH}_3)_5(\text{pyridine})](\text{BF}_4)_2$ in aqueous solution at $1.3 \times 10^{-4} \text{ M}$ (—) and acetonitrile at $1.1 \times 10^{-4} \text{ M}$ (---).

infrared spectra of the ruthenium(II) coordinated pyridyl ketone complexes exhibit a broadening and shift to lower frequency for the carbonyl stretch (Table 10). Representative infrared spectra are shown

Table 10. IR band in the CO stretching region for the pyridyl ketone pentaammineruthenium(II) tetrafluoroborates.

<u>Complex</u>	<u>$\nu_{\text{C=O}},^b \text{ cm}^{-1}$</u>	<u>(a)</u>
Ru2AP	1667-1676	(1701)
Ru3AP	1666-1685	(1690)
Ru4AP	1662-1673	(1700)
Ru2VP	1667	(1697)
Ru3VP	1665-1682	(1685)
Ru4VP	1672	(1698)
Ru Me3BP	1674	(1689)
Ru Me4BP	1672	(1693)
Ru Me4VP	1660	(1695)

^aNumbers in parenthesis refer to the corresponding free pyridyl ketones. ^bKBr pellets.

in Figures 23 and 24.

Complex stability

The pyridyl ketone ruthenium(II) complexes are extremely stable in terms of thermal ligand dissociation. When analyzed by gc, no dissociation of the pyridyl ketone ligand from the complex is seen up to injection port temperatures of 250°C. Dissociation does occur at injection port temperatures greater than 280°C, but it is not quantitative and the peaks are broad in comparison to the free ligand:

Injection port temperature:	250°C	280°C	320°C
Maximum fragmentation:	0%	18%	25%

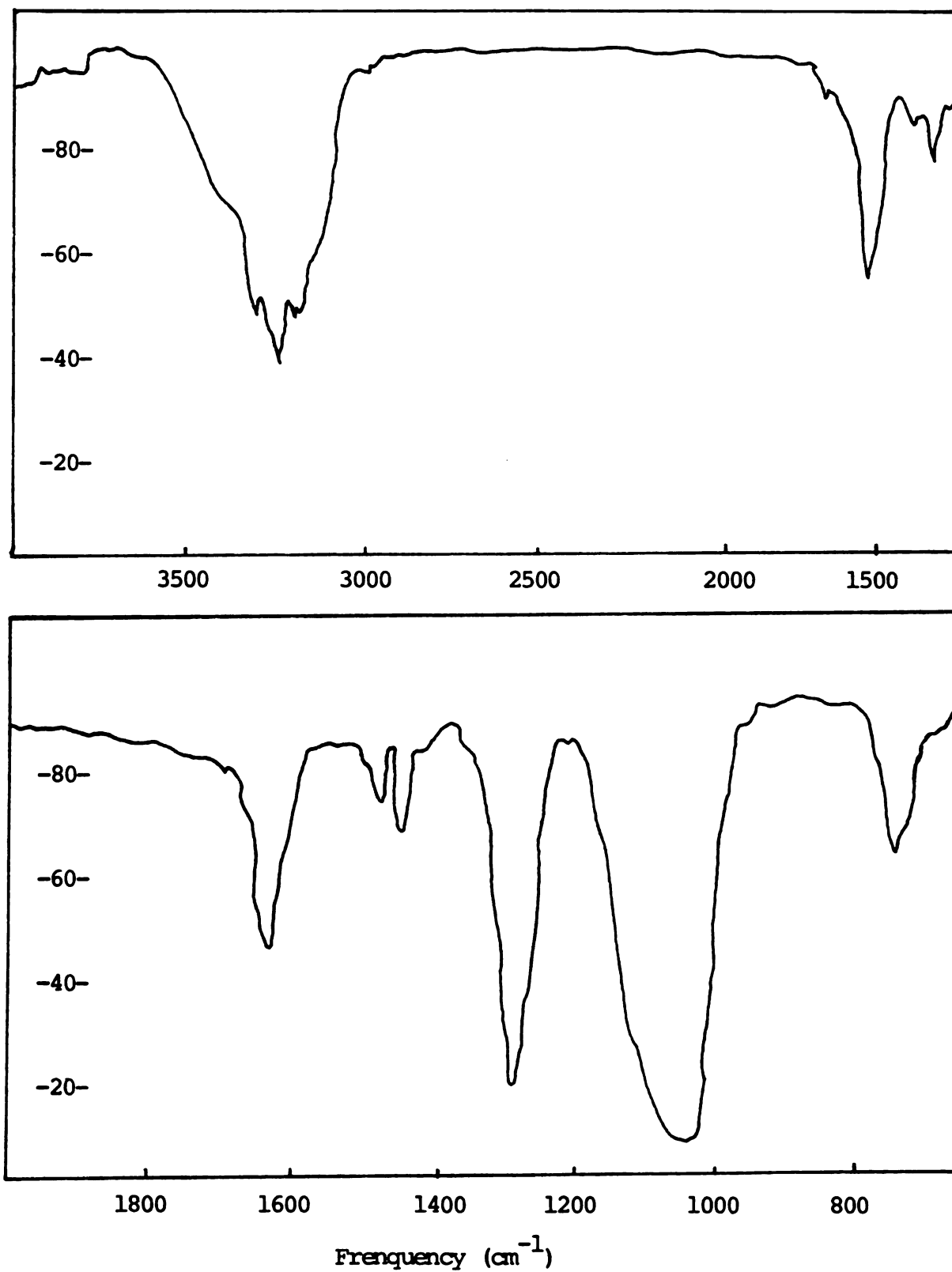


Figure 23. Infrared spectrum of $[\text{Ru}(\text{NH}_3)_5\text{pyridine}][\text{BF}_4]_2$.

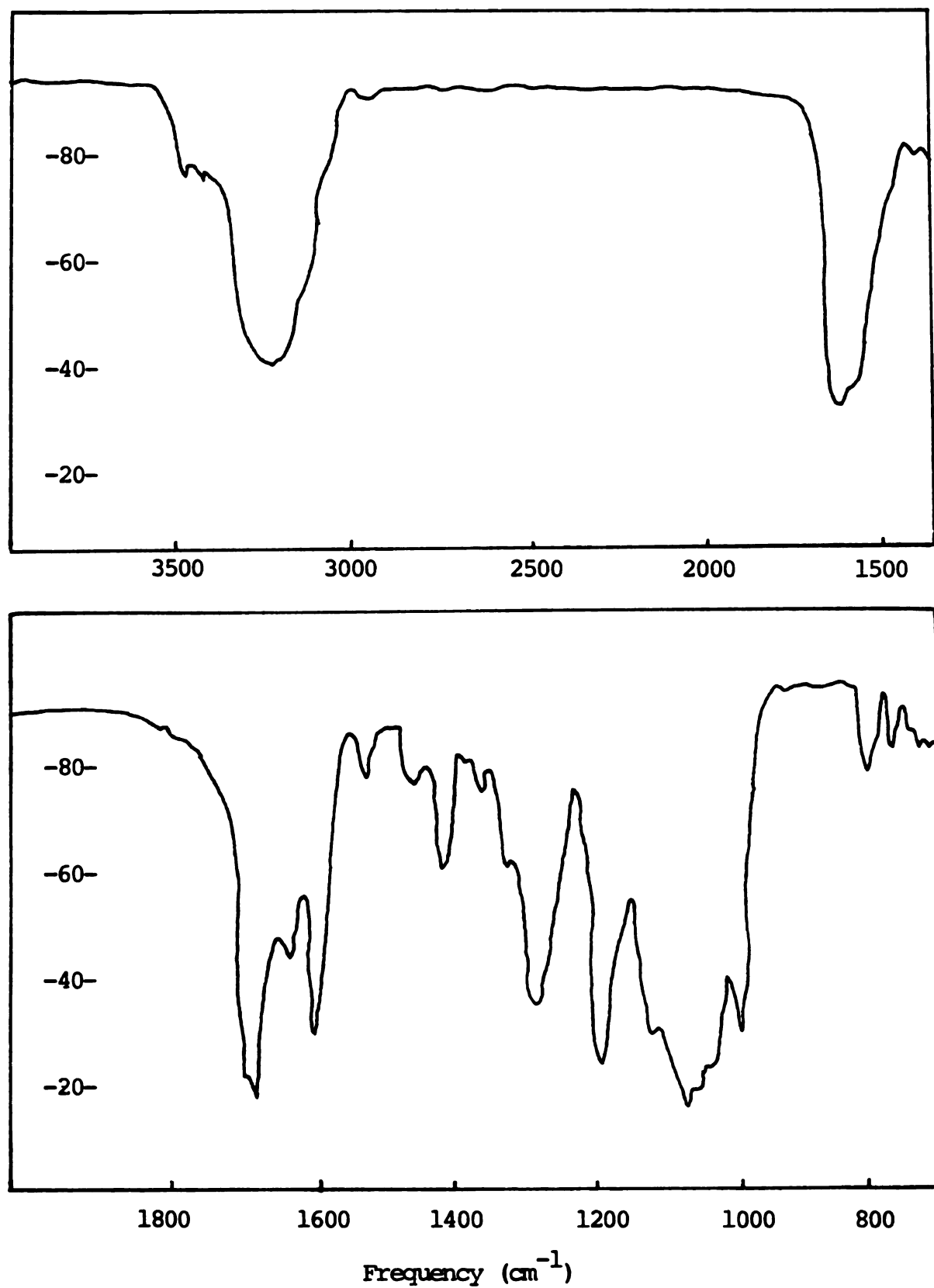


Figure 24. Infrared spectrum of $[\text{Ru}(\text{NH}_3)_5(1-(4\text{-pyridyl})\text{pentanone})] [\text{BF}_4]_2$.

Chemical methods to quantitatively fragment the complex were attempted prior to analysis. Solutions of the complex in both acetonitrile and butyronitrile were refluxed in the presence of excess triphenylphosphine or lithium chloride. This resulted in only 1% ligand fragmentation and was accompanied by a solution color change.

Solution stability of the pyridyl ketone pentaammineruthenium(II) pyridyl ketone complexes was assessed by examination of the absorption spectra. The spectral changes which occur for deaerated aqueous and acetonitrile solutions of pentaamine[4-methyl-1-(4-pyridyl)pentanone] ruthenium(II) tetrafluoroborate ($\gamma\text{MeRu4VP}$) are presented in Table 11.

Table 11. Solution stability of pentaamine[4-methyl-1-(4-pyridyl)pentanone]ruthenium(II) tetrafluoroborate.

<u>Aqueous solution:</u> ^a	<u>λ_{max}, nm (ϵ, $\text{M}^{-1}\text{cm}^{-1}$)</u>
original solution	518(10135) 267(3150) 223(5875)
in dark, 24 hr. (cold)	519(8430) 268(3400) 221(5550)
in dark, 24 hr. (rm.T.)	516(7060) 263(3120) 217(5455)
in light, 24 hr. (rm.T.)	515(1329) 317(3030) 287(3155) 217(7450)
<u>Acetonitrile solution:</u> ^b	
original solution	505(9995) 266(2285)
in dark, 24 hr. (cold)	503(7665) 265(2160)
in light, 24 hr. (rm.T.)	featureless in visible 265(2065)

^a $[\text{Ru}\gamma\text{Me4VP}] = 1.5 \times 10^{-5} \text{ M.}$ ^b $[\text{Ru}\gamma\text{Me4VP}] = 1.04 \times 10^{-5} \text{ M.}$

When kept in the cold and in the dark, acetonitrile solutions are more stable towards pyridyl ketone ligand dissociation than are aqueous solutions. Upon exposure to daylight, the optical density at the MLCT λ_{max} gradually decreases for $\text{Ru}\gamma\text{Me4VP}$ (Figure 25). The position of the

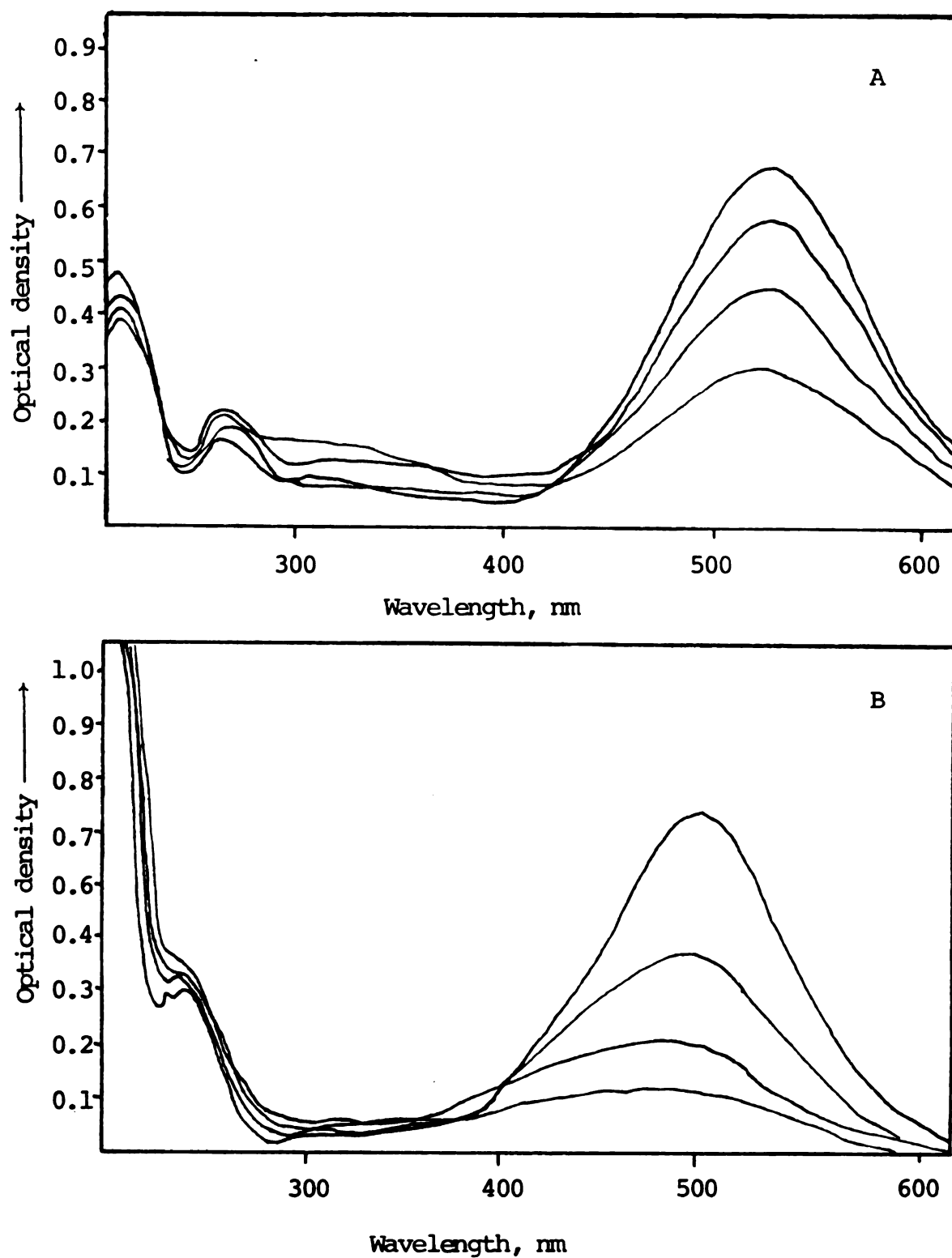


Figure 25. Solution stability upon exposure to light of Ru γ Me₄VP in:
A) aqueous solution. B) acetonitrile solution

MLCT band changes little in aqueous solution and undergoes a blue shift in acetonitrile solution; in both cases the optical density gradually decreases. All the pyridyl ketone ruthenium(II) complexes which were synthesized undergo the same type of decomposition illustrated here. The changes in MLCT band position and absorbance at the MLCT $\lambda_{\max}$ upon irradiation at 313 nm are listed in Table 12. All the complexes undergo the same photochemical decomposition illustrated here.

Table 12. Photochemical stability of pentaammine[4-methyl-1-(4-pyridyl)pentanone]ruthenium(II) tetrafluoroborate.^d

<u>Time, hr.</u>	<u>$\lambda_{\max}^b$, nm</u>	<u>Absorbance</u>	<u>$\lambda_{\max}^c$, nm</u>	<u>Absorbance</u>
0.0	519	0.619	505	0.719
2.0	518	0.563	499	0.532
4.5	518	0.473	490	0.317
6.5	517	0.368	475	0.105
18.0	517	0.246	460	0.072

^a[Ru^{Me}4VP] = 1.49×10^{-5} M in aqueous solution, 0.00017 einsteins/hr.

^b[Ru^{Me}4VP] = 1.05×10^{-5} M in acetonitrile, 0.0097 einsteins/ hr.

^c λ_{irr} = 313 nm.

Intramolecular Type II Reaction

Photoproduct Identification

Upon irradiation at 313 nm in acetonitrile solution all complexes produced alkene and some produced pyridyl ketone. The alkene produced in the irradiation of the ruthenium(II) pyridyl ketone complex was identified by comparison of the gc retention time with alkene produced by the irradiation of an uncomplexed pyridyl ketone sample. The alkene concentration determined by this method was found to be within $\pm 3\%$ of

the acetylpyridine concentration determined under analysis conditions for low ketone concentrations. The pyridyl ketones produced upon irradiation of the ruthenium(II) pyridyl ketone complexes were identified by comparison of the gc retention time with authentic samples. All samples were analyzed immediately after photolysis.

Quantum Yield and Quenching Studies

Quantum yields for product formation and Stern Volmer quenching constants were measured by the same methods as those for the pyridyl ketones and their hydrochloride salts. Alkene formation was quenched by ethyl sorbate. Conversions were kept below 3% for quantum yield studies and below 5% for the tube without quencher in the quenching studies. The error estimated in the quantum yield studies was determined by carrying out at least duplicate runs per complex and found to be $\pm 5\%$. Duplicate quenching runs indicate a $\pm 8\%$ error in the $k_q \tau$ determination. Table 13 lists the quantum yields obtained from the complexes synthesized using granular zinc chloride for the zinc mercury amalgam. Table 14 lists the quantum yields and $k_q \tau$ values obtained from the complexes synthesized using powdered mercuric chloride for the zinc mercury amalgam. The Stern Volmer plots for the compounds in Table 14 are presented in Figure 26.

Intermolecular Photoreduction

The irradiation procedures and methods of photoproduct identification were identical to those used in the intermolecular photoreduction studies of the pyridyl ketone hydrochloride salts. Irradiation of acetonitrile solutions of the acetylpyridine pentaammineruthenium(II) complexes in the presence of p-xylene, 1-phenylethanol or 2-propanol

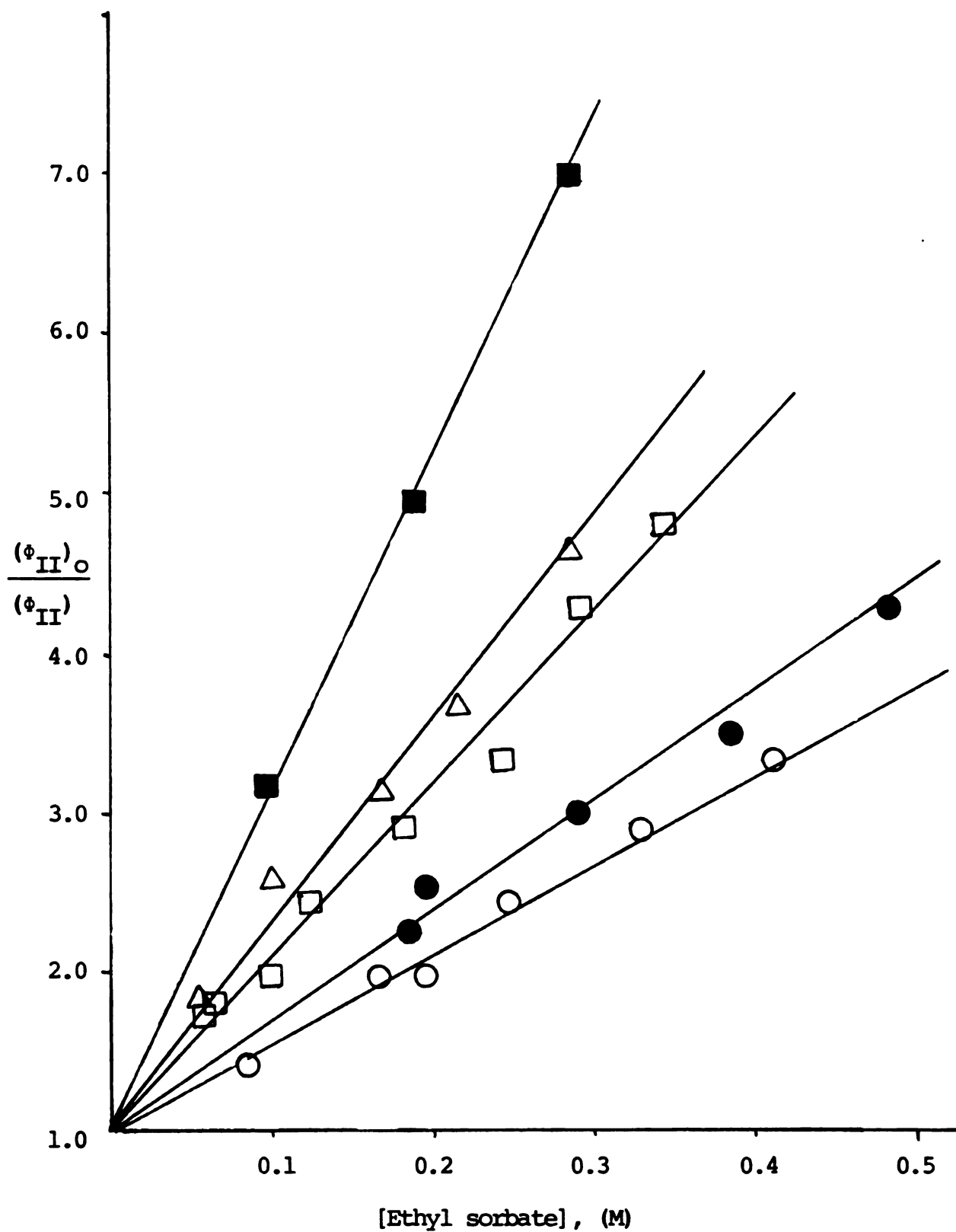
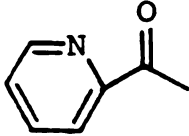
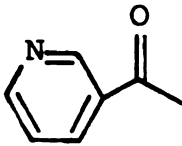
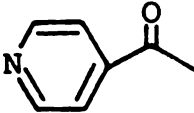


Figure 26. Stern Volmer plots for Ru⁴Me₄VP (○), Ru₄VP (●), Ru₃VP (□), Ru⁸Me₃BP (■) and Ru⁸Me₄BP (△) in acetonitrile. Formation of alkene monitored.

Table 13. Quantum yields for $[\text{Ru}(\text{NH}_3)_5\text{L}][\text{BF}_4]_2$ in acetonitrile.^a

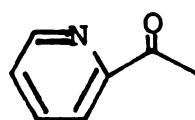
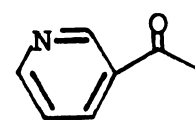
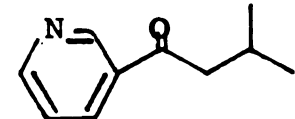
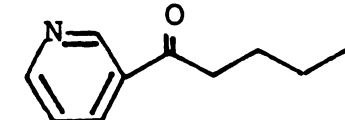
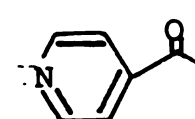
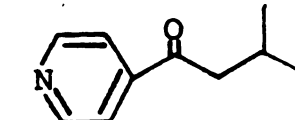
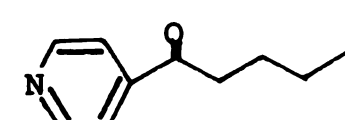
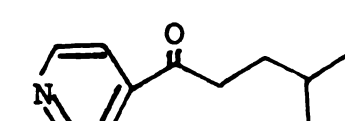
L	ϕ_{propene}	ϕ_{AP}	ϕ_{VP}
	0.0035 (0.00804)	0 (0)	0 (0)
	0.081 (0.12)	0.01 (0.04)	0.08 (0.063)
	0.0097 (0.0081)	0 (0)	0 (0)

^a0.01 M, irradiated at 313 nm; synthesized from granular zinc chloride for the zinc mercury amalgam; recrystallized from water; numbers in parenthesis refer to the quantum yield obtained in the presence of the sensitizer acetophenone.

was accompanied by decreases to various extents in the optical density of the MLCT band. Complete bleaching of the MLCT band resulted upon irradiation of the acetylpyridine pentaammineruthenium(II) complexes in the presence of *p*-xylene for the time required for measureable 1,2-di-*p*-tolylethane formation. In quantum yield studies with 2-propanol, a blue shift and less dramatic decrease in the optical density of the MLCT band accompanied acetone formation:

$[\text{Ru4AP}]_0, \text{M}$	0.0108	0.00998	0.00961	0.00990	0.00990
$[2\text{-propanol}], \text{M}$	1.005	0.804	0.603	0.403	0.201
$\lambda_{\text{max}}, \text{nm}$	503	500	500	500	500
$[\text{Ru4AP}], \text{M}$	0.00951	0.00893	0.00817	0.00753	0.00604

Table 14. Photokinetic data for $[\text{Ru}(\text{NH}_3)_5\text{L}][\text{BF}_4]_2^{\text{a}}$ in acetonitrile.

<u>L</u>	<u>ϕ_{propene}</u>	^b <u>ϕ_{AP}</u>	<u>ϕ_{L}</u>	<u>$k_{\text{q}}\tau, \text{M}^{-1}$</u>
	0.0	0.0	-	-
	0.0	0.028	-	-
	0.020	0.0	0.043	22.0
	0.020	0.0	0.081	10.5
	0.0	0.0	-	-
	0.023	0.0	0.0	13.0
	0.019	0.0	0.0	6.6
	0.020	0.0	0.0	5.7

^a0.01 M, irradiated at 313 nm; synthesized using powdered zinc chloride for the zinc mercury amalgam, recrystallized from water. ^bAP = acetylpyridine.

[Ru3AP] ₀ , M :	0.0100	0.0104	0.0104	0.00937	0.00949
[2-propanol], M:	0.999	0.799	0.599	0.400	0.199
λ_{max} , nm :	395	395	370	370	370
[Ru3AP], M :	0.00805	0.00793	0.00616	0.00495	0.00540

Formation of acetone was not detected in identical unirradiated samples. Plots of $\phi_{\text{acetone}}^{-1}$ versus $[2\text{-propanol}]^{-1}$ are linear (Figure 27) and values for the slope and intercept are listed in Table 15. Irradiation of 0.01 M acetonitrile solutions of pentaamminepyridine-ruthenium(II) tetrafluoroborate and pentaammine[1-(4-pyridyl)penta-none]ruthenium(II) tetrafluoroborate with 1.0 M 2-propanol produced acetone with quantum yields of 0.059 and 0.115, respectively.

Table 15. Photokinetic data for the intermolecular photoreduction of the pyridyl ketone pentaammineruthenium(II) tetrafluoroborate complexes in acetonitrile.^a

<u>Complex</u>	<u>Donor</u>	<u>Slope</u>	<u>Intercept</u>
Ru3AP	2-propanol	10.9	0.975
Ru4AP	2-propanol	5.75	2.1

^a0.01 M complex, irradiated at 313 nm; all slopes and intercepts analyzed by least squares.

Stern Volmer quenching studies were performed by the irradiation at 313 or 366 nm of acetonitrile solutions 0.01 M in acetylpyridine pentaammineruthenium(II) and containing a constant amount of 2-propanol and varying amounts of quencher. Conversions were kept below 7% for the tube without quencher and no quenching was observed for the following series of quenchers: naphthalene, 2-chloronaphthalene,

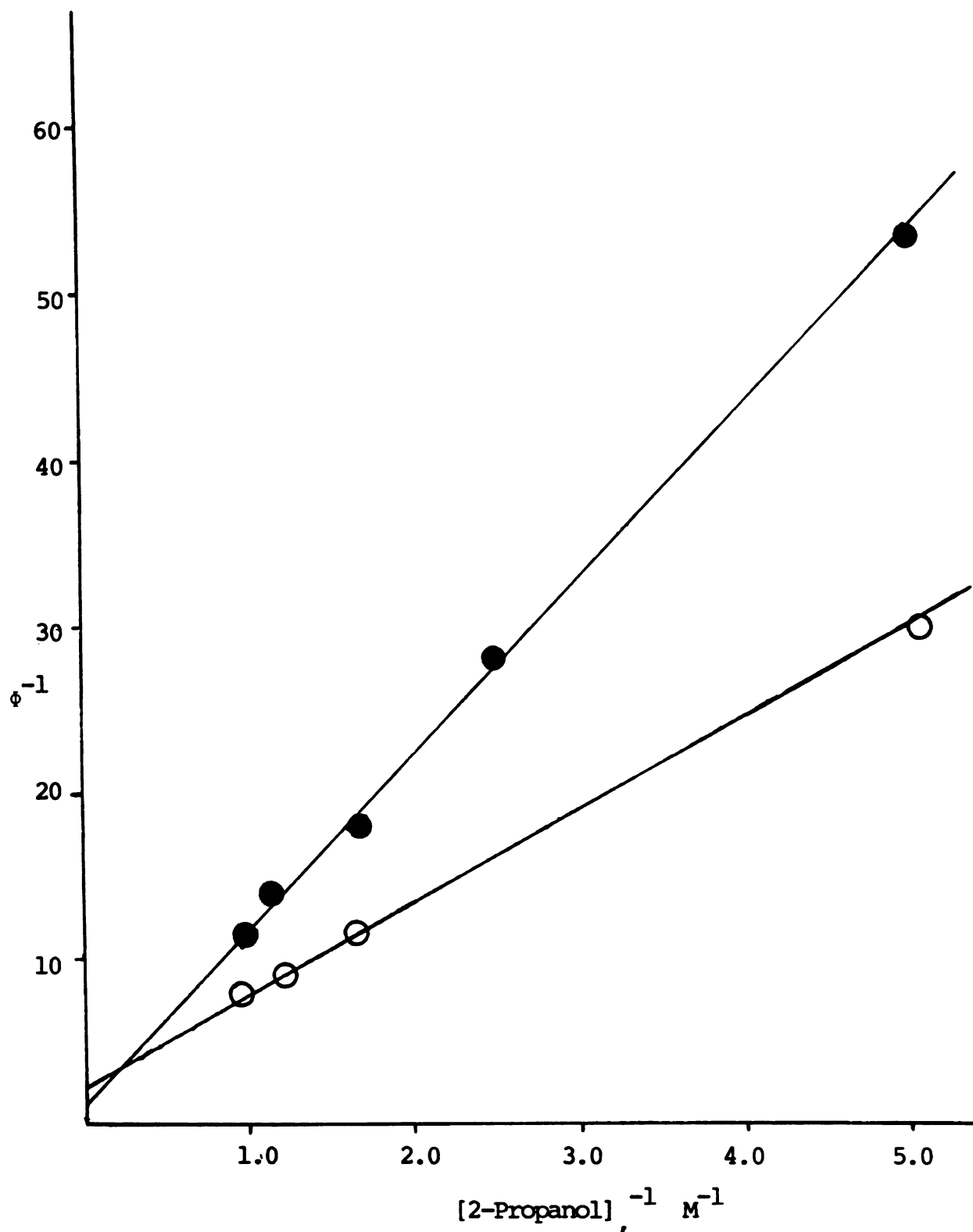


Figure 27. Dependence of quantum yield of acetone formation on 2-propanol concentration in acetonitrile, Ru4AP (○) and Ru3AP (●).

1-naphthylacetic acid, 1,3-cyclooctadiene, fumaronitrile, 2,3-dimethyl-2-butene and 2,4-hexadienol. The quenching observed with ethyl sorbate was nonlinear and nonreproducible.

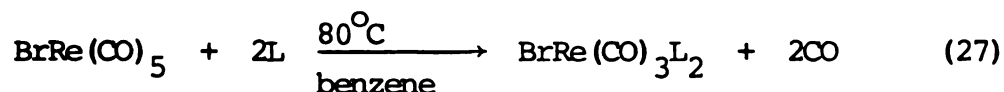
Emission Studies

No emission is observed for these complexes at room temperature and 77°K.

Rhenium Complexes

Preparation and Identification

The $\text{BrRe}(\text{CO})_3\text{L}_2$ complexes, where L is a pyridyl ketone, were synthesized by refluxing pentacarbonylbromorhenium(I) with the appropriate pyridyl ketone in benzene (27). The exact synthetic procedure is detailed in the Experimental Section. The absorption spectral data



are listed in Table 16, along with abbreviations for each complex. Representative absorption spectra are shown in Figures 28 and 29. All complexes have high energy absorption bands at 277 nm. The white ortho- and yellow para-substituted complexes exhibit distinct low energy MLCT bands, while a shoulder at 300 nm is observed for the red-orange meta-substituted complexes. The infrared spectra of the pyridyl ketone rhenium(I) complexes exhibit four bands in the CO stretch region (Table 17). The three high frequency bands are consistent with the facial arrangement of the three carbon monoxide ligands⁶¹ and the lowest frequency band results from the CO stretch of the carbonyl of the pyridyl ketone ligand. A slight shift is observed for

Table 16. Absorption spectral data for the bromotricarbonylrhenium(I) pyridyl ketone complexes.

Complex	$\lambda_{\max}$, nm (ϵ , $M^{-1}cm^{-1}$)	ϵ_{313nm} , $M^{-1}cm^{-1}$
$BrRe(CO)_5$	sh $\sim$ 350 (180) 326 (545)	355
$BrRe(CO)_3$ (N C_5H_5) ₂ (Repy)	sh $\sim$ 300 (8620) 277 (10075)	6835, 1025 ^b
$BrRe(CO)_3$ (N $\text{C}_5\text{H}_4\text{C(=O)CH}_3$) ₂ (Re2AP)	468 (4165) 277 (13170)	6700
$BrRe(CO)_3$ (N $\text{C}_5\text{H}_4\text{C(=O)CH}_2\text{CH}_2\text{CH}_3$) ₂ (Re2BP)	465 (3100) 277 (9695)	4325
$BrRe(CO)_3$ (N $\text{C}_5\text{H}_4\text{C(=O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ₂ (Re2VP)	468 (2265) 277 (8230)	3590
$BrRe(CO)_3$ (N $\text{C}_5\text{H}_3\text{C(=O)CH}_3$) ₂ (Re3AP)	sh $\sim$ 300 (8290) 277 (10900)	8290
$BrRe(CO)_3$ (N $\text{C}_5\text{H}_3\text{C(=O)CH}_2\text{CH}_2\text{CH}_3$) ₂ (Re3BP)	sh $\sim$ 305 (2745)	2210
$BrRe(CO)_3$ (N $\text{C}_5\text{H}_3\text{C(=O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ₂ (Re3VP)	sh $\sim$ 300 (10050) 277 (13430)	10050, 2800 ^b
$BrRe(CO)_3$ (N $\text{C}_4\text{H}_4\text{C(=O)CH}_3$) ₂ (Re4AP)	345 (8230) 277 (9175)	5850
$BrRe(CO)_3$ (N $\text{C}_4\text{H}_4\text{C(=O)CH}_2\text{CH}_2\text{CH}_3$) ₂ (Re4BP)	377 (3100)	2440
$BrRe(CO)_3$ (N $\text{C}_4\text{H}_4\text{C(=O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ₂ (Re4VP)	344 (10270) 277 (10320)	720, 8140 ^b

^a Benzene solvent. ^b Extinction coefficient at 366 nm.

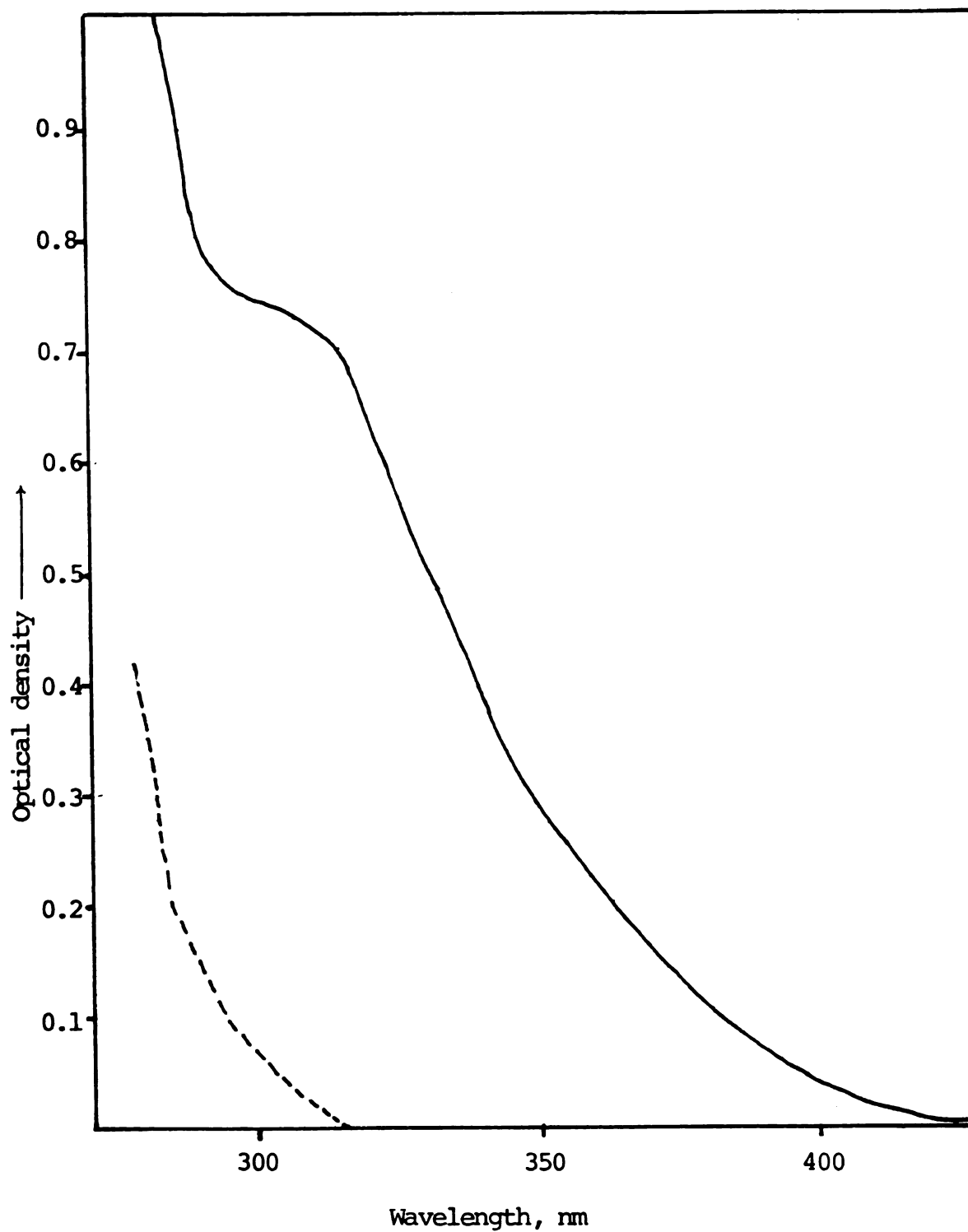


Figure 28. Absorption spectra of $7.7 \times 10^{-5} \text{ M BrRe(CO)}_3[1-(3\text{-pyridyl})\text{pentanone}]$ (—) and $2.52 \times 10^{-4} \text{ M } 1-(3\text{-pyridyl})\text{pentanone}$ (---) in benzene.

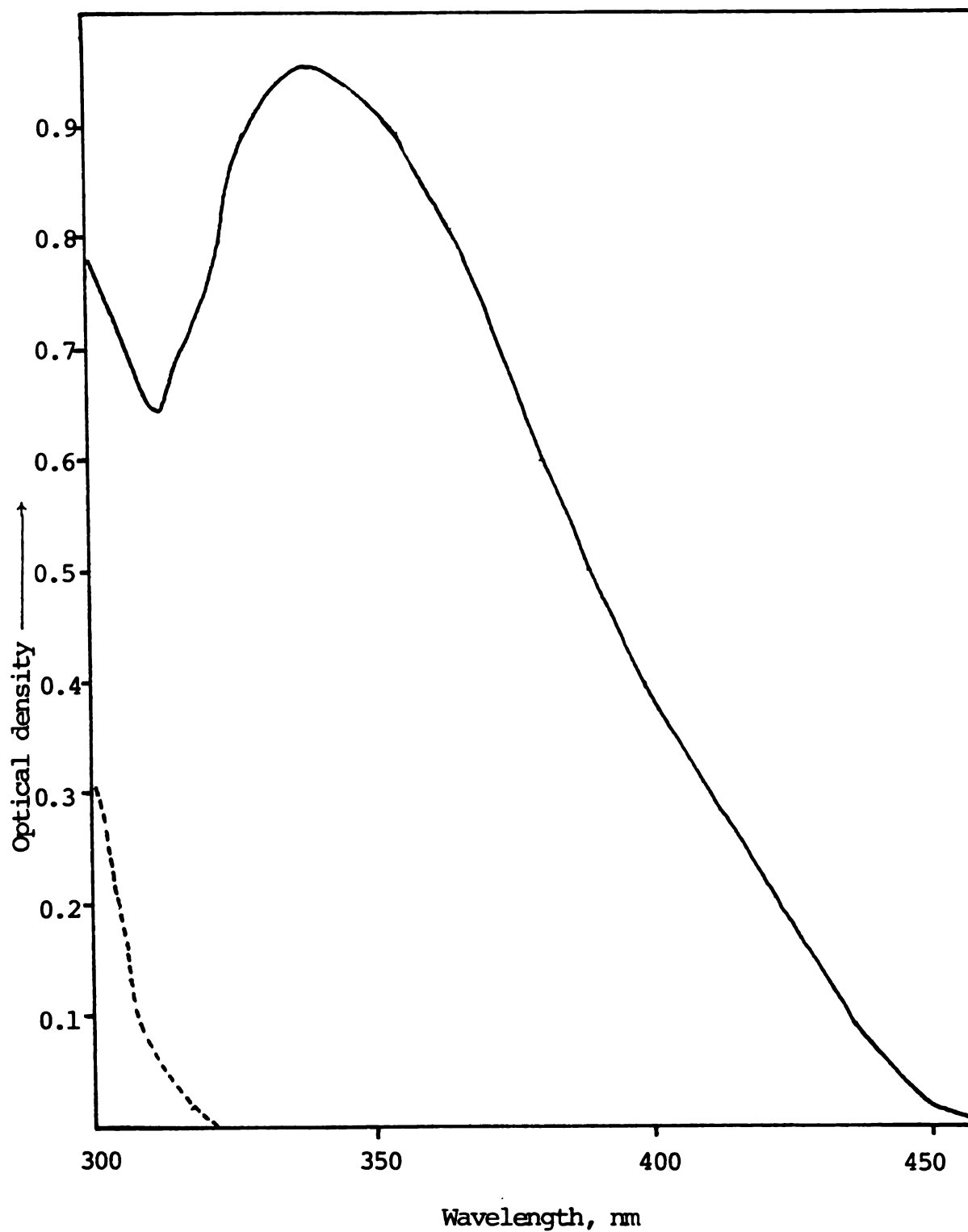


Figure 29. Absorption spectra of 1.01×10^{-4} M $\text{BrRe}(\text{CO})_3[\text{l}-(4\text{-pyridyl})\text{pentanone}]$ (—) and 2.54×10^{-4} M $\text{l}-(4\text{-pyridyl})\text{pentanone}$ (---) in benzene.

Table 17. IR bands in the CO stretching region for the pyridyl keton-bromotricarbonylrhenium(I) complexes.

Complex	$\nu_{\text{CO}},^b \text{ cm}^{-1}$ (a)			
BrRe(CO) ₅	2050	1990		
Repy	2025	1926	1885	
Re2AP		1933	1908	1621(1698)
Re2BP	2027	1927	1908	1615(1694)
Re2VP	2026	1926	1888	1618(1691)
Re3AP	2030	1929	1893	1693(1691)
Re3BP	2025	1925	1894	1693(1687)
Re3VP	2022	1922	1883	1698(1690)
Re4AP	2050	1930	1890	1690(1697)
Re4BP	2039	1939	1902	1695(1695)
Re4VP	2025	1923	1886	1675(1701)

^aNumbers in parenthesis refer to the corresponding free pyridyl ketones in methylene chloride. ^bMethylene chloride.

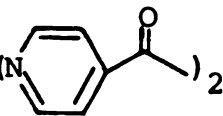
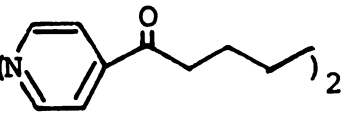
the meta and para complexes, while a larger shift (80 cm⁻¹) to lower frequency is observed for the ortho complexes. Mass spectral data show that the loss of carbon monoxide competes with the loss of pyridyl ketone. Chemical ionization using methane as the carrier gas gave the pyridyl ketone ligand as the base peak. Electron impact gave ligand fragmentation of the meta and para complexes to the same base peak as that observed for the free pyridyl ketones. The m/e value observed for Re2VP suggests coordination of both nitrogen and oxygen in the ortho-substituted complexes as described in the Discussion Section.

Complex Stability

The complexes were found to be stable in solution and not sensitive to air or daylight. When analyzed by vpc, the dissociation of the

pyridyl ketone from the rhenium(I) complex is dependent on the temperature of the injection port (Table 18). The pyridyl ketones were identified by comparison of the gc retention time with an authentic sample. The maximum ligand dissociation observed for each complex is listed in Table 19 and quantitative dissociation is observed for only R34AP, Re3VP and Re4VP.

Table 18. Variation of pyridyl ketone ligand dissociation from the rhenium(I) complexes with injection port temperature.^a

<u>Complex</u>	<u>Temperature</u>	<u>% Fragmentation</u>
$\text{BrRe}(\text{CO})_3$ 	145	19 ± 2
	190	36 ± 4
	200	79 ± 3
	210	82 ± 3
	235	94 ± 3
$\text{BrRe}(\text{CO})_3$ 	140	41 ± 4
	180	53 ± 2
	195	91 ± 3
	208	100 ± 2
	223	96 ± 3
	230	97 ± 2

^aBenzene solution.

Table 19. Maximum ligand dissociation of pyridyl ketone observed for $\text{BrRe}(\text{CO})_3\text{L}_2$ in benzene.

<u>L</u>	<u>Injection Port Temperature (°C)</u>	<u>% Fragmentation</u>
2AP	250	50 ± 5
2BP	235	37 ± 4
2VP	250	66 ± 2
3AP	250	66 ± 4
3BP	235	43 ± 2
3VP	230	99 ± 2
4AP	235	97 ± 1
4BP	240	42 ± 4
4VP	230	98 ± 2

Photoproduct Identification and Quantum Yield Studies

All complexes produced only the starting ketone upon irradiation at 313 nm, which was identified by comparison of the vpc retention time with an authentic sample. Alkene and acetylpyridine were not detected.

The quantum yield studies for photoproduct formation were carried out using the same method as that used for the pyridyl ketones. Benzene solutions containing 0.01 M bromotricarbonylrhenium(I) butyryl and valeryl pyridine complexes were irradiated in parallel with 0.1 M solutions of valerophenone actinometer in benzene. Only the original ligand was detected after the irradiation at 313 nm. Alkene and acetylpyridine were not detected. All photoproducts were identified by comparison of the gc retention time with an authentic sample. The results are shown in Table 20. While no Type II fragmentation was observed, some of the pyridyl ketone ligand disappeared and a color change occurred. The infrared spectra showed neither the appearance

Table 20. Results for the quantum yield studies on $\text{BrRe}(\text{CO})_3\text{L}_2$.^a

<u>L</u>	<u>t_{irr} (hr.)</u>	<u>Color change</u>		<u>ϕ_{AP}^b</u>	<u>$\phi_{-\text{L}}^b$</u>
2VP	2.5	Red	Deep red	0(0)	0.511(0.315)
	24.0	Red	Deeper red	0(0)	0.052(0.075)
3VP	2.0	Colorless	Yellow	0(0)	0.140(0.181)
	24.0	Colorless	Yellow	0(0)	0.072(0.046)
4AP	8.0	Yellow	Orange	-	0.073
4VP	2.5	Yellow	Orange	0(0)	0(0)
	8.0	Yellow	Orange-red	0(0)	0.011
	24.0	Yellow	Red	0(0)	0.029(0.035)

^a Benzene solvent, irradiation at 313 nm, $[\text{Re2VP}] = 0.006 \text{ M}$, $[\text{Re3VP}] = 0.0094 \text{ M}$, $[\text{Re4AP}] = 0.011 \text{ M}$, $[\text{Re4VP}] = 0.01 \text{ M}$. ^b Numbers in parenthesis refer to the quantum yields observed in the presence of acetophenone.

of new peaks nor a change in the position or size of the bands in the carbonyl region. The concentration change calculated from the change in optical density of the low energy MLCT band or shoulder at 300 nm was less than that seen by vpc analysis. This data suggests that a change has occurred in the oxidation state of the rhenium metal ion as discussed later.

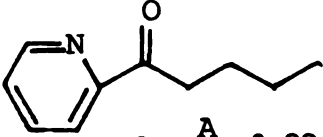
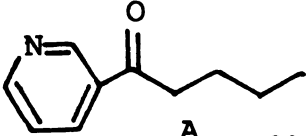
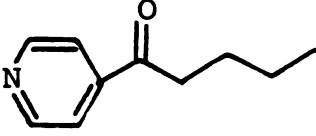
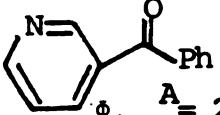
Intersystem Crossing Yields

The quantum yield of isomerization and the efficiency of intersystem crossing were determined using the same method as that for the free pyridyl ketones. The results of the irradiations with cis-1,3-pentadiene at 313 nm and trans-stilbene at 366 nm are given in Table 21. The plot of $(\phi_{O \rightarrow T})^{-1}$ versus quencher concentration is linear as illustrated for some of the complexes using cis-1,3-pentadiene as a quencher in Figure 30. When trans-stilbene is used as a quencher, no changes were observed in the infrared spectra and all stilbene was accounted for after photolysis.

Emission Spectra

Corrected emission spectra (see Experimental Section) were obtained at room temperature and at 77°K in methyltetrahydrofuran (MeTHF), a 5:1 mixture of methylcyclohexane:2-methylbutane and a 5:5:2 mixture of ethyl ether:2-methylbutane:ethanol (EPA). Concentrations of the pyridyl ketone rhenium(I) complexes were approximately 2.0×10^{-4} M. No emission was detected at room temperature and all emission bands at 77°K were broad and featureless. The same $\lambda_{\max}$ emission band was observed in all cases, with or without the phosphoroscope attachment. The emission maxima of the pyridyl ketone bromotricarbonylrhenium(I) complexes are listed in Table 22.

Table 21. Sensitization of diene isomerization by $\text{BrRe}(\text{CO})_3\text{L}_2$.^a

L	$Q_A = \text{cis-1,3-Pentadiene}$		$Q_B = \text{trans-Stilbene}$	
	$[\text{Q}], \text{M}$	$\phi_{\text{c} \rightarrow \text{t}}^b$	$[\text{Q}], \text{M}$	$\phi_{\text{t} \rightarrow \text{c}}^b$
 $\phi_{\text{isc}}^A = 0.083$ $\phi_{\text{isc}}^B = 0.17$	0.40	0.0245	0.008	0.00045
	0.50	0.0234	0.01	0.00920
	0.66	0.0322	0.02	0.0158
	1.01	0.0294	0.04	0.0855
 $\phi_{\text{isc}}^A = 0.22$	0.040	0.0044		
	0.50	0.0061 (0.502)		
	0.68	0.0085 (0.503)		
	1.01	0.0106 (0.0516)		
 $\phi_{\text{isc}}^A = 0.93$ $\phi_{\text{isc}}^B = 0.98$	0.40	0.34	0.0083	0.208
	0.50	0.37 (0.45)	0.0104	0.238
	0.66	0.43	0.0207	0.286
	1.00	0.41 (0.51)	0.414	0.396
 $\phi_{\text{isc}}^A = 2.5$ $\phi_{\text{isc}}^B = 2.8$	0.40	0.68 (0.36)	0.008	0.66
	0.50	0.70 (0.39)	0.01	0.56
	0.66	0.80 (0.42)	0.02	0.92
	1.00	1.01 (0.45)	0.04	1.05
 $\phi_{\text{isc}}^A = 2.3$ $\phi_{\text{isc}}^B = 0.78$	0.40	0.40	0.008	0.33
	0.50	0.47	0.102	0.35
	1.00	0.69	0.203	0.41
			0.41	0.51

^a Benzene solvent, irradiation at 313 nm for cis-1,3-pentadiene, irradiation at 366 nm for trans-stilbene, $[\text{Repy}] = 0.00049 \text{ M}$, $[\text{Re2VP}] = 0.0028 \text{ M}$, $[\text{Re3VP}] = 0.0002 \text{ M}$, $[\text{Re4VP}] = 0.0004 \text{ M}$. ^b Numbers in parenthesis are the $\phi_{\text{c} \rightarrow \text{t}}$ for the free pyridyl ketones in benzene.

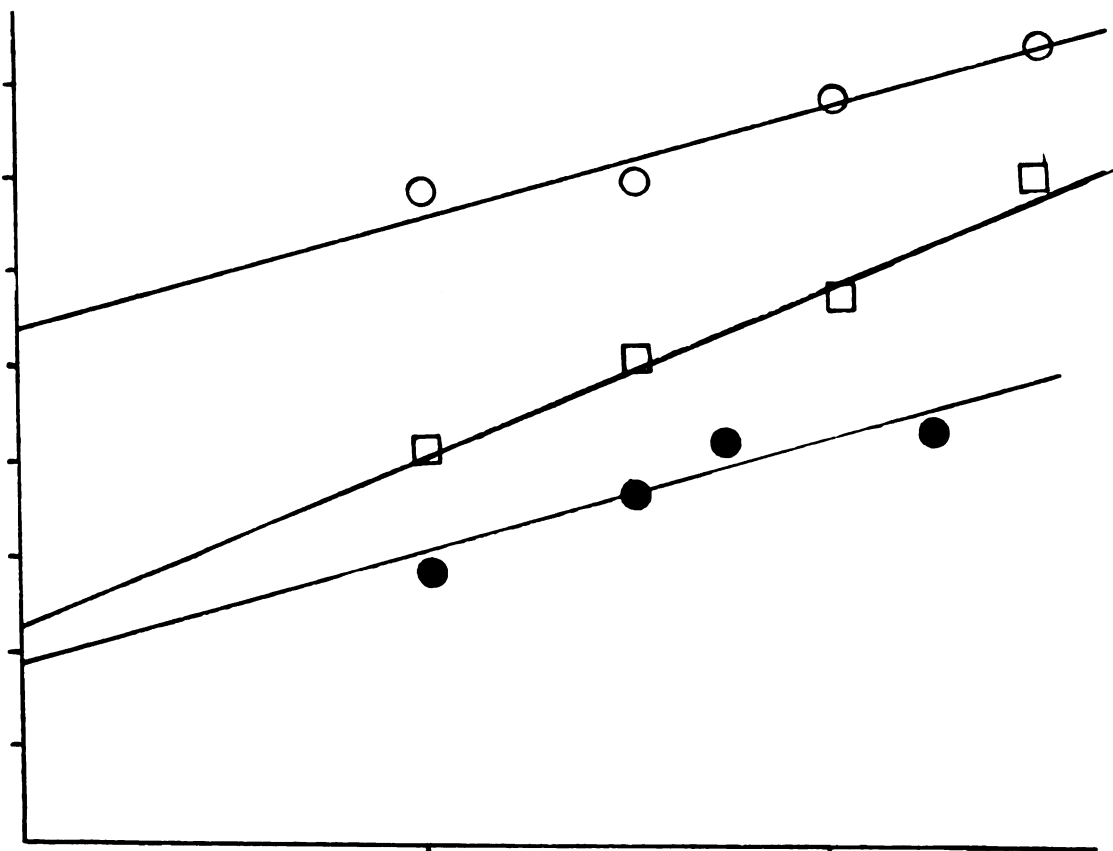


Figure 30. The sensitized isomerization of cis-1,3-pentadiene by Re3VP (○), Re4VP (●) and Re3-benzoylpyridine (□) in benzene.

Representative emission spectra are shown in Figures 31 and 32. The emission λ_{max} of the meta-pyridyl ketone bromotricarbonylrhenium(I) complexes is essentially independent of the wavelength of excitation. The emission λ_{max} of the para-pyridyl ketone bromotricarbonylrhenium(I) complexes shifts to lower energy when the energy of excitation is increased.

Table 22. Emission maxima of the pyridyl ketone bromotricarbonylrhenium(I) complexes at 77°K.^a

<u>Complex</u>	<u>λ_{exc}, nm</u>	<u>λ_{em}, nm</u>	<u>E_T, kcal/mol</u>
Re3AP	267	488	58.6
	303	478	59.8
Re4AP	277	542	52.7
	367	500	57.2
Re3VP	267	477	60.0
	303	477	60.0, 58.7, ^b 60.4 ^c
Re4VP	277	546	52.4, 53.5 ^b
	367	493	57.9

^aEPA solvent unless otherwise noted. ^b5:1 methylcyclohexane:2-methylbutane. ^cMeTHF.

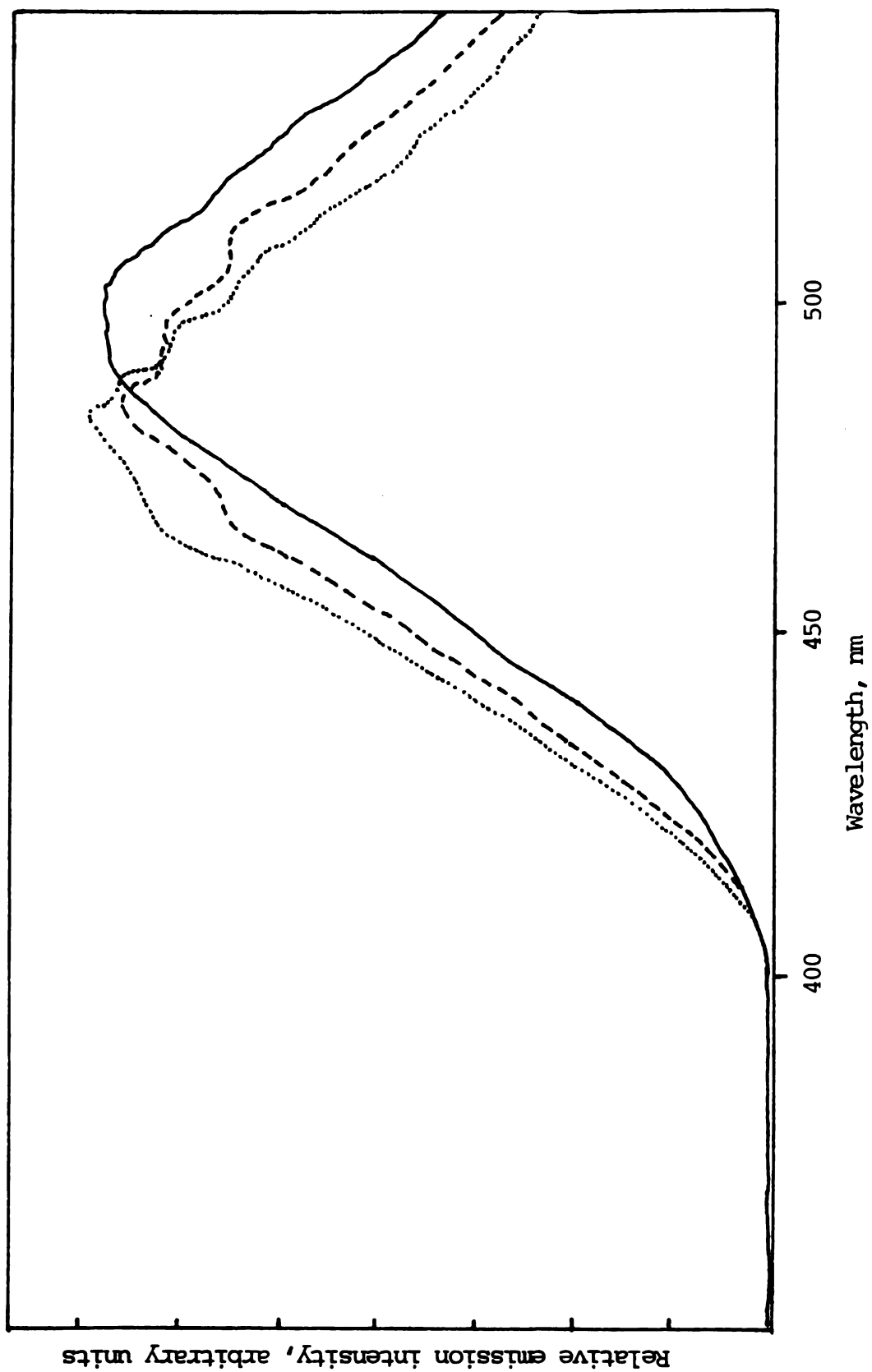


Figure 30. The emission spectra of Re3VP in 5:1 methylcyclohexane:2-methylbutane (—) ; methyltetrahydrofuran (---) and EPA (.....) at 77K.

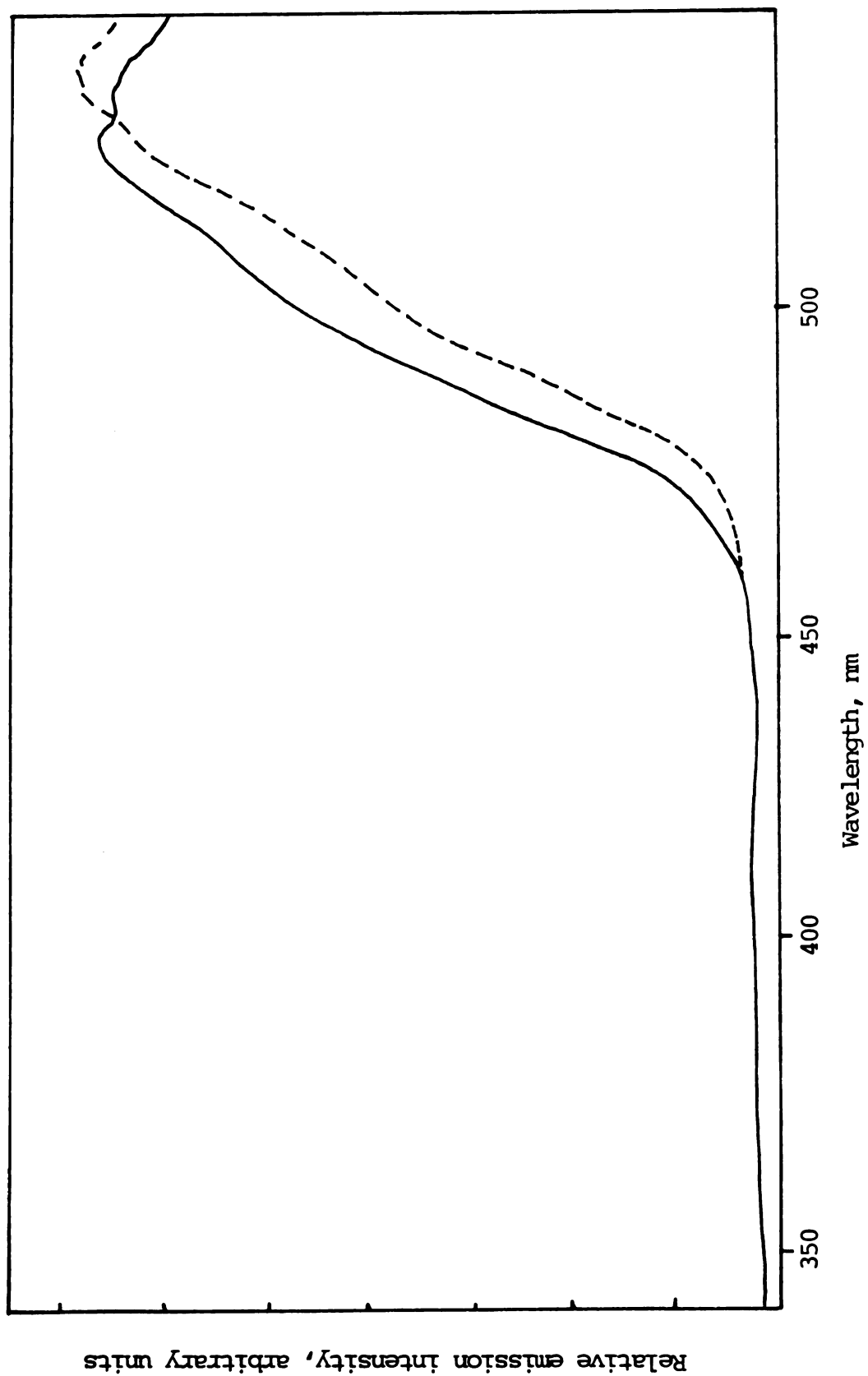


Figure 31. The emission spectra of Re4VP in 5:1 methylcyclohexane:2-methylbutane (—) and EPA (---) at 77K.

DISCUSSION

The goal of this work was to measure the rate of internal conversion between the IL excited state and the MLCT excited states. The discussion is divided into three parts. The first section deals with the photochemistry of the ligand pyridyl ketones and the pyridyl ketone hydrochloride salts which are used as models for the metal complexed ketones. The second section deals with the preparation and characterization of the inorganic complexes. The last section discusses the photochemistry of the pentaammineruthenium(II) and bromotricarbonylrhenium(I) pyridyl ketone complexes.

Pyridyl Ketone Photochemistry

Quantum Yields

In benzene solution, the fragmentation quantum yields for the pyridyl ketones are lower than those observed for the corresponding phenyl alkyl ketones (Table 23) and show more dependence on the aza position than on the nature of the alkyl side chain.¹³⁹ In polar solvents, the fragmentation quantum efficiencies increase, although the quantum yields are not unity in all cases, even when cyclobutanol formation is taken into account.⁷³ The pyridyl ketone disappearance quantum yields in acetonitrile are also not unity (0.67-0.87).

In agreement with previous observation,¹⁹⁹ the relatively low quantum yields of the pyridyl ketones are not due to quenching impurities or to pyridyl ketone self-quenching. The quantum yields were

found to increase as the concentration of the pyridyl alkyl ketone was increased (Figure 7). A concentration effect of this type has been interpreted as solvation of the biradical by ground state ketone. The quantum yield then increases in the same manner as observed with added polar solvents.⁷¹ These concentration effects also suggest that decreases of the quantum yield in the tert-butyl alcohol studies are not due to quenching impurities, but to some interaction of alcohol with the excited state.

Protonation of the pyridine nitrogen results in drastic changes in photochemical behavior. Very low quantum efficiencies are observed even when acetonitrile is the irradiation solvent. The negligible change in quantum yield with increasing ketone concentration rules out self quenching. In the tert-butyl alcohol studies, the increase in quantum efficiency is minor, although the maximum quantum efficiency occurs at the same concentration as for the corresponding free pyridyl ketone. The similarity of quantum yields in acetonitrile and with added tert-butyl alcohol rules out any further quenching from solvent impurities. The best interpretation of the low quantum yields is that they are due to the presence of H^+ and Cl^- . Lifetime measurements, (vide infra), indicate that inefficiency does not result from competitive triplet excited state reactions. Furthermore, material balances of 50% suggest that competitive biradical processes occur. Studies of the free pyridyl ketones in the presence of added salts were limited by the solubility of such additives. Nonetheless, the decreased quantum yields are comparable to the fragmentation quantum yields of the pyridyl ketone hydrochloride salts.

Quenching Studies

For comparison with the pyridyl ketones studied in this thesis, triplet lifetime data for the parent phenyl ketones are presented in Table 23. In tert-butyl alcohol, the quantum yield of ketone disappearance for the phenyl alkyl ketones rises to unity so that $1/\tau$

Table 23. Photochemical data for the parent phenyl alkyl ketones in benzene solution.^a

Ketone		ϕ_{II}	$k_q\tau, M^{-1}$	$\tau, 10^{-9}s^b$	$k_r, 10^7 s^{-1}$
$PhCOCH_2CH_2CH_3$	(BP)	0.35	670.	134.	0.75
$PhCOCH_2CH_2CH(CH_3)_2$	(β MeBP)	0.36	245.	49.	2.0
$PhCOCH_2CH_2CH_2CH_3$	(VP)	0.33	36.	7.2	14.0
$PhCOCH_2CH_2CH_2CH(CH_3)_2$	(γ MeVP)	0.25	11.	2.2	45.0

^aRef. 140. ^b $k_q = 5 \times 10^9 M^{-1}cm^{-1}$ in benzene, Ref. 69 and 141.

equals the rate of gamma hydrogen abstraction (k_r).⁷¹ Although the quantum yields for the pyridyl ketones are not unity, the fact that the fragmentation yields are constant for the same aza substituent allows for determination of k_r in the same manner. The Norrish Type II fragmentation proceeds through the biradical intermediate in (32) and the fragmentation quantum yield is the product of probabilities in (36).





$$\phi_{II} = \phi_{isc} \phi_{BR} \phi_P = \phi_{isc} \left(\frac{k_r}{k_r + k_d} \right) \left(\frac{k_p}{k_p + k_{cyc} + k_{-r}} \right) \quad (36)$$

Sensitization studies using the valerylpyridines indicate inter-system crossing to the triplet states (30) occurs with unit efficiency. Inefficiency must then result from triplet ketone decay (31), inefficient biradical fragmentation (33) or a combination of (31) and (33). In order for the quantum yield to remain constant for each aza substituent while k_r varies, the aza substituent must affect only the probability of product formation (ϕ_P) and not the probability of biradical formation (ϕ_{BR}).¹³² Thus $k_d \ll k_r$, $1/\tau$ equals k_r and the quantum yields less than unity result from inefficient fragmentation of the biradical. The photochemical kinetic data for the pyridyl ketones in benzene and acetonitrile are presented in Tables 24 and 25. The rate of hydrogen abstraction by the triplet carbonyl (k_r) parallels the hydrogen bond strength in the order $3^O > 2^O > 1^O$. The ratio of reactivity for the ortho pyridyl ketones ($1^O : 2^O : 3^O = 1 : 23 : 80$) differs from that of the meta ($1^O : 2^O = 1 : 11$) and para ($1^O : 2^O : 3^O = 1 : 11 : 46$) pyridyl ketones. An unusually low value of τ for ortho butyrylpyridine would nicely explain the discrepancy observed for the ortho isomers. The shorter lifetime results from the low quantum yields of

Table 24. Photokinetic data for the pyridyl alkyl ketones in benzene.

<u>Ketone</u>	<u>ϕ_{II}</u>	<u>$\tau, 10^{-9} \text{ sec}^a$</u>	<u>$k_r, 10^7 \text{ s}^{-1}$</u>
2BP	0.16	107.5	0.93
2VP	0.20	4.65	21.5
γ Me2VP	0.19	1.34	74.7
3BP	0.44	38.0	2.63
β Me3BP	0.31	18.0	5.56
3VP	0.35	3.48	28.7
4BP	0.20	16.0	6.25
β Me4BP	0.16	-	-
4VP	0.23	1.46	68.5
γ Me4VP	0.18	0.35	289.

^aValues of τ are estimated on the basis that k_q equals $5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in benzene.^{69,141}

Table 25. Photokinetic data for the pyridyl alkyl ketones in acetonitrile.

<u>Ketone</u>	<u>ϕ_{II}</u>	<u>$\tau, 10^{-9} \text{ sec}^a$</u>	<u>$k_r, 10^7 \text{ s}^{-1}$</u>
2BP	0.25	58.1	1.72
2VP	0.70	5.59	17.9
γ Me2VP	0.73	1.34	74.7
3BP	0.70	54.1	1.86
β Me3BP	0.76	10.8	9.3
3VP	0.84	3.1	32.3
4BP	0.63	20.4	4.90
β Me4BP	0.60	4.11	24.3
4VP	0.60	1.00	100.
γ Me4VP	0.58	0.25	400.

^aValues of τ are estimated on the basis that k_q equals $1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ in acetonitrile.⁷¹

2-acetylpyridine. This suggests that competitive reactions from the triplet excited state are occurring as previously observed for 2-butyrylpyrimidine.^{129,130}

The triplet lifetimes of the pyridyl ketone hydrochloride salts are much shorter than those of the corresponding free pyridyl ketones. Equating $1/\tau$ to k_r for the meta ($1^{\circ} : 2^{\circ} = 1 : 8$) and para ($1^{\circ} : 2^{\circ} : 3^{\circ} = 1 : 8 : 12$) compounds indicated a decrease in hydrogen atom selectivity (Table 27). To determine whether $1/\tau$ contains an appreciable k_d , k_d was independently measured. The photokinetic data for the bimolecular photoreduction of the meta and para acetylpyridine hydrochloride salts are presented in Table 26.

Table 26. Kinetic data for the intermolecular photoreduction of 3- and 4-acetylpyridine hydrochloride in acetonitrile.

Ketone	Donor	$k_r, M^{-1}sec^{-1}$	k_d, sec^{-1}	ϕ_{max}^a
3APHCl	2-Propanol	2.8×10^7	1.5×10^8	0.55
4APHCl	2-Propanol	2.8×10^8	1.9×10^8	0.86
4APHCl	1-Phenylethanol	2.8×10^8	9.0×10^8	-

^aQuantum yield of acetone formation.

The initial photochemical steps, including intersystem crossing and the mechanism of hydrogen abstraction by the reactive triplet ketone excited state, are the same as in intramolecular photoreduction. The maximum quantum yields of acetone formation indicate that hydrogen abstraction is an efficient reaction. The efficiency of intersystem crossing must be at least 60% and 90% respectively,

for the meta and para compounds. The rate constants of triplet reactions, however, are much higher than those observed for the tert-butoxy radical ($k_r = 1.86 \times 10^6 \text{ M}^{-1}\text{sec}^{-1}$),¹⁴² acetophenone ($k_r = 1.8 \times 10^6 \text{ M}^{-1}\text{sec}^{-1}$)⁹⁰ and benzophenone ($k_r = 1.3 \times 10^6 \text{ M}^{-1}\text{sec}^{-1}$)⁹⁰ when 2-propanol is the hydrogen donor. These results suggest that the first step is not direct hydrogen abstraction. The mechanism may be similar to that observed for trifluoroacetophenone which involves charge transfer interactions.¹¹⁵ Further experimental evidence for the occurrence of charge transfer upon irradiation of the pyridyl ketone hydrochloride salts is the fact that the Type II fragmentation of 4VP is not quenched by *p*-xylene whereas that of 4VPHCl is quenched at a rate of $5 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$. Since the triplet energy of *p*-xylene (80 kcal/mol) lies well above the triplet energy of 4VPHCl ($E_T = 70.9 \text{ kcal/mol}$), exothermic energy transfer cannot occur and quenching must result from charge transfer. Under these experimental conditions, the rate of *p*-xylene charge transfer quenching is faster than naphthalene quenching of the triplet ketone. The lack of quenching of 4VP must be interpreted as the absence of charge transfer interactions with free ketone. The higher ionization potential of benzene (IP = 9.25 eV)¹⁴⁴ makes it less reactive than *p*-xylene (IP = 8.44 eV),¹⁴⁴ and, as expected,¹¹⁴ quenching of 4VPHCl is not observed.

Regardless of the exact nature of the bimolecular reduction mechanism, the kinetic analysis allows for an unbiased determination of k_d . The high values of k_d and the observation of two different values of k_d for 4APHCl were quite unexpected. Possible causes are ground state processes influencing the quantum yields. However, the

enhanced decay could also be rationalized from charge transfer interactions. The high k_d for 4APHC1 with 1-phenylethanol, $9.0 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$, is inconsistent with product quantum yields in the corresponding intramolecular photoreactions. Specifically, this would not allow for product formation with 4BP where $1/\tau = 4.3 \times 10^8 \text{ s}^{-1}$. The ionization potential of 2-propanol (IP = 10.15 eV)¹⁴⁴ would not allow for charge transfer interaction. Using the experimentally determined values of k_d from 2-propanol, the rates of gamma hydrogen abstraction for the pyridyl ketone hydrochloride salts were determined and are presented in Table 27. The rate of gamma hydrogen abstraction also parallels the strength of the gamma hydrogen bond ($3^\circ > 2^\circ > 1^\circ$). The high percentage of decay predicted for the meta (73%) and para (42%) butyrylpyridine hydrochlorides contradicts the observed minimal changes in quantum yield. This suggests that k_d determined from the 2-propanol studies is unaccountably high and most likely represents

Table 27. Photokinetic data for the pyridyl ketone hydrochloride salts in acetonitrile.

Ketone	ϕ_{II}	$1/\tau, 10^8 \text{ s}^{-1}$	$k_r, 10^8 \text{ s}^{-1} \text{ }^a$	$k_d, 10^8 \text{ s}^{-1}$
3BPHCl	0.23	2.4	0.9	1.5
β Me3BPHCl	0.19	7.6	6.1	1.5
3VPHCl	0.27	20.4	18.9	1.5
4BPHCl	0.092	4.3	2.5	1.8
β Me4BPHCl	0.16	13.5	11.7	1.8
4VPHCl	0.12	33.0	21.2	1.8
γ Me4VPHCl	0.13	50.0	48.0	1.8

^aValues of τ are estimated on the basis that k_q equals $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile.⁷¹ ^b $k_r = (\tau)^{-1} - k_d$.

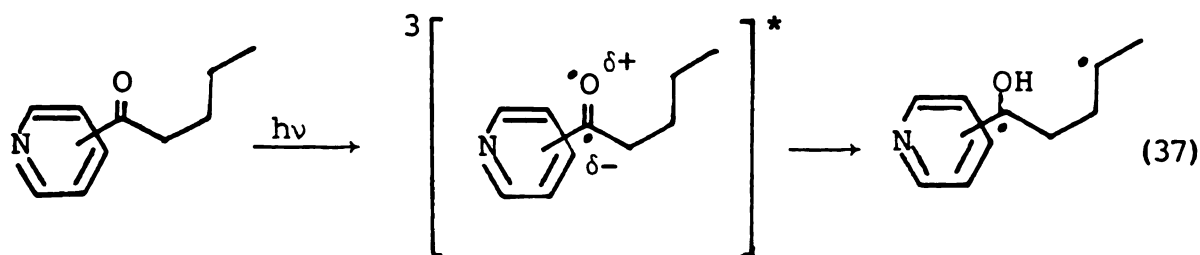
a maximum value for decay.

The gamma hydrogen selectivity for the pyridyl ketone hydrochloride salts ($1^\circ : 2^\circ : 3^\circ = 1 : 9 : 20$) differs from the selectivity of the pyridyl alkyl ketones ($1^\circ : 2^\circ : 3^\circ = 1 : 11 : 46$) and phenyl alkyl ketones ($1^\circ : 2^\circ : 3^\circ = 1 : 12 : 55$). This decrease in selectivity may be related to similar observations for cation radicals. The hydrogen atom transfers observed for the molecular cation radicals of ketones (McLafferty rearrangement)¹⁴⁵ are known to be similar to the gamma hydrogen abstractions observed for triplet ketones.¹⁴⁶ These reactions involving the breaking of carbon-hydrogen bonds occur with the expected wide range of deuterium isotope effects. Deuterium isotope effects are not found in the mass spectroscopy study of 2-hexanone-5-d₁.¹⁴⁷ Green and coworkers¹⁴⁸ also observed the lack of deuterium isotope effects in the Hoffman-Loeffler-Freytag rearrangement of deuterated N-chloro-2-hexylamine. The electron deficient character of both sources of reactivity for the radical cation was hypothesized to lead to abstraction of the carbon bound hydrogen with lower energy of activation compared to neutral molecules. By analogy, the electron deficient triplet carbonyl excited states of the pyridyl ketone hydrochloride salts abstract the gamma hydrogens with a lower energy of activation than the free pyridyl ketones, resulting in decreased selectivity.

Reactivity and Efficiency

Enhanced reactivity of the pyridyl ketones is expected since the nitrogen atom of the pyridine ring is an electron withdrawing substituent¹⁴⁹ and activates the electron deficient n, π^* triplet excited

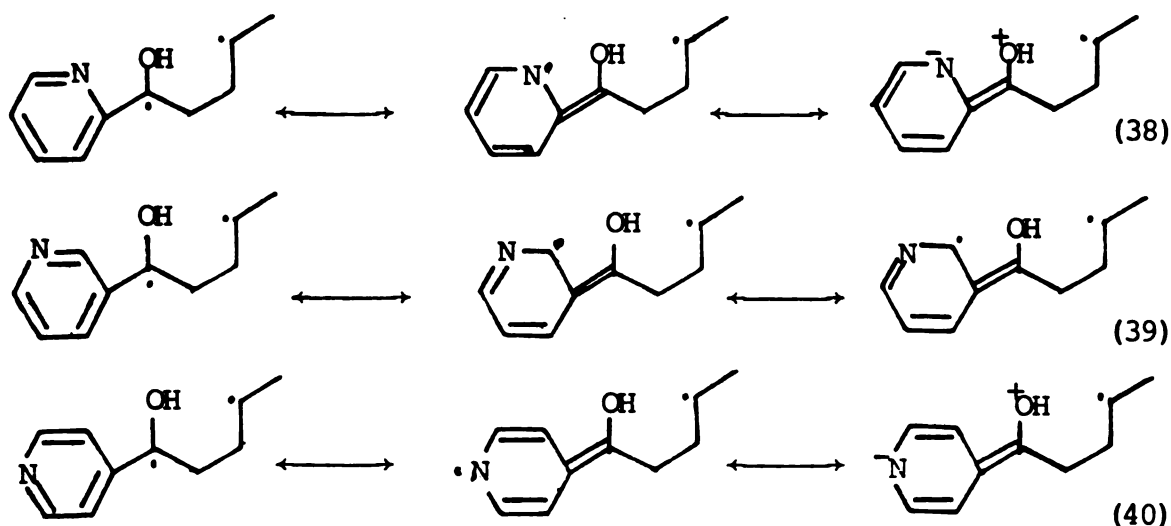
state towards gamma hydrogen abstraction (37) Protonation of the



nitrogen renders it more electron deficient and the triplet carbonyl is further activated. Previous spectroscopic work¹¹⁹ suggests that the n, π^* triplet excited states for the pyridyl ketones lie lower (para < ortho < meta $\approx$ phenyl) and the π, π^* triplet excited states of the pyridyl ketones lie higher (para > ortho > meta > phenyl) relative to those of the phenyl alkyl ketones in nonpolar solvents. Since the n, π^* triplet states are of lowest energy, the exact energy of the π, π^* triplet excited states cannot be measured. The same order of reactivity is observed in both benzene and acetonitrile solutions, $k_r(\text{para}) > k_r(\text{meta}) > k_r(\text{ortho})$. The underlying reason for this observed order is not clear. Decreased mixing of the triplet states predicts $k_r(\text{para}) > k_r(\text{ortho}) > k_r(\text{meta})$; while induction, where nitrogen acts as an electron withdrawing group, predicts $k_r(\text{ortho}) > k_r(\text{meta}) > k_r(\text{para})$. The rate data indicate that induction plays a minor role in influencing the rate of gamma hydrogen abstraction since the aza substituent has the greatest effect on enhancing triplet reactivity when it is farthest away.

Low quantum efficiencies may be attributed to a combination of low efficiencies of intersystem crossing, biradical formation and biradical fragmentation. The high rates of biradical formation (k_r) versus decay (k_d) rule out inefficient biradical formation. The unit efficiency of intersystem crossing observed for the pyridyl ketones

leaves only an inefficient biradical fragmentation as the cause of the low quantum yields. Delocalization of the carbon radical electron into the pyridine ring ((38)-(40)) is consistent with the fact that nitrogen is an electron withdrawing group and alkyl radicals are electron donating groups.¹⁵⁰ Only in the case of meta substitution, can the carbon radical electron not be delocalized onto the nitrogen. The meta aza substituent has no effect on the stability of the biradical and the quantum efficiency is similar to that observed for the parent phenyl alkyl ketones. For ortho and para substitution, electron delocalization creates the charge separation illustrated in (38) and (40). The partial positive charge on oxygen is best relieved by reverse gamma hydrogen transfer and the quantum yield is decreased in comparison to the phenyl alkyl ketones.



If intersystem crossing occurs with comparable efficiency in the pyridyl ketone hydrochloride salts, inefficient biradical fragmentation is again responsible for the low quantum yields. The actual reason for the extensive decrease is unknown. However, very fast

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reverse gamma hydrogen transfer is possible. Furthermore, the low mass balances suggest competitive biradical reactions may also occur.

Synthesis and Properties of the Inorganic Complexes

The background on the excited state behavior of the ruthenium and rhenium complexes in the Introduction illustrates the wide range of photochemical behavior normally observed for organometallic complexes. The energy levels which affect the photochemical behavior are derived from molecular structure⁶⁵ and an examination of the physical properties is necessary to interpret the results of the photochemical studies.

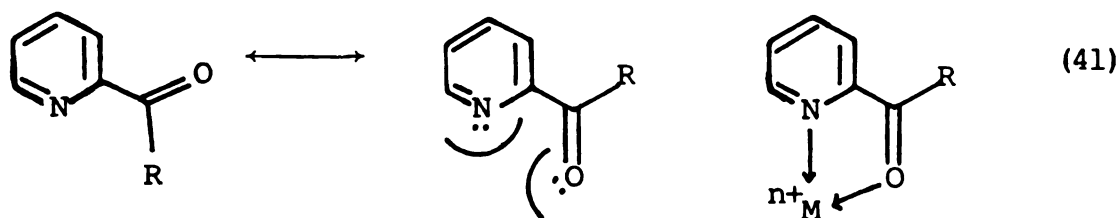
Pyridyl Ketone Pentaammineruthenium(II) Complexes

The synthesis and purification of the pentaammineruthenium(II) pyridyl ketone complexes proved somewhat difficult, as has been experienced by other workers.^{151,152,153} The spontaneous color changes often observed, e.g. in the synthesis of chloropentaammineruthenium(II) dichloride, were first observed in 1804¹⁵⁴ for acidic ruthenium metal complex solutions and are unexplained to date.¹⁵⁵ The reduction of chloropentaammineruthenium(III) complex under the same experimental conditions, but using different forms of mercuric chloride for the zinc-mercury amalgam, gave complexes with comparable absorption spectra but different elemental analyses and different photochemistry.

The characteristic features of the absorption spectra of the pyridyl ketone pentaammineruthenium(II) complexes are the π bands in the ultra-violet region and intense MLCT bands¹⁵⁶ in the visible region. The π, π^* pyridyl ketone transition is shifted to higher energy upon coordination of nitrogen ($\lambda_{\max}(\text{Ru}^{2+}) < \lambda_{\max}(\text{HCl salt}) < \lambda_{\max}(\text{free ketone})$). Coordination also removes the n, π^* transition associated

with the ring nitrogen and thus produces a sharper π, π^* band. The enhancement of absorption in the carbonyl n, π^* transition region (313 nm) is most likely due to underlying metal d-d transitions as observed in the corresponding pyridine complex.

The position of the MLCT band for the complexes is dependent on the position of the acyl group relative to the pyridine nitrogen and independent of the nature of the alkyl side chain (Table 9). It is interesting that meta acyl substitution on the pyridine ring produces little change in the energy of the MLCT band. The occurrence of low energy bands in the ortho complexes might indicate coordination of both pyridine nitrogen and carbonyl oxygen to the ruthenium(II) metal center.^{157,158} To minimize dipole moment, the pyridine nitrogen and carbonyl oxygen are usually trans,¹⁵⁹ but in the presence of metal ions, the cis conformation is often preferred (41).¹⁶⁰ Bidentate



ligand behavior is normally accompanied by a $40\text{--}60\text{ cm}^{-1}$ red shift in the infrared carbonyl frequency;^{161,162,163} however the ortho complexes do not show an appreciable shift from the meta and para pyridyl ketone pentaammineruthenium(II) complexes. No infrared data are reported for the ortho coordinated ruthenium(II) complexes in the literature¹⁵⁷ so the exact nature of bonding in the ortho pyridyl ketone ruthenium (II) complexes is uncertain.

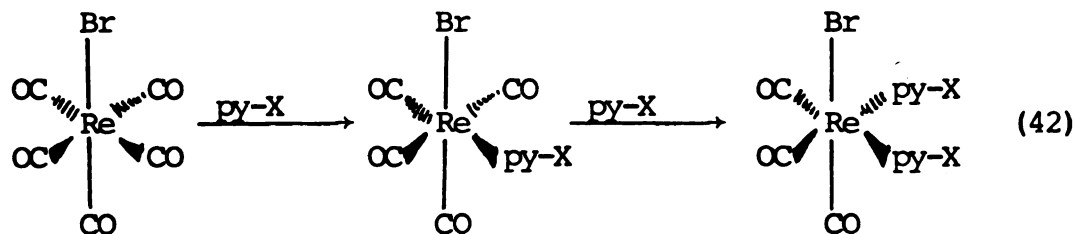
The pyridyl ketone pentaammineruthenium(II) complexes have a propensity towards decomposition in solution, most likely through oxidation⁴⁵ or ligand substitution. They are unexpectedly stable toward gc fragmentation, even though other ruthenium(II) complexes are known to fragment quantitatively at temperatures greater than 200°C.¹⁶⁴ Whitten^{51,52} displaced 4-stilbazole from $[\text{Ru}(\text{bipy})_2(4\text{-stilbazole})_2]^{2+}$ using triphenylphosphine and Dwyer¹⁶⁵ displaced pyridine from $\text{cis-}[\text{Ru}(\text{phen})_2(\text{py})_2]^{2+}$ with chloride ion. The application of these methods and others did not result in quantitative displacement of the pyridyl ketone ligand from the pentaammineruthenium(II) complex. It is known that when not influenced by the "trans" effect, ligands which are good donors (e.g. NH_3 , pyridines, N_2) are not very labile in solution,⁴⁵ presumably due to π -back bonding from the metal center.^{165,166,167} Since the pyridyl ketone infrared carbonyl stretch frequencies are shifted to lower energy in the complexes, ruthenium(II) back bonding may be a possible reason for the lack of fragmentation.

The meta and para pyridyl ketone pentaammineruthenium(II) complexes were used for photochemical studies. The complexes are in the +2 oxidation state, since the corresponding ruthenium(III) complexes have no MLCT band.^{42,169} The complexes contain only one pyridyl ketone ligand. A dipyridyl tetraammineruthenium(II) complex would have a MLCT λ_{max} twice as large as that observed. The correct carbon analysis verifies that only one pyridyl ketone is present. The low nitrogen and hydrogen analysis suggest that one of the ammine groups in the complex has been replaced by water or chloride ion. Any trace amounts of hydroxy or chloro tetraammineruthenium(II) complex would

be too small to be detected and unable to be distinguished by spectroscopic analysis since the absorption characteristics would be similar to the pentaammineruthenium(II) complex.^{42,170}

Pyridyl Ketone Bromotricarbonylrhenium(I) Complexes

In contrast to the pyridyl ketone pentaammineruthenium(II) complexes, the solubility properties of the pyridyl ketone bromotricarbonylrhenium(I) complexes allow for easy isolation and purification. The infrared of each complex exhibits a band for the carbonyl stretch of the pyridyl ketone and the metal-carbonyl three band pattern associated with the facial arrangement of the carbon monoxide ligands.⁶¹ Pyridyl ketone bromotricarbonylrhenium(I) complex formation occurs through the stepwise "trans-effect" mechanism (42). As a result, the



pyridyl ketone groups lie cis to each other. Attempts to substitute further CO groups in other systems have been unsuccessful.⁵⁵

The main bands in the absorption spectrum are associated with the high energy $\pi\pi^*$ transitions and the rhenium to pyridyl ketone MLCT transition.⁶¹ The $\pi\pi^*$ band of the pyridyl ketone rhenium(I) complex occurs at approximately the same energy as that of the free pyridyl ketone. As with other $\text{fac-XRe(CO)}_3\text{L}_2$ complexes,⁶¹ the extinction coefficient of the band is at least twice the magnitude of the free pyridyl ketone. The position of the lower energy MLCT band is dependent upon the position of the carbonyl group relative to the

pyridine nitrogen and independent of the nature of the alkyl side chain. Meta acyl substitution on the acyl pyridine ring produces very little change in the MLCT band energy.

While all the bromotricarbonylrhenium(I) complexes with the aza substituent in the same ring position have the same MLCT λ_{max} , the extinction coefficients at the λ_{max} and at 313 nm vary significantly. Some complexes, particularly the butyrylpyridine complexes, may have occluded solvent upon recrystallization. Although the complexes also display temperature dependent pyridyl ketone ligand dissociation and do not undergo quantitative ligand dissociation upon gc analysis, the probability of only one pyridyl ketone coordinated to the rhenium(I) metal center is unlikely. The infrared carbonyl stretch frequencies of $\text{Ph}_3\text{PRe}(\text{CO})_3\text{Br}$,¹⁷¹ the only monosubstituted rhenium(I) metal carbonyl complex in the literature, do not correspond to those of the synthesized pyridyl ketone bromotricarbonylrhenium(I) complexes in Table 17. Furthermore, the same carbonyl stretch and relative band intensities are observed for all the complexes.^{59,60,61} The ortho pyridyl ketone rhenium(I) complexes are peculiar. The mass spectral fragmentation pattern is suggestive of an ortho coordinated rhenium(I) species, however, the IR spectra are slightly different from those reported for other ortho-metallated complexes.¹⁷² The low frequency infrared stretch observed for the ortho pyridyl ketone rhenium(I) complexes has no literature precedence.

Photochemistry of the Organometallic Complexes

Pyridyl Ketone Pentaammineruthenium(II) Complexes

The physical properties of the pyridyl ketone pentaammineruthenium (II) complexes placed a limitation on the scope of the photochemical

studies. The spectral characteristics of some of the pyridyl ketone pentaammineruthenium(II) complexes, even though in agreement with the literature values (i.e. Rupy,¹⁵⁶ Ru4AP⁵⁰) were found not to be a good measure of complex purity¹⁶⁶ and only those complexes with satisfactory elemental analyses were used for the photokinetic studies. The unknown nature of the pyridyl ketone bonding, in addition to the unsatisfactory elemental analysis for the ortho pyridyl ketone pentaammineruthenium(II) complexes, are the basis for their elimination from the photochemical Type II fragmentation studies. The nondissociation of the pyridyl ketone ligand from the pyridyl ketone pentaammineruthenium(II) complexes under vpc analysis conditions also limited the study to pyridyl ketone ligands whose alkene fragmentation products could be measured accurately. Propylene and iso-butylene analyses were accurate to 3%. Analysis for ethylene was nonreproducible and eliminated the butyryl-pyridyl ketones as ligands for photochemical studies. The nondissociation of the pyridyl ketone ligands from the pyridyl ketone pentaammineruthenium(II) complexes under vpc analysis conditions did however allow for the direct measurement of the photodissociated pyridyl ketone ligand.

The use of spectroscopic analysis by Ford^{41,43,49} to monitor photosubstitution of the py-X ligands is complicated by the effects on the MLCT λ_{max} optical density of additional decay pathways. Gc analysis of alkene and pyridyl ketone are absolute measures of the upper and lower excited state reactions. With spectroscopic analysis, the accuracy of the photosubstitution quantum yield rests on the assumption that the decrease in optical density of the MLCT λ_{max} rises solely from pyridine aquation. While cis- and

trans-[Ru(NH₃)₄(py)(H₂O)]²⁺ (λ_{max} = 407 nm; $\epsilon_{\text{MLCT}}(\text{trans})$ 7700, $\epsilon_{\text{MLCT}}(\text{cis})$ 6400 M⁻¹cm⁻¹)⁴² and [Ru(NH₃)₅py]²⁺ (λ_{max} = 407 nm, ϵ 7762 M⁻¹cm⁻¹)¹⁵⁶ have similar spectral characteristics, oxidation of ruthenium(II) to ruthenium(III) as [Ru(NH₃)₅py]³⁺ (λ_{max} = 262 nm, ϵ 4539 M⁻¹cm⁻¹)¹⁵⁶ causes a decrease in the MLCT λ_{max} optical density without the aquation of pyridine. The quantitative evaluation of any ruthenium(III) complex formed is complicated by the fact that all the reactants and products have some absorbance at these wavelengths and ion exchange elution analysis^{41,42} failed to give quantitative or qualitative agreement with the spectroscopic analysis.

The quantum yield of alkene formation thus represents Type II fragmentation while quantum yields of pyridyl ketone formation represent photodissociation (Table 14). Acetylpyridine formation was not observed upon irradiation for any of the butyrylpyridine and valerylpyridine complexes, so none of the pyridyl ketone formed by photodissociation undergoes Type II fragmentation. The meta pyridyl ketone complexes which exhibit high energy MLCT bands at 412 nm are photolabile, while the para pyridyl ketone complexes with lower energy bands at 503 nm do not photodissociate in acetonitrile solution. This is consistent with Ford's model of photolabilization occurring only when the λ_{max} of the MLCT absorption band is less than 460 nm.⁴⁹

Ford also found that a linear relation exists between the wavelength of irradiation and $\log \phi_{\text{py-X}}$.⁴⁹ He observed photolabilization for Ru4AP in acetonitrile; extrapolation of his data predicts $\phi_{4\text{AP}}$ of 0.83 upon irradiation at 313 nm! While bleaching of the MLCT band is observed upon irradiation of the para pyridyl ketone

complexes at 313 nm (Figure 25), no free para pyridyl ketone is detected upon gc analysis. The decrease in MLCT λ_{max} must then be the result of another reaction such as oxidation of ruthenium(II) to ruthenium(III).

The pentaammineruthenium(II) valerylpyridyl ketone complexes exhibited photochemical behavior which was dependent upon the type of mercuric chloride used for the synthesis of the reductive zinc mercury amalgam. Initial photochemical studies were carried out on the complexes synthesized using granular mercuric chloride. The photochemical results shown in Table 13 differ from those shown in Table 14 where the complexes were synthesized using powdered mercuric chloride. While the elemental analyses of the former complexes were poor, the spectral properties matched those of the literature and free valerylpyridyl ketone was not detected by gc analysis prior to photolysis. Further work on the characterization of the pentaammine-ruthenium(II) complexes indicated that only those complexes synthesized with the powdered mercuric chloride gave suitable analysis; further photochemical study was restricted to those.

Coordination of the pyridine nitrogen to the ruthenium(II) metal center results in drastic changes in the photochemical behavior of the pyridyl ketone. The Type II fragmentation efficiencies are very low (~2%) when compared to the corresponding hydrochloride salts (10-15%) or free pyridyl ketones (70-90%). This results primarily from the different absorption characteristics of the metal complexed ketone and the corresponding free pyridyl ketone and hydrochloride salt. Bonding to the ruthenium(II) metal center and formation of the hydrochloride salt both involve coordination of the lone

electron pair on nitrogen. If hydrochloride salt formation has the same effect as metal coordination in the absence of orbital mixing, multiplying the ϕ_{II} of the ruthenium(II) complex by the ratio of the extinction coefficient of the complex to its corresponding hydrochloride salt corrects for total light absorption by the pyridyl ketone chromophore. Taking into account the experimental error resulting from the variance in complex extinction coefficient, the corrected Type II fragmentation quantum yields of the ruthenium(II) complexes are comparable to the quantum yields of the pyridyl ketone hydrochloride salts (Table 28).

Table 28. Type II fragmentation quantum yields for the hydrochloride salts and pentaammineruthenium(II) complexes of the pyridyl ketones in acetonitrile solution.

Pyridyl Ketone	Hydrochloride Salts		Ruthenium(II) Complexes	
	ϕ_{II}^a	R^b	ϕ_{actual}	$\phi_{corrected}^c$
β Me3BP	0.13	5.7	0.020	0.120
3VP	0.14	7.6	0.0195	0.150
β Me4BP	0.13	4.4	0.0228	0.099
4VP	0.085	5.0	0.0185	0.093
γ Me4VP	0.13	5.7	0.0228	0.096

^aQuantum yield of acetylpyridine extrapolated to zero ketone concentration. ^b $R = (\epsilon_{313 \text{ nm}}(\text{Ru}^{2+} \text{ complex})) / (\epsilon_{313 \text{ nm}}(\text{HCl salt}))$. ^c $\phi_{corrected} = (\phi_{original})(R)$.

The lifetimes of the ligand derived triplet excited states of the pentaammineruthenium(II) pyridyl ketone complexes are longer than the lifetimes of the corresponding pyridyl ketone hydrochloride salts. Equating $1/\tau$ to k_T for an initial evaluation of the triplet carbonyl

reactivity for the meta ($1^{\circ} : 2^{\circ} = 1 : 2$) and para ($1^{\circ} : 2^{\circ} : 3^{\circ} = 1 : 1.9 : 2.3$) pyridyl ketone complexes indicated a dramatic decrease in gamma hydrogen selectivity (Table 29). In the pyridyl ketone pentaammineruthenium(II) complexes, decay to the lower energy metal-ligand excited states can compete with the intrinsic decay of the ligand derived triplet excited state. Kinetically, these two rates of decay cannot be separately determined. Their sum however may be determined from the bimolecular photoreduction of the corresponding pentaammineruthenium(II) acetylpyridine complexes.

Table 29. Photokinetic data for $[\text{Ru}(\text{NH}_3)_5\text{L}][\text{BF}_4]_2$ in acetonitrile.

<u>L</u>	<u>$\phi_{\text{II}}^{\text{corr}}$</u>	<u>$1/\tau, 10^8 \text{ sec}^{-1}$</u>
βMe3BP	0.120	4.5
3VP	0.150	9.5
βMe4BP	0.099	7.7
4VP	0.088	15.0
γMe4VP	0.096	17.5

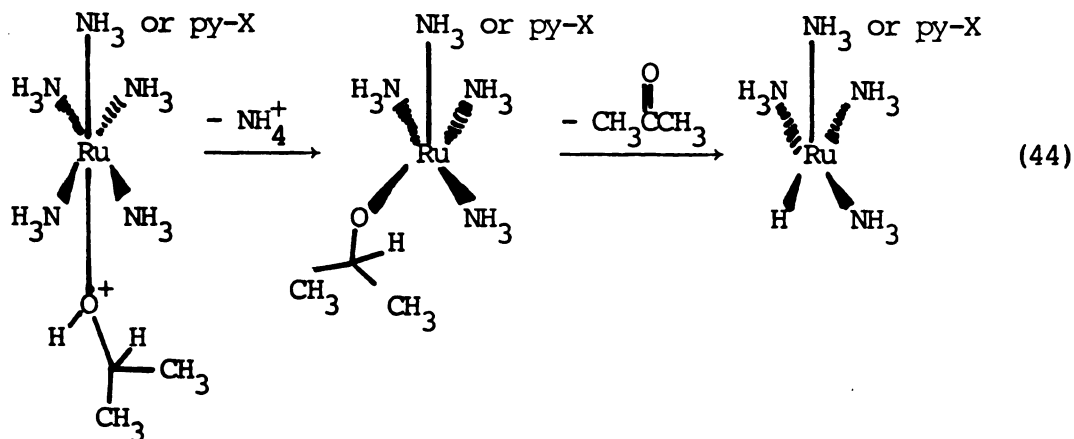
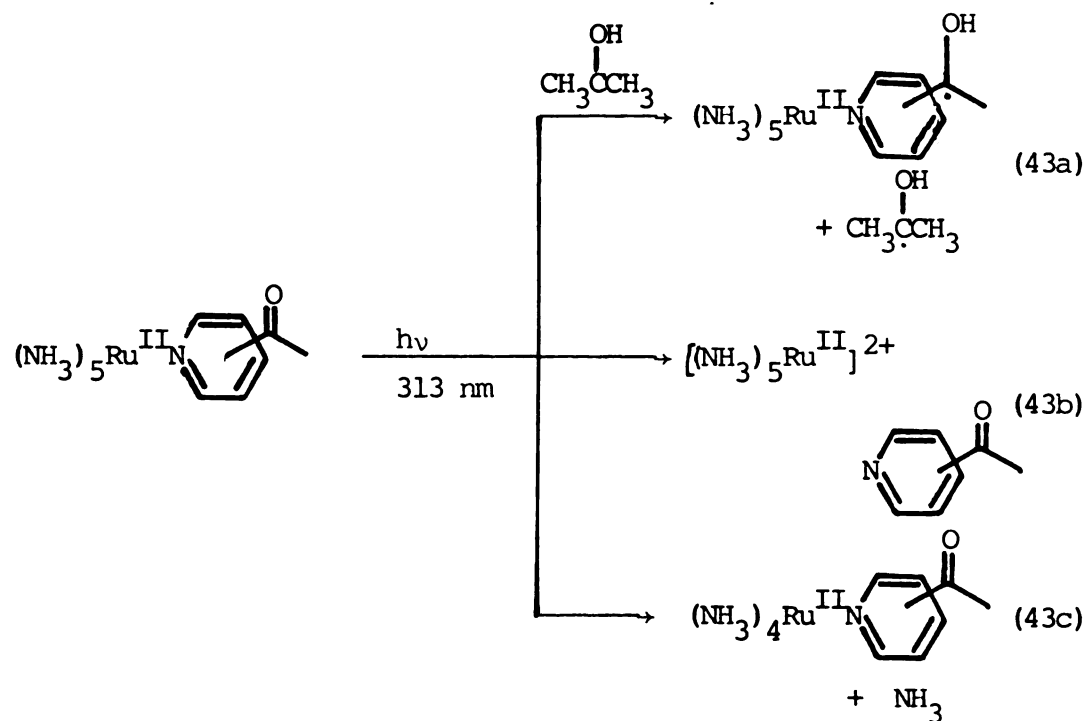
^aValues of τ are estimated on the basis that k_q equals $1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ in acetonitrile.

Irradiation of acetylpyridine pentaammineruthenium(II) complexes in the presence of various hydrogen donors was complicated by competing complex decomposition. Intermolecular photoreduction processes are normally slower than intramolecular photoreductions and strongly dependent upon the reactivity of the hydrogen donating substrate, i.e. acetophenone ($1.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ with toluene,¹⁵⁵ $7.0 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ with p-xylene,¹¹⁴ and $1.8 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ with 2-propanol⁹⁰) versus valerophenone ($1.4 \times 10^8 \text{ sec}^{-1}$).¹⁷³ Irradiation of Ru3AP

or Ru4AP with the less reactive hydrogen donors toluene and p-xylene resulted in complete bleaching of the MLCT λ_{max} without formation of any bibenzyl product. Irradiation of Ru3AP or Ru4AP with 2-propanol produced acetone and was accompanied by only 10-20% complex decomposition. However, the production of acetone could not be quenched by any triplet quencher used. This lack of quenching was quite unexpected. Additional experiments indicated that the formation of acetone could also be the result of other competing reactions. Irradiation of an acetonitrile solution of pentaamminepyridineruthenium(II) tetrafluoroborate with 2-propanol produced acetone, indicating that the presence of a carbonyl group on the pyridine ring is not required for the oxidation of 2-propanol. Under identical conditions, equivalent amounts of acetone were produced upon irradiation of Ru4AP, Ru4VP or pyridine complex in acetonitrile.

The existence of competing side reactions in this inorganic system is likely in light of the redox behavior observed with other ruthenium(II) complexes. While $[\text{Ru}(\text{bipy})_3]^{2+}$ stoichiometrically reduces water to hydrogen, the analogous reaction with $[\text{Ru}(\text{trpy})_2]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{bipy})_2(\text{py})_2]^{2+}$ shows ligand reduction, solvent reduction and loss of ligand competing with hydrogen production.¹⁷⁴ Catalytic quantities of $[(\text{trpy})(\text{bipy})\text{RuO}]^{2+}$ have been found to quantitatively oxidize 2-propanol to acetone.¹⁷⁵ In the absence of external hydrogen acceptors, ruthenium(II) complexes have been found to cause the dehydration of alcohols.¹⁷⁶ The pentaammineruthenium(II) system has not been studied as extensively as the polypyridyl ruthenium(II) systems. The loss of ligands indicated by the decrease in the MLCT λ_{max} optical density (43b) and the shift of the MLCT λ_{max} (43c)

suggests that a similar mechanism for dehydrogenation¹⁷⁶ is occurring upon irradiation with 2-propanol (44).



In terms of pentaammineruthenium(II) pyridyl ketone photoreactivity, the observation of Type II fragmentation is positive proof that reaction from the ligand triplet excited state (k_r) is able to compete with decay down to the lower energy excited states and the ground

state ($k_d + k_{ic}$). The lack of quenching of acetone formation and its probable formation by other pathways indicates that the bimolecular photoreduction experiments cannot be used to quantitatively determine the rate of ligand triplet excited state decay. The rate of internal conversion can then be calculated by comparing the photoelimination data for the pyridyl ketone pentaammineruthenium(II) complexes and the corresponding hydrochloride salts as follows. Coordination to the ruthenium(II) metal center can be viewed as introducing two unknowns into the triplet state lifetime: an inductive effect on the rate constant for gamma hydrogen abstraction, k_r ; and competitive decay to the lower energy metal-ligand excited states with rate constant k_{ic} . In equation (45), k_r^O is the known triplet rate constant for gamma hydrogen abstraction by the corresponding pyridyl ketone hydrochloride salt. The unknown rate factor on gamma hydrogen abstraction introduced

$$\frac{1}{\tau} = k_r + k_{ic} = a(k_r^O) + k_{ic} \quad (45)$$

by ruthenium(II) metal coordination is a . Substituting the values for $1/\tau$ (Table 29) and k_r^O (Table 27) into (45) and solving the pair of simultaneous equations for the meta coordinated pyridyl ketones gives $a = 0.39$ and $k_{ic} = 2.1 \times 10^8 \text{ sec}^{-1}$. The three simultaneous equations for the para coordinated pyridyl ketones do not give a real solution, $a = 0.37$ and $k_{ic} = +1.1 \times 10^8 \text{ sec}^{-1}$. This is best rationalized as resulting from the compression of the pyridyl ketone ruthenium(II) complex lifetime ratios ($1/\tau(\text{Ru}^{\text{II}}\text{Me}4\text{BP}) : 1/\tau(\text{Ru}4\text{VP}) : 1/\tau(\text{Ru}^{\text{II}}\text{Me}4\text{VP}) = 1 : 2 : 2$).

Comparison of the k_{ic} value for the meta pyridyl ketone pentaammineruthenium(II) complexes with the observed quantum yields

indicates that this value of k_{ic} overestimates the actual rate of decay. Calculation of k_r from k_r^0 for the meta complexes gives k_r (Ru β Me3BP) = $2.48 \times 10^8 \text{ sec}^{-1}$ and k_r (Ru3VP) = $7.4 \times 10^8 \text{ sec}^{-1}$.

Substitution into (12) gives the following expressions for the Type II quantum yields:

$$\phi_{II} = 0.53\phi_{isc}\phi_P \quad (\text{Ru}\beta\text{Me3BP}) \quad (46)$$

$$\phi_{II} = 0.78\phi_{isc}\phi_P \quad (\text{Ru3VP}) \quad (47)$$

For meta substitution, ϕ_{isc} and ϕ_P are constant. Since the ϕ_{II} are constant (ϕ (Ru β Me3BP) = 0.20, ϕ (Ru3VP) = 0.195). $k_{ic} < k_r$. To account for the constant quantum yields observed for the para pyridyl ketone complexes, the ϕ_{BR} must also be constant with $k_{ic} < k_r$. Thus, $k_r = 1/\tau$; and k_{ic} for both the meta and para pyridyl ketone complexes must be less than 10^8 sec^{-1} .

An excited state manifold incorporating k_{ic} is illustrated in Figure 33. The retention of orbital parentage in radiationless transitions¹⁸⁴ and enhanced intersystem crossing from the heavy atom induced spin orbit coupling^{27,184} in organometallic complexes has been interpreted to indicate that $k_{isc} \gg k_{ic}$. Intersystem crossing in the pyridyl ketone ruthenium(II) complexes must be at least as efficient as in the corresponding hydrochloride salts (ϕ_{isc} (meta) = 0.90, ϕ_{isc} (para) = 0.60) since the ϕ values are similar. Reaction from the ligand excited state is then dependent upon the rate of reaction of the ligand derived excited state (k_r) relative to the rates of internal conversion to the lower energy metal-ligand excited states (k_{ic}), decay to the ground state (k_d) and emission (k_{em}).

Pyridyl ketone photoreduction is a known triplet state reaction.⁶⁷

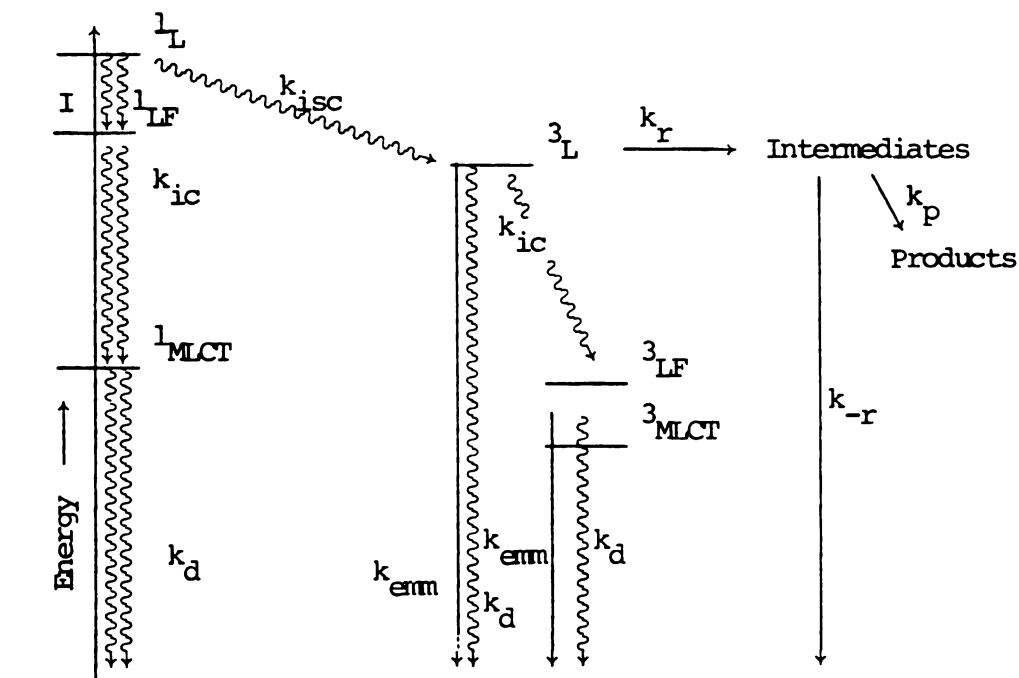


Figure 33. Jablonski diagram for a pyridyl ketone organometallic complex.

The value determined above for k_{ic} as $< 10^8 \text{ sec}^{-1}$ must measure triplet state conversion. Relatively little data exists on the rates of $T_n \rightarrow T_1$ internal conversion. For example, Gillispie and Lim¹⁹⁹ as well as Liu & workers²⁰⁰ measured a k_{ic} of $1 \times 10^{10} \text{ sec}^{-1}$ for $T_2 \rightarrow T_1$ internal conversion of 9,10-dibromoanthracene. The rate of internal conversion in the organometallic system thus differs by a factor of at least 10^2 . This difference may be attributed to the combined effects of energy level separation and orbital overlap. Liu²⁰¹ has indicated that the $T_2 \rightarrow T_1$ energy gap for 9,10-dibromoanthracene and anthracene should be similar (31.9 kcal/mol). The energy level differences in the penta-ammineruthenium(II) pyridyl ketone system may not be quantitatively determined because these complexes do not emit. The pyridyl ketone

ligand triplet state is expected to lie at approximately the same energy as the pyridyl ketone hydrochloride salt (~ 70 kcal/mol). The MLCT energy may be estimated as below the λ_{max} absorption bands (E_{MLCT} (para) ~ 56 kcal/mol, E_{MLCT} (meta) ~ 69 kcal/mol). The expected smaller separation of energy levels in the organometallic system does not lead to an enhanced rate. In the organometallic system, the $p-\pi$ orbitals of the pyridyl ketone overlap with the d_{z^2} orbitals of the ruthenium(II) metal ion. Although the carbonyl and ruthenium(II) metal center are not very far apart, the coplanar n and d_{xz} orbitals are highly directed and almost perpendicular to each other. Therefore it is both the poor orientation of the orbitals and intervening pyridine nuclei which give poor orbital overlap resulting in a slower rate of internal conversion.

In the corresponding system $[\text{Ru}(\text{bipy})_2(4\text{-stilbazole})_2]^{2+}$, Whitten suggested a k_{ic} value of $5 \times 10^{12} \text{ sec}^{-1}$.⁵² This rate is also much faster than the k_{ic} value determined for the pentaammineruthenium(II) pyridyl ketone complexes. This discrepancy raises the question as to whether k_{ic} in an organometallic system is dependent only upon the metal center or whether it is also affected by the ligands. The limited experimental data, at this point consisting of only two cases for the ruthenium(II) system, lend themselves to the following evaluation. Whitten did not measure the reaction rates for the stilbazole ruthenium(II) complexes. Isomerization efficiency was attributed to ruthenium(II) catalyzed intersystem crossing to an unreactive triplet, evidenced by a ten fold lower sensitized isomerization efficiency. He attributed complexed stilbazole isomerization to a singlet reaction. The tentatively determined k_{ic} is comparable to values

observed in other singlet systems.¹⁷⁷ Crosby et. al.¹⁷⁸ have proposed that singlet and triplet spin labelling in organometallic complexes is inappropriate due to orbital mixing. However, the ligand photoreactions in the two systems apparently occur from states of different multiplicities since pyridyl ketone photoreduction is a known triplet reaction.⁶⁷ It would then appear reasonable that the value of k_{ic} will also be affected by the nature of the ligand excited state.

Pyridyl Ketone Bromotricarbonylrhenium(I) Complexes

The physical properties of the bromotricarbonyl rhenium(I) pyridyl ketone complexes did not restrict the pyridyl ketone used as a ligand for the photochemical studies. Dissociation of the pyridyl ketone ligand from the rhenium(I) complex upon gc analysis allowed for direct analysis of both acetylpyridine photoproduct and ligand pyridyl ketone disappearance. However, pyridyl ketone ligand dissociation could not be detected. Unfortunately, Type II fragmentation was not observed for any of the pyridyl ketone bromotricarbonylrhenium(I) complexes. In comparison, the corresponding styrylpyridine bromotricarbonylrhenium(I) complexes undergo ligand isomerization in a manner almost identical to that of the free ligand.^{53,60} The underlying reasons for the different photochemical behavior in these two complexes are the reactive chromophore's ability to absorb light and the nature of the lowest lying excited state. The enhancement of absorption at 313 nm for pyridyl ketone rhenium(I) complexes results from additional dd transitions. If hydrochloride salt formation and metal coordination have the same effect on light absorbance of the carbonyl chromophore, only 1.4-1.7% of the light goes into the ligand carbonyl chromophore. Irradiation over

the 24 hour period (Table 20) could result in only 0.003 einstein absorption by the ligand. With no internal conversion, this would produce only 5×10^{-4} M acetylpyridine, corresponding to an observed quantum yield of 0.0015. A 10^{-4} M concentration could have been measured. Furthermore, the MLCT state is lower in energy than the ligand triplet excited state. Thus the lack of ligand photoreaction is a consequence of the ligand's weak absorption of light as well as competitive complex decomposition. In contrast, metal coordination of styrylpyridine in the rhenium(I) complex shifts the IL $\lambda_{\max}$ ($\lambda_{\max}$ (meta) = 297 nm (ϵ 45300 M⁻¹cm⁻¹); $\lambda_{\max}$ (para) = 330 nm (ϵ 53200 M⁻¹cm⁻¹)) but has a negligible effect on the extinction coefficient in comparison to the free ligand ($\lambda_{\max}$ (para) = 308 nm (ϵ 27000 M⁻¹cm⁻¹); $\lambda_{\max}$ (meta) = 308 nm (ϵ 19300 M⁻¹cm⁻¹)). The alkene chromophore absorbs all the light and isomerization quantum yields and photostationary states are identical to the free ligand.⁵³

The color changes after irradiation are a further indication that photoreactions occur from the lower energy MLCT states. Normally carbon monoxide dissociation is the primary photoprocess observed upon irradiation of metal carbonyl complexes.^{179,180} However, with the lack of observable CO dissociation in other bromotricarbonyl-rhenium(I) systems,⁶¹ this was not expected to be a competing photoprocess. The absence of change in the infrared and absorption spectra implied that pyridyl ketone ligand dissociation from the complex did not occur. Even if pyridyl ketone ligand dissociation were to occur, free pyridyl ketone Type II fragmentation would not be expected to compete with complexed pyridyl ketone fragmentation since the rhenium

complex would still absorb a major amount of the light and the presence of bromotricarbonylrhenium(I) complexes suppressed fragmentation quantum yields of the free ligand in independent experiments (Table 6). The fact that gc analysis of irradiated solutions of the pyridyl ketone bromotricarbonylrhenium(I) complexes show more disappearance of pyridyl ketone ligand than the concentration change calculated from the change in MLCT λ_{max} optical density suggests a situation similar to that observed in the pentaammineruthenium(II) system. Although new products are not detected by gc analysis, the broadness of the MLCT band may obscure the spectral characteristics of products with similar absorption properties formed after prolonged irradiation.

The lack of IL photobehavior in the pyridyl ketone tricarbonyl-bromorhenium(I) complexes is paralleled in the emission spectra. The IL emission of 1-(3-pyridyl)pentanone (3VP) is compared to the MLCT emission of Re3VP in Figure 34. Like the free pyridyl ketones, no emission is observed from the corresponding bromotricarbonylrhenium(I) complexes at room temperature. At 77°K the red shifted, broad, structureless emission of the para pyridyl ketone complexes is indicative of MLCT character. The low energy emission of the meta alkyl pyridyl ketone complexes also has MLCT character, unlike the ligand character seen with the corresponding benzoylpyridine complex. The spectral properties of the pyridyl ketone bromotricarbonylrhenium(I) complexes are compared to the tricarbonylrhenium(I) systems exhibiting IL character in their emission spectra (Table 30). The 3-valerylpyridine and 3-benzoylpyridine complexes have the same absorption energies. The emission energies at 77°K are not identical for the 3-benzoylpyridine (69.2 kcal)⁶² and acetonitrile phenanthroline

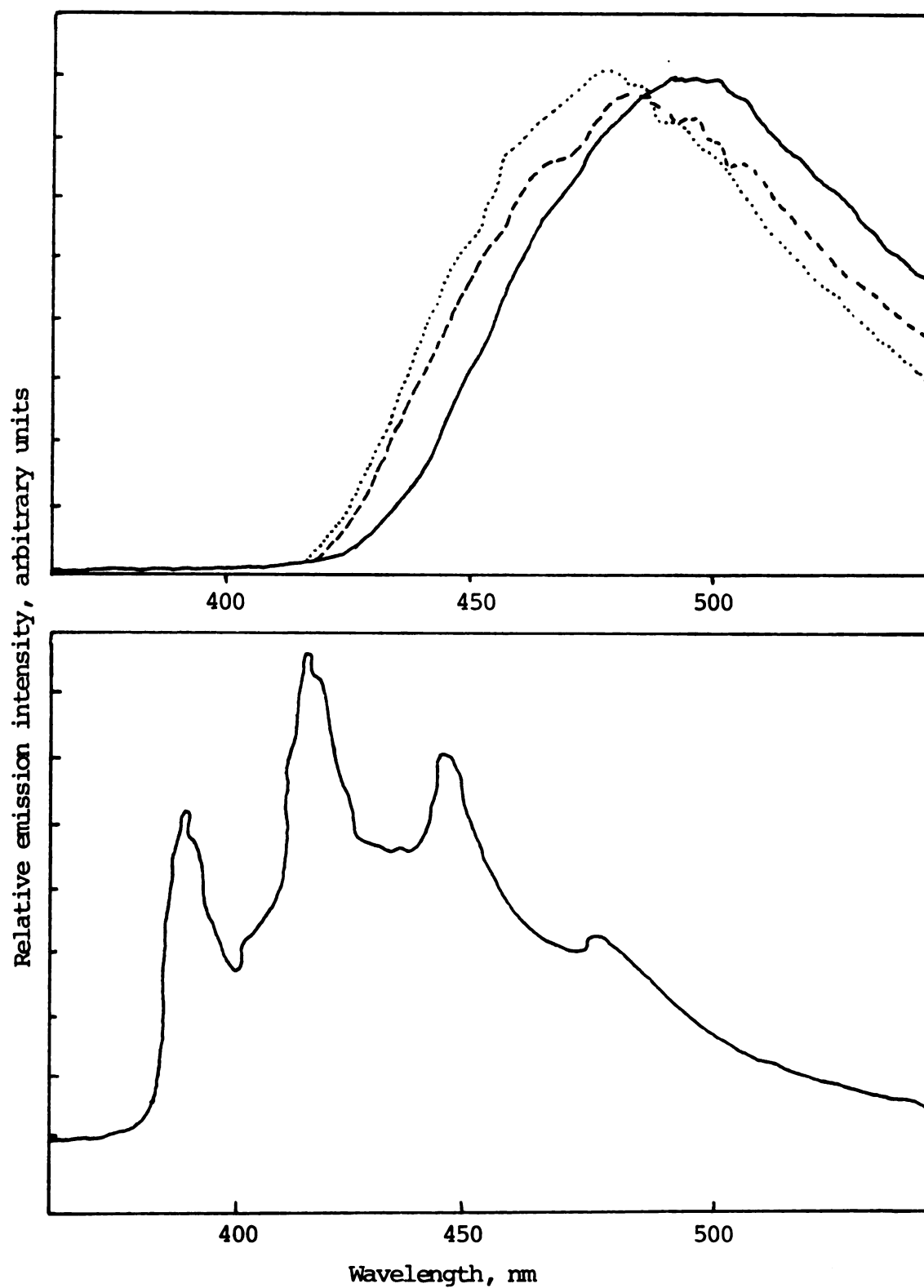


Figure 34. Comparison of the emission spectra of Re3VP and 3VP in 5:1 methylcyclohexane:iso-pentane (—); methyltetrahydrofuran (--) and EPA (.....) at 77K.

Table 30. Spectral properties of some $\text{BrRe}(\text{CO})_3\text{L}_2$ complexes.

Complex	Absorption ^c		Emission $\lambda_{\text{max}}, \text{nm}(\tau, \mu\text{s})^{\text{d}}$	
	$\lambda_{\text{max}}, \text{nm}$	$(\epsilon, \text{M}^{-1}\text{cm}^{-1})$	298°C	77°K
$\text{BrRe}(\text{CO})_3(3\text{-benzpy})_2^{\text{a}}$	sh ~ 295		546 (<0.5)	Total: 413,444,478 (12.5 + 1300) Long Lived: 413,442 478,518 (1300)
$\text{BrRe}(\text{CO})_3(4\text{-benzpy})_2^{\text{a}}$	330 (10000)		602 (<0.5)	Total: 513 (38) Long Lived: none
$\text{BrRe}(\text{CO})_3(3\text{VP})_2$	sh ~ 300 (10050)		none	Total: 476 Long Lived: 476
$\text{BrRe}(\text{CO})_3(4\text{VP})_2$	334 (10270)		none	Total: 493 Long Lived: 493
$\text{ClRe}(\text{CO})_3\text{phen}^{\text{b}}$	sh ~ 409		577 (0.85)	Total: 535 (9) Long Lived: 493
$(\text{CH}_3\text{CN})\text{Re}(\text{CO})_3\text{phen}^{\text{b}}$	360 (6410)		532 (0.80)	Total: 455,487,517 (11 + 75) Long Lived: 452,482 517 (75)

^aRef. 62. ^bRef. 63. ^cBenzene solvent. ^dEPA solvent.

(62.9 kcal) rhenium(I) complexes, yet only those complexes in the series with the blue shifted absorption and emission bands show structured emission at low temperature. It is evident that a correlation cannot be drawn between the existence of IL character in the emission spectra and the energy levels of the IL and MLCT states.

The absence of IL character in the pyridyl ketone rhenium(I) complexes could also indicate that the initially populated ligand excited states undergo internal conversion to the lower energy MLCT excited states faster than reaction from the ligand excited state. Sensitization of alkene isomerization by rhenium(I) complexes resulted in isomerization quantum yields of varying efficiency. The linear plots show a variation in the efficiency of intersystem crossing

dependent upon the alkene quencher, aza substituent and substituent on the pyridine carbonyl group. While dependence upon the latter two factors is expected, dependence of the intersystem crossing efficiency on the quencher suggests that alkene isomerization does not occur by the accepted bimolecular mechanism.¹²⁵ This is further substantiated by the fact that Repp causes alkene isomerization with efficiency comparable to that observed for other metal complexes under similar conditions.^{181,182} Wrighton et.al.¹⁸² speculated that alkene isomerization resulted from the dissociation of carbon monoxide, followed by reversible binding of the alkene.

SUMMARY

The results described in this thesis have shown that the photo-processes of pyridyl ketones coordinated to metal atoms are very dependent on the metal ion and the nature of the other ligands. Irradiation with high energy light at 313 nm does not always lead to photochemical reactions from the pyridyl ketone ligand excited state. The underlying reason is the existence of additional pathways of decay for an organic ligand, L, when coordinated to a metal ion in an organometallic complex. (Figure 32).

The intramolecular photoreduction reaction from the upper excited state of the pyridyl ketone pentaammineruthenium(II) complexes is fast enough to compete with decay to the lower energy excited states. Decreased ability to absorb light directly into the carbonyl chromophore lowers the Type II fragmentation efficiency. Correction of ϕ_{II} for light absorption and comparison to ϕ_O^∞ of the pyridyl ketone hydrochloride salts indicates that with coordination of the nitrogen lone pair, the same effects operate on the 1,4-biradical. Ligand phot substitution occurs only with the meta pyridyl ketone pentaamine-ruthenium(II) complexes from the LF^* excited state. Side reactions, among them complex decomposition, compete with the intermolecular photoreduction reaction and the rate of decay of the ligand derived triplet excited state cannot be quantitatively lifetimes of the triplet carbonyl excited state in the pyridyl ketone

pentaammineruthenium(II) complexes were compared to the lifetimes of the corresponding hydrochloride salts to determine a rate of decay to the lower energy excited states of less than 10^8 sec^{-1} .

The lack of Type II fragmentation for the bromotricarbonylrhenium(I) pyridyl ketone complexes suggests that the rate of internal conversion to the lower energy states is faster than the rate of gamma hydrogen abstraction. If metal complexation were to have the same effect on excited state behavior as hydrochloride salt formation, the lifetime of the ligand carbonyl triplet state and the rate of gamma hydrogen abstraction would be expected to decrease and increase respectively. Sensitization studies show that triplet state population occurs upon excitation. The decreased ability of light absorbance by the ketone chromophore would result in inefficient Type II fragmentation. Ligand photoreduction is then unable to compete with complex decomposition.

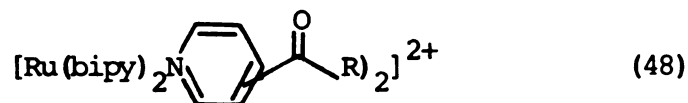
In conclusion, reaction resulting directly from the upper excited state in an organometallic complex has been observed. Observation of ligand pyridyl ketone photoreduction has been found to be dependent upon the ability of the ketone chromophore to absorb light. Most significantly, where ligand photoreduction is efficient enough to compete with complex decomposition, the lifetime of the ligand excited state may be used to determine the rate of decay of the upper excited state to the lower excited states. The rate of internal conversion in the pyridyl ketone pentaammineruthenium(II) complexes ($k_{ic} < 10^8 \text{ sec}^{-1}$) is slower than the rate of conversion in organic compounds ($k_{ic} = 10^{11}-10^{13} \text{ sec}^{-1}$).¹⁸⁶

Suggestions for Further Study

The field of organometallic photochemistry is rich with opportunity and the results in this dissertation indicate that further work is necessary to increase understanding of the organometallic excited state manifold. Study should be focused primarily on systems where ligands undergo reactions from upper excited states to allow further determination of the rates of internal conversion of the excited states. Now that it is established that a pyridyl ketone coordinated to a metal center can undergo Type II fragmentation before complex decomposition, two different courses of study could be pursued. Pyridyl ketones could be used as ligands in other metal systems. Since the observation of photoreduction depends strongly on the ability of the carbonyl chromophore to absorb light, irradiation of complexes which are transparent in the 313 nm region would be expected to provide valuable information.

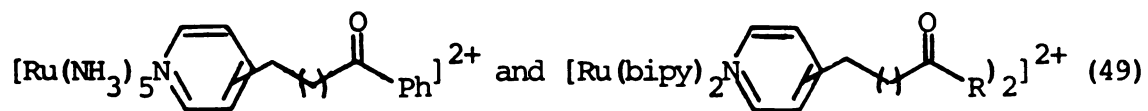
The second course of study would be related directly to the photochemistry which has been observed in the ruthenium(II) system:

- 1) Synthesis and investigation of the photochemical properties of the pyridyl ketone bisbipyridylruthenium(II) complexes in (48) where ligand photodissociation would not be expected to be a competing side reaction.



- 2) Synthesis and photochemical study of the complexes in (49) to determine the intramolecular effect of metal coordination on the Type II photoprocesses when the metal is not conjugated

to the carbonyl chromophore.



The low quantum efficiencies and high rates of reactivity of the pyridyl ketone hydrochloride salts indicate that these compounds will exhibit interesting photochemistry in their own right. It is apparent that the two reactions leading to product formation, radical formation and reaction of these radicals, are in competition with reactions whose nature at this point can only be ascribed to a charge transfer interaction. Further work especially involving the bimolecular photo-reduction and flash experiments are necessary.

EXPERIMENTAL

Instrumentation

All compounds were identified on the basis of their physical and spectral properties using the instruments described below. Samples for irradiation were greater than 99.5% pure as determined from gas phase chromatography (gc).

Nuclear resonance spectra (NMR) at 60 MHz were obtained with a Varian T-60 NMR Spectrophotometer. All chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). Infrared absorption spectra (IR) were determined on a Perkin Elmer 237B Grating Infrared Spectrophotometer calibrated at 1601 cm^{-1} with a polystyrene film. Low resolution mass spectra (ms) were determined on a Hitachi Perkin Elmer RMU-6 mass spectrophotometer or on a Finnigan 4021 GC-MS at an ionization potential of 70 ev for electron impact and 40 ev for chemical ionization (methane carrier gas). Melting points (mp) were determined with a Thomas Hoover capillary melting point apparatus. All melting points are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan 49951.

Absorption spectra were measured with a Cary 17 or Unicam SP-800 spectrophotometer. Emission spectra were measured on a Perkin Elmer MPF-44A Fluorescence Spectrophotometer equipped with a Differential Corrected Spectra Unit and Hitachi Phosphorescence Accessory.

Preparative scale separations were done on a Varian Aerograph

model 920 gas chromatograph fitted with a thermal conductivity detector. Analytical analyses were done on Varian Aerographs: Hi-Fy Model 600D, Model 1200 and Model 1400 gas chromatographs fitted with flame ionization detectors. Relative peak areas were determined using an Infotronics CRS 309 Computing Integrator for Chromatography.

Chemicals

Solvents

Benzene: 3.5 liters of thiophene free benzene (Fischer Scientific or Mallinckrodt Chemical Company) was stirred over several changes of concentrated sulfuric acid (200 ml) until the sulfuric acid remained colorless. It was washed with distilled water (2x300 ml), then saturated sodium bicarbonate (3x300 ml) until a white precipitate no longer formed. The benzene was then washed with distilled water (2x200 ml) and dried with anhydrous magnesium sulfate. It was refluxed over phosphorous pentoxide overnight and distilled through a one meter column packed with stainless steel helices, the first and last 250 ml being discarded; bp = 80.0° C.

Acetonitrile: Acetonitrile (Fischer Scientific Company) was purified according to the procedure of O'Donnell.¹⁸⁷ Practical grade acetonitrile was distilled from 10 g anhydrous Na₂CO₃ and 15 g KMnO₄, made slightly acidic with H₂SO₄ (conc), decanted from the precipitated ammonium sulfate and distilled through a half meter column packed with stainless steel helices; bp = 82° C. Mallinckrodt SpectAR, Aldrich Gold Label and MCB OmniSolv were used as received.

Pyridine: Pyridine (Mallinckrodt Chemical Company) was dried over KOH, decanted and distilled from barium oxide through a half meter

column packed with stainless steel helices. The middle 70% was collected; bp = 115°C .¹⁸⁸

tert-Butyl Alcohol: tert-Butyl alcohol (J. T. Baker Company) was distilled from freshly cut sodium (1g/ 1 of alcohol) through a 45 cm glass helix packed column. The middle 60% was collected; bp = 83°C .

2-Methyltetrahydrofuran: 2-Methyltetrahydrofuran (Matheson, Coleman and Bell) was refluxed overnight over cuprous chloride, then distilled through a 40 cm vigreux column. The first and last 10% were discarded. It was then triply distilled from lithium aluminum hydride, the first and last 10% being discarded; bp = 79°C .¹⁸⁹

2-Methylbutane: Gold Label Grade 2-methylbutane was used as received from Aldrich Chemical Company.

Ethanol: Ethyl alcohol was used as received from Aaper Alcohol and Chemical Company.

Ethyl Ether: Anhydrous ethyl ether (Mallinckrodt) was refluxed for 24 hr over freshly cut pieces of sodium and distilled from a 30 cm vigreux column packed with stainless steel helices. The middle 60% was collected; bp = 34.5°C . When used for emission studies at 77°K , ether was distilled freshly prior to use. Emission spectrum at 77°K showed no impurities immediately after distillation; however, with time, impurities appeared.

Methylcyclohexane: Methylcyclohexane (Eastman Chemical Company) was purified according to the procedure of Foster.¹⁹⁰ 500 ml of methylcyclohexane was stirred over several changes of concentrated sulfuric acid (100 ml) until the sulfuric acid remained colorless. It was washed with distilled water (3x100 ml), saturated sodium bicarbonate (3x100 ml), distilled water (2x100 ml) and dried over

magnesium sulfate. It was then distilled through a half meter stainless steel helix column. The first and last 20% was discarded; bp = 101°C.

Water: Distilled water was passed through three Sargent-Welch mixed ion-exchange columns.

Hydrogen Donors

Toluene: Toluene (Mallinckrodt) was purified in the same manner as benzene with the exception that the toluene was kept in an ice bath while being washed with sulfuric acid to prevent sulfonation of the ring. The middle 60% was collected from distillation; bp = 110°C.

p-Xylene: p-Xylene (Mallinckrodt) was purified in the same manner as toluene. The middle 60% was collected from distillation; bp = 138°C.

2-Propanol: 2-Propanol (Matheson, Coleman and Bell) was distilled from freshly cut metallic sodium through a 20 cm glass helix packed column. The first and last 10% was discarded; bp = 82.5°C.

1-Phenylethanol: 1-Phenylethanol (Aldrich) was purified by stirring over sodium borohydride to reduce acetophenone, washed with distilled water and distilled under reduced pressure; bp = 89°C (10 mm).

Internal Standards

Cyclohexane: Cyclohexane (Matheson, Coleman and Bell, Spectrophotometric grade) was recrystallized twice from itself by Dr. H. Frerking.

Hexadecane: Hexadecane was obtained from Aldrich Chemical Company and purified by washing with sulfuric acid, then distilling by Dr. Peter J. Wagner; bp = 146°C (10 mm).

Heptadecane: Heptadecane was obtained from Aldrich Chemical

Company and purified by washing with sulfuric acid then distilling by Dr. Peter J. Wagner; bp = 158° C (8 mm) .

Octadecane: Octadecane was obtained from Aldrich Chemical Company and purified by recrystallization from ethanol by Dr. Peter J. Wagner.

Nonadecane: Nonadecane was obtained from Chemical Samples Company and purified by recrystallization from petroleum ether by Dr. Peter J. Wagner.

Eicosane: Eicosane was obtained from Chemical Samples Company and purified by recrystallization twice from 200 proof ethanol by Elizabeth Seibert.

Heneicosane: Heneicosane was obtained from Chemical Samples Company and purified by recrystallization from ethanol by Dr. Peter J. Wagner.

Quenchers

2,5-Dimethyl-2,4-hexadiene: this diene was obtained from Chemical Samples Company and upon refrigeration sublimed up around the sides of the bottle. The sublimed material was used.

cis- and trans-1,3-Pentadiene: this diene was used as received from Chemical Samples Company.

cis-1,3-Pentadiene: this diene was used as received from Chemical Samples Company (98.8% pure by gc) .

trans-Stilbene: this olefin was used as received from J. T. Baker Company.

Ethyl sorbate: this diene was used as received from Aldrich Chemical Company.

Naphthalene: Naphthalene (Matheson, Coleman and Bell) was purified by several recrystallizations from ethanol by Dr. A. E. Puchalski; mp =

79.5–80.5° C.

Phenylalkyl Ketones

Acetophenone: Matheson, Coleman and Bell acetophenone was distilled under reduced pressure by Dr. A. E. Puchalcki.

Benzophenone: Aldrich Chemical Company benzophenone was purified by recrystallization from ethanol by W. B. Mueller.

Valerophenone: Valerophenone was prepared by the Friedel Crafts acylation of benzene by valeryl chloride. The acid chloride was dripped slowly into a two-fold excess of benzene containing a ten percent excess of aluminum chloride and refluxed one hr. Upon cooling, the mixture was poured onto cracked ice and concentrated HCl, the layers separated and the aqueous layer was washed with benzene. The combined organic layers were washed with 5% NaOH (100 ml) and saturated sodium chloride solution (100 ml). Removal of the solvent under reduced pressure gave a brown oil (85%). Two distillations gave 99.7% pure product bp = 88° C (1.2 mm).

Pyridylalkyl Ketones

2-Acetylpyridine (2AP): 2-Acetylpyridine (Aldrich Chemical Company) was distilled; bp = 65° C (10 mm). Physical properties: IR (neat) 3040, 2970, 1700, 1585, 1565, 1350, 1275, 1230, 1100, 970 cm^{-1} ; NMR (CDCl_3) δ 2.68 (s, 1H), 7.21–8.67 (m, 4H, aromatic); UV (acetonitrile) 275 nm (ϵ 2810 $\text{M}^{-1}\text{cm}^{-1}$); m/e (rel int) 121(65), 93(23), 79(100), 78(79).

3-Acetylpyridine (3AP): A solution containing 20 g (0.14 m) of methyl iodide in 80 ml of anhydrous ether was added dropwise to a well stirred mixture of 3.5 g (0.14 m) of magnesium turnings and 20 ml of anhydrous ether. When the mixture cooled to room temperature, a

solution containing 10.4 g (0.10 m) of 3-cyanopyridine in 80 ml of ether was added dropwise, then the mixture was refluxed for 12 hr. Upon cooling to room temperature, 100 ml of a 5% sulfuric acid solution was added, the ether was removed by distillation and the reaction mixture was refluxed 1.5 hr. Upon cooling, the solution was saturated with solid potassium carbonate and extracted several times with ether. The ether extracts were combined, washed with saturated salt solution and dried over magnesium sulfate. Removal of ether under reduced pressure left a brown oil (crude yield 10 g - 83%) which was distilled; bp = 89-90^o C (7 mm), and characterized as 3-acetylpyridine on the basis of its physical and spectral properties: IR(neat) 3010, 1700, 1590, 1420, 1370, 1275, 1015, 800, 700 cm⁻¹; NMR(CDCl₃) δ2.57 (s, 1H), 7.29-9.05 (m, 4H, aromatic); UV(acetonitrile) 266 nm (ε 2510 M⁻¹cm⁻¹); m/e (rel int) 121(54), 106(97), 79(17), 78(100); UV(heptane) 267 nm (ε 2630 M⁻¹cm⁻¹).

4-Acetylpyridine (4AP): A solution containing 20 g (0.14 m) of methyl iodide in 80 ml of anhydrous ether was added dropwise to a well stirred mixture of 3.5 g (0.14 m) of magnesium turnings and 20 ml of anhydrous ether. After the reaction was complete, a solution of 10.4 g (0.10 m) of 4-cyanopyridine in 100 ml of anhydrous ether was added dropwise. The resultant solution was refluxed 12 hr. Upon cooling, 100 ml of 5% aqueous sulfuric acid solution was added and the reaction mixture was refluxed 1.5 hr. Upon cooling, the solution was saturated with solid potassium carbonate and extracted with ether. The ether extracts were combined, washed with saturated salt solution and dried over anhydrous potassium carbonate. Removal of the ether under reduced pressure left a brown oil (crude yield 5.2 g - 41%) which was distilled;

bp = 108-110° C (25 mm), and identified as 4-acetylpyridine on the basis of its physical and spectral properties:¹⁹¹ IR(neat) 3020, 1700, 1600, 1560, 1415, 1272, 810 cm^{-1} ; NMR(CDCl_3) δ 2.6 (s, 3H) 7.38-8.57 (dd, 4H, aromatic); UV(acetonitrile) 279 nm (ϵ 2210 $\text{M}^{-1}\text{cm}^{-1}$); UV(heptane) 278 nm (ϵ 2240 $\text{M}^{-1}\text{cm}^{-1}$); m/e (rel int) 121(94), 106(100), 79(29), 78(77), 51(35).

1-(2-pyridyl)butanone (2BP): A solution containing 35.2 g (0.29 m) of n-propyl bromide in 80 ml of anhydrous ether was added dropwise to a well stirred mixture of 6.9 g (0.28 m) of magnesium turnings and 30 ml of anhydrous ether. After the reaction subsided, it was cooled to and kept at 2°C while a solution containing 30 g (0.29 m) of 2-cyanopyridine in 80 ml of anhydrous ether was added dropwise over a period of two hours. The resultant black solution was stirred under reflux 12 hr. Upon cooling, the black solution was poured into 200 ml of 10 M hydrochloric acid. The ether was removed by distillation and the reaction mixture was refluxed for 8 hr. Upon cooling, the solution was made basic by the addition of solid potassium carbonate. Filtration removed the precipitated salts and the precipitate was washed with ether. The aqueous solution was extracted with ether until the ether extracts were colorless. The ether extracts were combined, washed with saturated salt solution, dried with anhydrous potassium carbonate and filtered. Removal of the ether under reduced pressure left a black oil (crude yield - 42.1 g - 97%) which was distilled twice under reduced pressure to obtain a sample suitable for photolysis. The ketone was identified as 2-butyrylpyridine on the basis of its physical and spectral characteristics: bp = 85-87° C (4.5 mm); IR(neat) 3040, 2970, 1700, 1585, 1565, 1350, 1275, 1230, 1100, 970 cm^{-1} ; NMR(CDCl_3) δ 0.98

(t, 3H), 1.45-2.03 (m, 2H), 3.1 (t, 2H), 7.2-8.7 (m, 4H, aromatic); UV(acetonitrile) 267 nm (ϵ 4190 M⁻¹cm⁻¹); m/e (rel int) 149(48), 134(100), 121(62), 80(45), 79(90), 78(57), 51(64).

1-(3-pyridyl)butanone (3BP): A solution of 23.6 g (0.19 m) of n-propyl bromide in 80 ml of anhydrous ether was added dropwise to a well-stirred mixture of 4.7 g (0.19 m) of magnesium turnings in 20 ml of anhydrous ether. This solution of n-propylmagnesium bromide was added dropwise to a stirred solution containing 20 g (0.19 m) of 3-cyanopyridine in 80 ml of anhydrous ether and 20 ml of benzene. The reaction mixture was stirred at 25°C for 3 hr. The reaction was quenched by the addition of 200 ml of 10 M hydrochloric acid solution. The ether was removed by distillation and the reaction mixture was refluxed for 3 hr. Upon cooling, the solution was made basic by the addition of solid potassium carbonate. Filtration removed the precipitated salts and the precipitate was washed with ether. The aqueous solution was extracted with ether until the ether extracts were colorless. The ether extracts were combined, washed with saturated salt solution, dried with anhydrous potassium carbonate and filtered. Removal of the ether under reduced pressure left a brown oil (crude yield 28 g - 100%) which was distilled twice under reduced pressure followed by a spinning band distillation under reduced pressure to obtain a sample suitable for photolysis. The ketone was identified as 3-butyrylpyridine on the basis of the following data: bp = 101-102°C (1.9 mm); IR(neat) 3040, 2960, 1690, 1585, 1420, 1220, 1010, 800, 700 cm⁻¹; NMR(CDCl₃) δ 1.0 (t, 3H), 1.74 (m, 2H), 2.92 (t, 2H), 7.59-9.42 (m, 4H, aromatic); UV(acetonitrile) 266 nm (ϵ 4300 M⁻¹cm⁻¹); UV(heptane) 276 nm (ϵ 4100 M⁻¹cm⁻¹); m/e (rel int) 149(4), 121(2), 106(91), 78(100).

1-(4-pyridyl)butanone (4BP): A solution containing 59 g (0.48 m) of n-propyl bromide in 80 ml of anhydrous ether was added dropwise to a well stirred mixture of 11.7 g (0.50 m) of magnesium turnings and 30 ml of anhydrous ether. After the reaction subsided, a solution containing 25 g (0.24 m) of 4-cyanopyridine in 60 ml of anhydrous ether and 40 ml of benzene was added to the stirred solution over 5 min. The resultant mixture was refluxed with stirring for 7 hr. Upon cooling, it was poured into 200 ml of 10 M hydrochloric acid solution, then refluxed 12 hr. Upon cooling, the solution was made basic by the addition of solid potassium carbonate. Filtration removed the precipitated salts and the precipitate was washed with ether. The aqueous solution was extracted with ether until the ether extracts were colorless. The ether extracts were combined, washed with saturated salt solution, dried with anhydrous potassium carbonate and filtered. Removal of the ether under reduced pressure left a brown oil (crude yield 33 g - 93%) which was distilled three times under reduced pressure to obtain a sample suitable for photolysis. The ketone was identified as 4-butyrylpyridine based on the following data: bp = 100-102° C (4 mm);^{191,192} IR (neat) 3040, 3010, 2960, 1698, 1550, 1415, 1220, 800, 750 cm⁻¹; NMR (CDCl₃) δ 0.98 (t, 3H), 1.8 (m, 2H), 7.56-8.4 (m, 4H, aromatic); UV (acetonitrile) 275 nm (ε 1640 M⁻¹cm⁻¹); UV (heptane) 277 nm (ε 1890 M⁻¹cm⁻¹); m/e (rel int) 149(33), 121(31), 106(100), 79(16), 78(80), 51(45).

1-(2-pyridyl)pentanone (2VP) was synthesized by the general method used for 1-(2-pyridyl)butanone using 27.5 g (0.20 m) of n-bromobutane, 4.8 g (0.21 m) of magnesium turnings and 21.2 g (0.20 m) of 2-cyanopyridine. The synthesis gave a black oil (crude yield - 29 g - 88%) which was distilled twice under reduced pressure to give a sample pure

enough for photolysis. The ketone was identified as 2-valerylpyridine on the basis of the following data: bp = 92-93°C (4.3 mm); IR(neat) 3040, 2960, 1700, 1580, 1210, 1015, 760 cm^{-1} ; NMR(CDCl_3) δ 0.95 (t, 3H), 1.56 (m, 4H), 3.14 (t, 2H), 7.19-8.6 (m, 4H, aromatic); UV(acetonitrile) 267 nm (ϵ 3670 $\text{M}^{-1}\text{cm}^{-1}$); m/e (rel int) 163(13), 134(35), 121(59), 106(88), 79(74), 78(100), 51(38).

1-(3-Pyridyl)pentanone (3VP) was synthesized by the general method used for 1-(3-pyridyl)butanone using 26.3 g (0.19 m) of *n*-bromobutane, 4.7 g (0.19 m) of magnesium turnings and 20 g (0.19 m) of 3-cyanopyridine. The synthesis gave a brown oil (crude yield - 45 g - 99%) which was distilled twice under reduced pressure to give a sample suitable for photolysis. The ketone was identified as 3-valerylpyridine based on the following data: bp = 114-115°C (2 mm); IR(neat) 3040, 1690, 1585, 1420, 1270, 1220, 1010, 790, 700 cm^{-1} ; NMR(CDCl_3) δ 0.95 (t, 3H), 1.59 (m, 4H), 2.94 (t, 2H), 7.18-8.71 (m, 4H, aromatic); UV(acetonitrile) 266 nm (ϵ 3350 $\text{M}^{-1}\text{cm}^{-1}$); UV(heptane) 267 nm (ϵ 3225 $\text{M}^{-1}\text{cm}^{-1}$); m/e (rel int) 163(8), 121(81), 106(100), 78(78), 51(32).

1-(4-Pyridyl)pentanone (4VP) was synthesized by the general method used for 1-(4-pyridyl)butanone using 79 g (0.58 m) of *n*-butylbromide, 14 g (0.59 m) of magnesium turnings and 30 g (0.29 m) of 4-cyanopyridine. The synthesis gave a brown oil which was distilled (crude yield 45 g - 99%) twice under reduced pressure to give a sample suitable for photolysis. The ketone was identified as 4-valerylpyridine^{191,192} based on the following data: bp = 114-115°C (4mm); IR(neat) 2950, 2930, 2875, 1700, 1550, 1400, 1205, 1200, 805, 780 cm^{-1} ; NMR(CDCl_3) δ 0.94 (t, 3H), 1.83 (m, 4H), 2.94 (t, 2H), 7.37-8.56 (dd, 4H, aromatic); UV(acetonitrile) 276 nm (ϵ 2075 $\text{M}^{-1}\text{cm}^{-1}$); UV(heptane) 277 nm (ϵ 2150 M^{-1}

cm^{-1}); m/e (rel int) 163(20), 121(100), 106(90), 77(16), 78(66).

4-Methyl-1-(2-pyridyl)pentanone (γMe2VP) was synthesized by the general method used for 1-(2-pyridyl)butanone using 43 g (0.28 m) of 1-bromo-3-methylbutane, 6.9 g (0.29 m) of magnesium turnings and 30 g (0.29 m) of 2-cyanopyridine. The synthesis gave a black oil (crude yield 40 g - 88%) which was distilled three times under reduced pressure to give a sample suitable for photolysis. The ketone was characterized as γMe2VP on the basis of the following data: bp = 103-104 $^{\circ}$ C (2.3 mm); IR(neat) 3040, 2960, 1690, 1580, 1460, 990, 750 cm^{-1} ; NMR (CDCl_3) δ 0.95 (d, 6H), 1.65 (t, 3H), 3.2 (d, 2H), 7.25 - 8.3 (m, 4H, aromatic); UV(acetonitrile) 270 nm (ϵ 3585 $\text{M}^{-1}\text{cm}^{-1}$); UV(benzene) 277 nm (ϵ 2980 $\text{M}^{-1}\text{cm}^{-1}$); m/e (rel int) 177(2), 163(3), 149(1), 134(43), 121(28), 106(30), 93(17), 80(18), 79(100), 78(84).

3-Methyl-1-(3-pyridyl)butanone (βMe3BP) was synthesized using the general method used for 1-(3-pyridyl)butanone using 39 g (0.29 m) of 1-bromo-2-methylpropane, 6.9 g (0.29 m) of magnesium turnings and 30 g (0.29 m) of 3-cyanopyridine. The reaction gave a yellow oil (crude yield 33 g - 70%) which was purified by distillation under reduced pressure, repeated recrystallization from the hydrochloride salt from methylene chloride and *n*-pentane and finally a spinning band distillation of the free ketone under reduced pressure. The ketone was characterized as βMe3BP based on the following data: bp = 104 $^{\circ}$ C (2.4 mm); IR(neat) 3040, 2960, 1690, 1580, 1410, 1360, 1270, 1210, 970, 775, 690 cm^{-1} ; NMR(CDCl_3) δ 0.9 (s, 3H), 1.3 (s, 3H), 2.25 (m, 1H), 2.8 (d, 2H), 7.12-8.7 (m, 4H, aromatic); UV(acetonitrile) 266 nm (ϵ 2070 $\text{M}^{-1}\text{cm}^{-1}$); m/e (rel int) 163(8), 148(8), 106(100), 79(11), 78(62), 51(32).

3-Methyl-1-(4-pyridyl)butanone (βMe4BP) was synthesized by the

general method used for 1-(4-pyridyl)butanone using 41 g (0.30 m) of 1-bromo-2-methylpropane, 7 g (0.30 m) of magnesium turnings and 31 g (0.30 m) of 4-cyanopyridine. The reaction gave a brown oil (crude yield 43 g - 88%) which was distilled three times under reduced pressure. The ketone was converted to the corresponding hydrochloride salt and recrystallized twice from methylene chloride and *n*-pentane to give a sample suitable for photolysis. The ketone was characterized as β Me4BP on the basis of the following data: bp = 116^o C (5.5 mm); IR(neat) 3020, 2950, 1695, 1585, 1395, 1250, 1185, 970, 800 cm⁻¹; NMR(CDCl₃) δ 1.1 (d, 6H), 2.3 (m, 1H), 2.8 (d, 2H), 7.62-8.7 (m, 4H, aromatic); UV(acetonitrile) 275 nm (ϵ 2170 M⁻¹cm⁻¹) UV(heptane) 273 nm (ϵ 2250 M⁻¹cm⁻¹); m/e (rel int) 163(30), 148(13), 122(8), 121(80), 107(9), 106(100), 79(22), 78(64), 57(26).

4-Methyl-1-(2-pyridyl)pentanone (γ Me4VP) was synthesized by the general method used for 1-(4-pyridyl)pentanone using 87 g (0.58 m) of 1-bromo-3-methylbutane, 14 g (0.61 m) of magnesium turnings and 20 g (0.60 m) of 4-cyanopyridine. The reaction gave a brown oil (crude yield 31.5 g - 93%) which was distilled four times under reduced pressure to give a sample suitable for photolysis. The ketone was characterized on the basis of the following data: bp = 97-99^o C (2.2 mm); IR(neat) 3020, 2960, 1690, 1405, 1270, 1200, 980, 810 cm⁻¹; NMR(CDCl₃) δ 0.91 (d, 6H), 1.6 (m, 3H), 2.9 (t, 2H), 7.5-8.7 (m, 4H, aromatic); UV(acetonitrile) 277 nm (ϵ 2310 M⁻¹cm⁻¹); UV(heptane) 278 nm (ϵ 2300 M⁻¹cm⁻¹); m/e (rel int) 177(9), 122(38), 121(100), 106(98), 93(13), 78(70), 51(53).

Pyridyl Ketone Hydrochloride Salts

All hydrochloride salts were prepared by bubbling hydrogen

chloride gas through an ether solution of the pyridyl ketones. The salts were purified by repeated recrystallization from methylene chloride and *n*-pentane, washed with ether and then dried under vacuum. All salts were greater than 99.5% pure by gc analysis on Column B.

2-Acetylpyridine hydrochloride (2APHCl): 100° C, decomposes; IR(KBr) 3040, 2975, 1700, 1590, 1350, 1270, 1230, 1100, 975 cm^{-1} ; UV(acetonitrile) 273 nm (ϵ 2930 $\text{M}^{-1}\text{cm}^{-1}$).

3-Acetylpyridine hydrochloride (3APHCl): 160° C, decomposes; IR(KBr) 3010, 1700, 1600, 1565, 1420, 1370, 1270, 1000, 800, 700 cm^{-1} ; UV(acetonitrile) 264 nm (ϵ 4230 $\text{M}^{-1}\text{cm}^{-1}$).

4-Acetylpyridine hydrochloride (4APHCl): 100° C, decomposes; IR(KBr) 3020, 1700, 1600, 1565, 1410, 1270, 810 cm^{-1} ; UV(acetonitrile) 278 nm (ϵ 4210 $\text{M}^{-1}\text{cm}^{-1}$).

1-(2-Pyridyl)butanone hydrochloride (2BPHCl): mp = 76-78° C; IR(KBr) 3040, 2960, 1695, 1575, 1440, 1215, 980, 760 cm^{-1} ; UV(acetonitrile) 274 nm (ϵ 2840 $\text{M}^{-1}\text{cm}^{-1}$).

1-(3-Pyridyl)butanone hydrochloride (3BPHCl): mp = 135-136° C; IR(KBr) 3040, 2960, 1695, 1590, 1420, 1220, 1010, 800, 700 cm^{-1} ; UV(acetonitrile) 262 nm (ϵ 4125 $\text{M}^{-1}\text{cm}^{-1}$).

1-(4-Pyridyl)butanone hydrochloride (4BPHCl): mp = 162-163° C; IR(KBr) 3040, 2960, 1700, 1555, 1420, 1220, 800, 750 cm^{-1} ; UV(acetonitrile) 273 nm (ϵ 3050 $\text{M}^{-1}\text{cm}^{-1}$).

1-(2-Pyridyl)pentanone hydrochloride (2VPHCl): mp = 89-90° C; IR(KBr) 3040, 2960, 1700, 1580, 1210, 1020, 770 cm^{-1} ; UV(acetonitrile) 273 nm (ϵ 2910 $\text{M}^{-1}\text{cm}^{-1}$).

1-(3-Pyridyl)pentanone hydrochloride (3VPHCl): mp = 128-129° C; IR(KBr)

3040, 1690, 1580, 1420, 1270, 1010, 800, 700 cm^{-1} ; UV(acetonitrile) 265 nm (ϵ 4600 $\text{M}^{-1}\text{cm}^{-1}$).

1-(4-Pyridyl)pentanone hydrochloride (4VPHCl): mp = 153-154 $^{\circ}$ C; IR (KBr) 3040, 2960, 1700, 1580, 1210, 1020, 770 cm^{-1} ; UV(acetonitrile) 272 nm (ϵ 3880 $\text{M}^{-1}\text{cm}^{-1}$).

4-Methyl-1-(2-pyridyl)pentanone hydrochloride (γ Me2VPHCl): mp = 97-98 $^{\circ}$ C; IR(KBr) 3040, 2960, 1695, 1580, 1460, 980, 780 cm^{-1} ; UV (acetonitrile) 274 nm (ϵ 2890 $\text{M}^{-1}\text{cm}^{-1}$).

3-Methyl-1-(3-pyridyl)butanone hydrochloride (β Me3BPHCl): mp = 129-130 $^{\circ}$ C; IR(KBr) 3040, 2960, 1690, 1580, 1410, 1350, 1210, 970, 780, 700 cm^{-1} ; UV(acetonitrile) 263 nm (ϵ 4320 $\text{M}^{-1}\text{cm}^{-1}$).

3-Methyl-1-(4-pyridyl)butanone hydrochloride (β Me4BPHCl): mp = 170-171 $^{\circ}$ C; IR(KBr) 3020, 1700, 1590, 1400, 1250, 1180, 970, 800 cm^{-1} ; UV(acetonitrile) 273 nm (ϵ 3900 $\text{M}^{-1}\text{cm}^{-1}$).

4-Methyl-1-(4-pyridyl)pentanone hydrochloride (γ Me4VPHCl): mp = 159-161 $^{\circ}$ C; IR(KBr) 3020, 2960, 1690, 1400, 1270, 1200, 990, 800 cm^{-1} ; UV(acetonitrile) 273 nm (ϵ 3850 $\text{M}^{-1}\text{cm}^{-1}$).

Photoreduction products

Bibenzyl: Bibenzyl (Aldrich) was used as received.

Bixylyl: 1,2-Di-p-tolyethane (Aldrich) was used as received.

2,3-Diphenyl-2,3-butanediol: was synthesized and purified by Dr.

M. J. Thomas.

2,3-di(4-Pyridyl hydrochloride)-2,3-butane diol: NMR(D_2O) δ 2.1 (s, 6H), 3.5 (s, 1H), 7.4-8.7 (m, 10H, aromatic); m/e (rel int) 245 (27), 123(100), 122(60), 121(7), 108(14), 106(24), 80(22); mp = 188-190 $^{\circ}$ C.

2,3-di(4-Pyridyl)-2,3-butanediol: mp = 191-195 $^{\circ}$ C; insoluble in

CDCl_3 and D_2O ; m/e (rel int) 245(47), 123(100), 122(58), 121(11), 106(16).

2,3-di(3-Pyridyl hydrochloride)-2,3-butanediol: mp = 193-194°C; NMR(CDCl_3) δ 2.1 (s, 6H), 3.3 (s, 1H), 7.3-9.1 (m, 10H, aromatic); m/e (rel int) 245(33), 123(100), 122(64), 121(9), 108(15).

2,3-di(3-Pyridyl)-2,3-butanediol: mp = 197-199°C; insoluble in CDCl_3 and D_2O ; m/e (rel int) 245(45), 123(100), 122(56), 120(15), 106(23).

Ruthenium Complexes

Unless otherwise noted, all operations were performed in a purified argon atmosphere and all solvents were degassed prior to use. Two methods were used for argon purification: Method 1: A chromous bubbler made by the reaction of an aqueous solution of 1 M chromic chloride with mossy amalgamated zinc.¹⁹³ Method 2: A column of BASF Catalyst R-3-11 heated at 150°C followed in line by a column of 4 Å molecular sieves.

Chloropentaammineruthenium(III)dichloride $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{Cl}]_2$

Method 1:^{194,195} Nitrogenpentaammineruthenium(II) $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$:

Ruthenium trichloride (Alfa-Ventron) (1.97 g, 9.5 mmol) was dissolved in 20 ml of distilled water under nitrogen at 25°C. Hydrazine hydrate (13.6 g, 0.27 m) was added dropwise over a period of 20 min. The dark red solution was stirred 12 hours, then used in the following step.

Chloropentaammineruthenium(III)dichloride: Concentrated hydrochloric acid was added dropwise to a filtered solution of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ until the pH was equal to 2. The solution was refluxed with stirring and became yellow, slowly precipitating yellow product. When no

further precipitation was observed, the mixture was cooled to 2°C and filtered. The precipitate was washed with 5 ml of 6 M hydrochloric acid, ethanol and acetone; crude yield - 1.3 g - 47%. Recrystallization: An aqueous slurry of product in 5 ml of distilled water was heated to 60°C. Concentrated ammonium hydroxide was added dropwise until the yellow complex dissolved to give a wine red solution which was filtered hot, then cooled in an ice bath. Concentrated hydrochloric acid was added dropwise to reprecipitate a mustard yellow product which was filtered, then washed with 5 ml of 6 M hydrochloric acid solution, water, ethanol and acetone and dried at 78°C over phosphorous pentoxide in vacuum; yield - 0.622 g - 28% based on RuCl_3 .

Method 2:^{156,196} Hexaammineruthenium(III)trichloride (Strem Chemical Inc.) (2.0 g, 6.5 mmol) was dissolved in 70 ml of 6 M hydrochloric acid solution with warming. The solution was refluxed for 4 h., during which a yellow precipitate formed. The mixture was cooled and filtered. The precipitate was washed with 10 ml of 6 M hydrochloric acid solution, then methanol and dried under vacuum. Yields of bright yellow crystals ranged from 66-88%; $\text{UV}(\text{H}_2\text{O})$ 327 nm (ϵ 1930 $\text{M}^{-1}\text{cm}^{-1}$); $\text{IR}(\text{KBr})$ 3100-3300, 1600, 1300, 700-800 cm^{-1} .

Pentaamminepyridineruthenium(II) tetrafluoroborate and the pyridine substituted derivatives: These complexes were synthesized by a modification of Ford and Taube's methods.^{42,156}

General synthetic procedure: Silver oxide (158 mg, 0.683 mmol) was dissolved in 4 ml of distilled water by the dropwise addition of trifluoroacetic acid with stirring. Chloropentaammineruthenium(III) dichloride (200 mg), 0.683 mmol) was added. The resultant mixture was stirred, then digested (heated to boiling to complete the precipitation

of silver chloride). After 20 min. the precipitate was filtered, then washed with two 5 ml portions of distilled water. The filtrate was diluted to 25 ml with distilled water and placed in an addition funnel. The pyridyl ketone ligand, in 3-10 molar excess, was flushed with argon in a 3-neck 100 ml round bottom flask covered with aluminum foil. When necessary, 2 ml of methanol was added to improve ligand solubility in the resultant aqueous solution.

Granular zinc (50 g) was washed with 50 ml of 1.2 M hydrochloric acid solution. A mixture of 50 g of granular zinc, 5 g of mercuric chloride, 5 ml of sulfuric acid and 150 ml of distilled water was stirred for 10 minutes.¹⁹³ The zinc mercury amalgam was washed with distilled water until the washings were slightly acidic, then packed into a column. The water was drained and the column was flushed with argon for 5 minutes. The column was fitted to the round bottomed flask and the addition funnel containing the ruthenium(III) solution was attached to the top of the column. The entire system was flushed with argon for 10 minutes.

The light yellow ruthenium(III) solution was passed through the reducing column over a period of 30 minutes, giving a deep yellow ruthenium(II) solution which was slowly added to the stirring ligand. After the addition was complete, two 10 ml portions of distilled water were passed through the column. Stirring was continued for 30 min and then ammonium tetrafluoroborate (72 mg, 0.683 mmol) was added directly to the flask. The resultant solution was refrigerated for a minimum of 12 hr. The water was then removed under reduced pressure. The resultant oil or precipitate was dissolved in 3 ml of acetone. This solution was added dropwise to 400 ml of anhydrous ether which was

being bubbled with argon, the resultant precipitate was immediately filtered. The precipitate was dried under vacuum for 12 hr, then stored in a vacuum dessicator at 3-4° C.

Purification procedure

Method 1 - Column Chromatography: Pentaammine[1-(4-pyridyl)penta-none]ruthenium(II) tetrafluoroborate (Ru4VP) was chromatographed on a 2.5 x 15 cm alumina column (80-200 mesh).

<u>Fraction</u>	<u>Elution Solvent</u>	<u>Volume (ml)</u>
1	benzene	17
2	benzene	22
3	1:1 benzene : methylene chloride	40
4	1:1 methylene chloride : acetonitrile	40
5	acetonitrile	65
6	1:1 acetonitrile : methanol	40
7	methanol	60

Method 2 - Reprecipitation: the metal-pyridyl ketone complex was dissolved in a minimum amount of acetone and added dropwise to anhydrous ether using the same method as original complex isolation.

Method 3 - Recrystallization: The metal-pyridyl ketone complex was dissolved in a minimum amount of distilled water and heated to 40°C. Two ml of a saturated aqueous solution of ammonium tetrafluoroborate was added dropwise and the solution was refrigerated to induce crystallization.

Pentaamminepyridineruthenium(II) tetrafluoroborate (Rupy) was synthesized using 200 mg (0.683 mmol) $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{Cl}]_2$ and 1 g (12.6 mmol) of pyridine; crude yield of mustard yellow solid - 224 mg (85%);

UV(water) 408 nm (ϵ 4580 M⁻¹cm⁻¹). Complex was recrystallized twice from acetone/ethyl ether to yield 50 mg (19%); UV(water) 407 nm (ϵ 6270 M⁻¹cm⁻¹) 244 nm (ϵ 4190 M⁻¹cm⁻¹); IR(KBr) 3150-3450, 1600, 1275, 1050-1150, 750 cm⁻¹. Anal. calcd. for RuC₅N₆H₂₀B₂F₈: C, 13.68; H, 4.55; N, 19.15. Found: C, 13.79, H, 4.29,; N, 19.10.

Pentaammine(2-acetylpyridine)ruthenium(II) tetrafluoroborate

(Ru2AP) was synthesized using 200 mg (0.683 mmol) of Ru(NH₃)₅Cl][Cl]₂ and 300 mg (3.8 mmol) of 2-acetylpyridine; crude yield of blue solid - 262 mg (85%); UV(acetonitrile) 624 nm (ϵ 4550 M⁻¹cm⁻¹) 387 nm (ϵ 3540 M⁻¹cm⁻¹) 273 nm (ϵ 7835 M⁻¹cm⁻¹); IR(KBr) 3150-3300, 1675-1665, 1640-1615, 1470, 1050-1125 cm⁻¹.

Pentaammine(3-acetylpyridine)ruthenium(II) tetrafluoroborate

(Ru3AP) was synthesized using 200 mg (0.683 mmol) of [Ru(NH₃)₅Cl][Cl]₂ and 300 mg (2.5 mmol) of 3-acetylpyridine; crude yield of brown solid - 290 mg (92%); UV(acetonitrile) 412 nm (ϵ 3350 M⁻¹cm⁻¹) 258 nm (ϵ 3750 M⁻¹cm⁻¹) 223 nm (ϵ 6740 M⁻¹cm⁻¹); IR(KBr) 3200-3300, 1685-1665, 1640-1620, 1425, 1100 cm⁻¹.

Pentaammine(4-acetylpyridine)ruthenium(II) tetrafluoroborate

(Ru4AP) was synthesized using 200 mg (0.683 mmol) of [Ru(NH₃)₅Cl][Cl]₂ and 300 mg (2.5 mmol) of 4-acetylpyridine; crude yield of purple solid - 320 mg - (99%) UV(acetonitrile) 505 nm (ϵ 11450 M⁻¹cm⁻¹) 266 nm (ϵ 4035 M⁻¹cm⁻¹); IR(KBr) 3200-3300, 1675-1665, 1590, 1475-1500, 1400-1425, 1075, 875 cm⁻¹.

Pentaammine[1-(2-pyridyl)pentanone]ruthenium(II) tetrafluoro-

borate (Ru2VP) was synthesized using 200 mg (0.683 mmol) of [Ru(NH₃)₅Cl][Cl]₂ and 350 mg (2.1 mmol) of 1-(2-pyridyl)pentanone; crude yield of blue solid - 247 mg (69%); UV(acetonitrile) 625 nm (ϵ 3010

$\text{M}^{-1}\text{cm}^{-1}$) 382 nm (ϵ 2565 $\text{M}^{-1}\text{cm}^{-1}$) 272 nm (ϵ 6200 $\text{M}^{-1}\text{cm}^{-1}$). Complex was recrystallized from water two times. Anal. Calcd. for $\text{RuC}_{10}\text{N}_6\text{H}_{31}\text{O}_2\text{F}_8$: C, 23.0; H, 5.4, N, 16.1. Found: C, 20.8; H, 3.4; N, 12.1; IR(KBr) 3150-3300, 1667, 1475-1500, 1400-1425, 1075, 875 cm^{-1} .

Pentaammine[1-(3-pyridyl)pentanone]ruthenium(II) tetrafluoroborate (Ru3VP) was synthesized using 200 mg (0.683 mmol) of $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{Cl}]_2$ and 400 mg (2.5 mmol) of 1-(3-pyridyl)pentanone; crude yield of brown solid - 156 mg (46%); UV(acetonitrile) 410 nm (ϵ 562 $\text{M}^{-1}\text{cm}^{-1}$) 290 nm (ϵ 680 $\text{M}^{-1}\text{cm}^{-1}$). Complex was reprecipitated twice from acetone/ethyl ether, UV(acetonitrile) 412 nm (ϵ 4460 $\text{M}^{-1}\text{cm}^{-1}$) 257 nm (ϵ 4780 $\text{M}^{-1}\text{cm}^{-1}$) 223 nm (ϵ 9990 $\text{M}^{-1}\text{cm}^{-1}$). Anal. Calcd. for $\text{RuC}_{10}\text{H}_{31}\text{N}_6\text{O}_2\text{F}_8$: C, 23.0; H, 5.4; N, 16.1. Found C, 13.5; H, 3.8; N, 14.8. Complex for photolysis studies was synthesized using powdered mercuric chloride for the zinc mercury amalgam and recrystallized from water-ethanol, UV(acetonitrile) 412 nm (ϵ 4760 $\text{M}^{-1}\text{cm}^{-1}$), 258 nm (ϵ 6930 $\text{M}^{-1}\text{cm}^{-1}$) 224 nm (ϵ 10300 $\text{M}^{-1}\text{cm}^{-1}$). Anal. Found: C, 23.4 and 23.37; H, 4.31 and 4.47; N, 12.80 and 12.66; IR(KBr) 3150-3300, 1680-1665, 1400-1425, 1050-1100 cm^{-1} .

Pentaammine[1-(4-pyridyl)pentanone]ruthenium(II) tetrafluoroborate (Ru4VP) was synthesized using 200 mg (0.683 mmol) of $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{Cl}]_2$ and 400 mg (2.5 mmol) of 1-(4-pyridyl)pentanone; crude yield of deep purple solid - 322 mg (95%); UV(acetonitrile) 506 nm (ϵ 9680 $\text{M}^{-1}\text{cm}^{-1}$) 268 nm (ϵ 2630 $\text{M}^{-1}\text{cm}^{-1}$). Complex was recrystallized from water twice, yield - 58 mg (17%); m/e (rel int) 163 (0.7), 49(100). Anal calcd. for $\text{RuN}_6\text{C}_{10}\text{H}_{31}\text{O}_2\text{F}_8$: C, 23.0; H, 5.4; N, 16.1. Found: C, 22.7; H, 4.5; N, 13.8. Complex for photolysis studies was recrystallized from water/ethanol, UV(acetonitrile) 503

nm (ϵ 11400 M⁻¹cm⁻¹) 268 nm (ϵ 2980 M⁻¹cm⁻¹). Anal. Found: C, 21.88 and 22.04; H, 4.89 and 4.99; N, 14.52 and 14.70; IR(KBr) 3200-3300, 1670, 1600, 1275, 1200, 1050-1075 cm⁻¹.

Pentaammine[4-methyl-1-(2-pyridyl)pentanone]ruthenium(II) tetrafluoroborate (Ru γ Me2VP) was synthesized using 200 mg (0.683 mmol) of [Ru(NH₃)₅Cl][Cl]₂ and 340 mg of 4-methyl-1-(2-pyridyl)pentanone; crude yield of blue solid - 246 mg (71%). Complex was recrystallized from water and found to be insoluble in acetonitrile; UV(water) 650 nm (ϵ 890 M⁻¹cm⁻¹) 376 nm (ϵ 770 M⁻¹cm⁻¹) 274 nm (ϵ 2125 M⁻¹cm⁻¹).

Pentaammine[3-methyl-1-(3-pyridyl)butanone]ruthenium(II) tetrafluoroborate (Ru β Me3BP) was synthesized using 200 mg (0.683 mmol) of [Ru(NH₃)₅Cl][Cl]₂ and 360 mg (2.2 mmol) of 3-methyl-1-(3-pyridyl)butanone; crude yield of brown solid - 419 mg (89%). Complex for photolysis studies was recrystallized from water/ethanol, UV(acetonitrile) 415 nm (ϵ 4700 M⁻¹cm⁻¹) 259 nm (ϵ 6020 M⁻¹cm⁻¹); UV(water) 412 nm (ϵ 4710 M⁻¹cm⁻¹) 259 nm (ϵ 5330 M⁻¹cm⁻¹) 227 nm (ϵ 7720 M⁻¹cm⁻¹); IR(KBr) 3200-3350, 1675, 1400-1425, 1275-1300, 1175-1200, 1025-1075 cm⁻¹.

Pentaammine[3-methyl-1-(4-pyridyl)butanone]ruthenium(II) tetrafluoroborate (Ru β Me4BP) was synthesized using 200 mg (0.683 mmol) of [Ru(NH₃)₅Cl][Cl]₂ and 452 mg (3.3 mmol) of 3-methyl-1-(4-pyridyl)butanone; crude yield of deep purple solid - 330 mg (93%). Complex for photolysis studies was recrystallized twice from water/ethanol, UV(water) 506 nm (ϵ 9820 M⁻¹cm⁻¹) 266 nm (ϵ 3350 M⁻¹cm⁻¹) 218 nm (ϵ 7000 M⁻¹cm⁻¹); IR(KBr) 3250-3350, 1672, 1590, 1300, 1200, 1025-1075 cm⁻¹.

Pentaammine[4-methyl-1-(4-pyridyl)pentanone]ruthenium(II) tetrafluoroborate (Ru γ Me4VP) was synthesized using 200 mg (0.683 mmol) of [Ru(NH₃)₅Cl][Cl]₂ and 370 mg (2.1 mmol) of 4-methyl-1-(4-pyridyl)

pentanone; crude yield of deep purple solid - 336 mg (97%). Complex for photolysis studies was recrystallized from water/ethanol, UV (water) 519 nm (ϵ 9970 $\text{M}^{-1}\text{cm}^{-1}$), 267 nm (3020 $\text{M}^{-1}\text{cm}^{-1}$) 222 nm (ϵ 5560 $\text{M}^{-1}\text{cm}^{-1}$); UV(acetonitrile) 505 nm (ϵ 9220 $\text{M}^{-1}\text{cm}^{-1}$) 265 nm (ϵ 3690 $\text{M}^{-1}\text{cm}^{-1}$) 221 nm (10440 $\text{M}^{-1}\text{cm}^{-1}$); IR(KBr) 3150-3350, 1660, 1400-1450, 1000-1200, 800 cm^{-1} .

Pentaammine[1-(4-pyridyl)pentanone]ruthenium(II) hexafluorophosphate was synthesized by Meyer's method.¹⁹⁷ Aquopentaammineruthenium(II) hexafluorophosphate monohydrate $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}][(\text{PF}_6)_2\cdot\text{H}_2\text{O}]$: A stirred mixture of 20 ml 0.1 M sulfuric acid and several pieces of zinc mercury amalgam was deaerated for 20 min. Chloropentaammineruthenium(II) dichloride (280 mg, 0.96 mmol) was added; after one hour a yellow-orange solution resulted, which was transferred to a 100 ml round bottomed flask. Saturated ammonium hexafluorophosphate (5 ml) was added and the solution was refrigerated 12 hr. Filtration gave a yellow solid which was washed with 3 ml of cold water (3-4°C), then with anhydrous ether and stored in a vacuum dessicator at 3-4°C; yield 150 mg (31%). Pentaammine[1-(4-pyridyl)pentanone]ruthenium(II) hexafluorophosphate: $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})][(\text{PF}_6)_2\cdot\text{H}_2]$ (119 mg, 0.23 mmol) was deaerated in a 50 ml Erlenmeyer flask fitted with a serum cap. A second flask containing 1-(4-pyridyl)pentanone (1 g, 6.1 mmol) was also deaerated. Five ml of acetone was added to each flask, the acetone solution of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ was slowly added to the pyridyl ketone solution and stirred for 15 min. The solution was added dropwise to 100 ml of anhydrous ether being bubbled with argon. The resultant precipitate was immediately filtered and washed twice with 30 ml of anhydrous ether; yield 96 mg (64%); UV(water) 521 nm (ϵ 4570

$\text{M}^{-1}\text{cm}^{-1}$), 273 nm (ϵ 2375 $\text{M}^{-1}\text{cm}^{-1}$) 223 nm (ϵ 7060 $\text{M}^{-1}\text{cm}^{-1}$).

Rhenium Complexes

All complexes were prepared by a modification of the procedure reported by Wrighton et. al.⁶⁰ $\text{BrRe}(\text{CO})_5$ was obtained from Pressure Chemical Company, pyridyl ketones were greater than 99.5% pure.

fac-Tricarbonylbromobis(pyridine)rhenium(I) (Repy): $\text{BrRe}(\text{CO})_5$ (200 mg, 0.492 mmol) and pyridine (97 mg, 1.2 mmol) were dissolved in 250 ml of benzene. The colorless solution was heated at 80°C with stirring in the dark under argon for 5 h. Removal of the benzene under reduced pressure left a white solid which was dissolved in 15 ml of methylene chloride. The addition of *n*-pentane precipitated the product which was filtered and washed with *n*-pentane (2x5 ml). Recrystallization twice from methylene chloride and *n*-pentane gave a white solid; yield - 111 mg (45%); IR(CH_2Cl_2) 2940, 2025, 1920, 1885 cm^{-1} ; UV(benzene) 300 nm(sh) (ϵ 8620 $\text{M}^{-1}\text{cm}^{-1}$) 227 nm (ϵ 10070 $\text{M}^{-1}\text{cm}^{-1}$); m/e (rel int) chemical ionization 80(100), electron impact 79(100).

fac-Tricarbonylbromobis(2-acetylpyridine)rhenium(I) (Re2AP): $\text{BrRe}(\text{CO})_5$ (204 mg, 0.51 mmol) and 2-acetylpyridine (122 mg, 1.1 mmol) were dissolved in 250 ml of benzene. The initially colorless solution was heated at 80°C in the dark under argon for 6 hr. Removal of the benzene under reduced pressure from the now burgundy colored solution left an orange-red solid which was dissolved in 15 ml of methylene chloride. *n*-Pentane was added to give a cloudy solution which was refrigerated for 12 hr. An orange-red solid was filtered and washed with *n*-pentane (2x5 ml). Recrystallization twice from methylene chloride and *n*-pentane gave an orange-red solid; yield 211 mg (71%);

IR(CH₂Cl₂) 2940, 2030, 1930, 1620, 1595-1575(br) cm⁻¹; IR(KBr) 2010, 1910-1890, 1610, 1585 cm⁻¹; UV(benzene) 408 nm (ϵ 4160 M⁻¹cm⁻¹) 277 nm (ϵ 13140 M⁻¹cm⁻¹).

fac-Tricarbonylbromobis(3-acetylpyridine)rhenium(I) (Re3AP):

BrRe(CO)₅ (207 mg, 0.51 mmol) and 3-acetylpyridine (124 mg, 1.0 mmol) were dissolved in 250 ml of benzene. The colorless solution was stirred and heated at 80°C in the dark under argon for 6 hr. Removal of the benzene under reduced pressure gave an off-white solid which was dissolved in 15 ml of methylene chloride. n-Pentane was added to give a cloudy solution which was refrigerated for 8 days until the oil solidified. The tan precipitate was filtered and washed with n-pentane (2x5 ml); yield - 262 mg (85%). Recrystallization twice from methylene chloride and n-pentane gave a white solid; IR(CH₂Cl₂) 2030, 1930, 1890, 1690-1700(br) cm⁻¹; UV(benzene) 300 nm(sh) (ϵ 8290 M⁻¹cm⁻¹) 277 nm (ϵ 10900 M⁻¹cm⁻¹).

fac-Tricarbonylbromobis(4-acetylpyridine)rhenium(I) (Re4AP):

BrRe(CO)₅ (200 mg, 0.49 mmol) and 4-acetylpyridine (135 mg, 1.1 mmol) were dissolved in 250 ml of benzene. The initially colorless solution was stirred and heated in the dark under argon at 80°C for 5 h. Removal of the benzene under reduced pressure from the now yellow solution left a yellow solid which was dissolved in 15 ml of methylene chloride. Addition of n-pentane precipitated a yellow solid which was filtered and washed with n-pentane (2x5 ml); yield - 184 mg (63%); IR(CH₂Cl₂) 2030, 1930, 1890, 1690 cm⁻¹; UV(benzene) 345 nm (ϵ 8230 M⁻¹cm⁻¹) 277 nm (ϵ 9180 M⁻¹cm⁻¹).

fac-Tricarbonylbromobis[1-(2-pyridyl)butanone]rhenium(I) (Re2BP):

BrRe(CO)₅ (200 mg, 0.50 mmol) and 1-(2-pyridyl)butanone (147 mg, 0.99

mmol) were dissolved in 250 ml of benzene. The initially colorless solution was stirred and heated at 80°C in the dark under argon for 11 hr. Removal of the benzene under reduced pressure from the now burgundy colored solution left a red-orange solid which was dissolved in 15 ml of methylene chloride. n-Pentane was added to give a cloudy solution which was refrigerated for 24 hr. The red-orange solid was filtered, washed with n-pentane (2x5 ml) and recrystallized twice from methylene chloride and n-pentane; yield - 180 mg (56%); IR(CH₂Cl₂) 2950, 2030, 1930, 1900, 1710 cm⁻¹; UV(benzene) 465 nm (ε 3100 M⁻¹cm⁻¹) 277 nm (ε 9700 M⁻¹cm⁻¹).

fac-Tricarbonylbromobis[1-(3-pyridyl)butanone]rhenium(I) (Re3BP):

BrRe(CO)₅ (200 mg, 0.49 mmol) and 1-(3-pyridyl)butanone (190 mg, 1.3 mmol) were dissolved in 250 ml of benzene. The initially colorless solution was heated at 70°C in the dark under argon for 11 hr. Removal of the benzene under reduced pressure from the now yellow solution left a yellow oil which was dissolved in 20 ml of methylene chloride. n-Pentane was added to cloudiness, the solution was refrigerated and the oil which formed did not solidify over a period of 3 weeks. The solvents were removed under reduced pressure, 3 ml of methylene chloride was added and the solution was added dropwise to n-pentane. An off-white solid formed which was filtered, washed with n-pentane and recrystallized twice from methylene chloride and n-pentane; yield - 296 mg (95%); IR(CH₂Cl₂) 2950, 2025, 1930, 1895, 1695, 1595 cm⁻¹; UV(benzene) 305 nm(sh) (ε 2760 M⁻¹cm⁻¹).

fac-Tricarbonylbromobis[1-(4-pyridyl)butanone]rhenium(I) (Re4BP):

BrRe(CO)₅ (198 mg, 0.49 mmol) and 1-(4-pyridyl)butanone (133 mg, 0.90 mmol) were dissolved in 250 ml of benzene. The initially colorless

solution was stirred and heated at 70°C in the dark under argon until the evolution of carbon monoxide ceased. Removal of the benzene under reduced pressure from the now yellow colored solution left a yellow oil which was dissolved in 20 ml of methylene chloride. n-Pentane was added to give a cloudy solution which was refrigerated for 20 d. The oil which formed did not solidify. The solvents were removed under reduced pressure, the oil was dissolved in 3 ml of methylene chloride, added dropwise to 250 ml of n-pentane and refrigerated for 2 days. A yellow solid formed which was filtered and washed with n-pentane and then recrystallized from methylene chloride and n-pentane; yield - 67 mg (20%); IR(CH₂Cl₂) 2940, 2040, 1940, 1900, 1700 cm⁻¹; UV(benzene) 337 nm (ϵ 3100 M⁻¹cm⁻¹).

fac-Tricarbonylbromobis[1-(2-pyridyl)pentanone]rhenium(I) (Re2VP):

BrRe(CO)₅ (204 mg, 0.50 mmol) and 1-(2-pyridyl)pentanone (164 mg, 1.0 mmol) were dissolved in 250 ml of benzene. The initially colorless solution was stirred and heated at 80°C in the dark under argon for 6 h. Removal of the benzene under reduced pressure left a red solid which was dissolved in 20 ml of methylene chloride. n-Pentane was added to give a cloudy solution which was refrigerated for 2 days. A red solid formed which was filtered and washed with n-pentane (2x5 ml) and then recrystallized twice from methylene chloride and n-pentane; yield - 195 mg (58%); IR(KBr) 2010, 1995, 1605, 1595 cm⁻¹; IR(CH₂Cl₂) 2030, 1930, 1890, 1620, 1595 cm⁻¹; UV(benzene) 468 nm (ϵ 2270 M⁻¹cm⁻¹) 277 nm (ϵ 8230 M⁻¹cm⁻¹); ms CI m/e 434(3.6), 164(100); EI m/e 514(2.2), 44(100).

fac-Tricarbonylbromobis[1-(3-pyridyl)pentanone]rhenium(I) (Re3VP):

BrRe(CO)₅ (199 mg, 0.49 mmol) and 1-(3-pyridyl)pentanone (168 mg, 1.03

mmol) were dissolved in 250 ml of benzene. The initially colorless solution was stirred and heated at 80°C in the dark under argon for 5 h. Removal of the benzene under reduced pressure from the now yellow solution left a yellow solid which was dissolved in 20 ml of methylene chloride. n-Pentane was added to give a cloudy solution which was refrigerated for 14 d. The oil which formed did not solidify. The solvents were removed under reduced pressure. The yellow solid was dissolved in 20 ml of methylene chloride, n-pentane was added to cloudiness and the solution was refrigerated for 10 d. A white solid formed which was filtered, washed with n-pentane (2x5 ml) and recrystallized twice from methylene chloride and n-pentane; yield - 296 mg (89%); IR(KBr) 2050, 1930-1890, 1700 cm^{-1} ; IR(CH_2Cl_2) 2030, 1930, 1890, 1700, 1620, 1590 cm^{-1} ; UV(benzene) 300 nm(sh) (ϵ 10500 $\text{M}^{-1}\text{cm}^{-1}$) 277 nm (ϵ 13400 $\text{M}^{-1}\text{cm}^{-1}$); ms CI m/e 204(2.8), 192(10.6), 164(100); EI m/e 163(4.1), 106(100).

fac-Tricarbonylbromobis[1-(4-pyridyl)pentanone]rhenium(I) (Re4VP): $\text{BrRe}(\text{CO})_5$ (199 mg, 0.49 mmol) and 1-(4-pyridyl)pentanone (191 mg, 1.2 mmol) were dissolved in 250 ml of benzene. The initially colorless solution was stirred and heated at 80°C in the dark under argon for 5 h. Removal of the benzene from the yellow solution left a yellow oil which solidified on the addition of n-pentane. The yellow solid was filtered, washed with n-pentane (2x5 ml) and recrystallized from methylene chloride and n-pentane; yield - 267 mg (81%); IR(CH_2Cl_2) 2950, 2030, 1925, 1890, 1685, 1260 cm^{-1} ; UV(benzene) 344 nm (ϵ 10270 $\text{M}^{-1}\text{cm}^{-1}$) 277 nm (ϵ 10320 $\text{M}^{-1}\text{cm}^{-1}$); ms CI m/e 192(15.3), 164(100); EI m/e 163(15.8), 121(100).

fac-Tricarbonylbromobis(3-benzoylpyridine)rhenium(I): $\text{BrRe}(\text{CO})_5$

(202 mg, 0.50 mmol) and 3-benzoylpyridine (184 mg, 1.0 mmol) were dissolved in 250 ml of benzene. The initially colorless solution was heated at 70°C in the dark under argon at 70°C for 7 hr. Removal of the benzene under reduced pressure from the cloudy yellow solution left a yellow oil which was dissolved in 20 ml of methylene chloride. n-Pentane was added to cloudiness and the solution was refrigerated for 14 d. The yellow oil which formed did not solidify. The solvents were removed under reduced pressure. The yellow solid was dissolved in 15 ml of methylene chloride, n-pentane was added to cloudiness and the solution was refrigerated for 12 h. A white solid formed which was filtered, washed with n-pentane (2x5 ml) and recrystallized twice from methylene chloride and n-pentane; yield - 266 mg (75%); IR(CH₂Cl₂) 2025, 1925, 1890, 1670 cm⁻¹; UV(benzene) no peaks before solvent cut-off at 275 nm; $\epsilon_{313 \text{ nm}} = 5810 \text{ M}^{-1}\text{cm}^{-1}$; ms EI m/e 184(100); CI m/e 183 (60), 105(100).

Methods and Techniques

Preparation of Samples

Photochemical Glassware: Class A pipets, Class A volumetric ware and pyrex syringes with chrome plated brass needles were used to prepare sample solutions for photolysis. All glassware was cleaned by rinsing with acetone, then distilled water, followed by heating in a distilled water solution of Alconox laboratory glassware detergent for a minimum of 24 hours and then heating two times for a minimum of 10 hours with fresh samples of distilled water. All glassware was dried at 140°C in an oven used only for photochemical glassware to avoid any contamination.

Irradiation Tubes: Photolysis tubes (13 x 100 mm Pyrex culture tubes) were cleaned in a manner analogous to the photochemical glassware. The necks were drawn out to the desired length by rotation in an oxygen flame.

Stock Solutions and Photolysis solutions: A Sartorius Model 2403 balance (accurate to ± 0.001) was used to weigh the desired amount of substrate into a volumetric flask which was then diluted to volume with the appropriate solvent. Solutions were used directly or by pipetting an appropriate aliquot into another volumetric flask and diluting to volume.

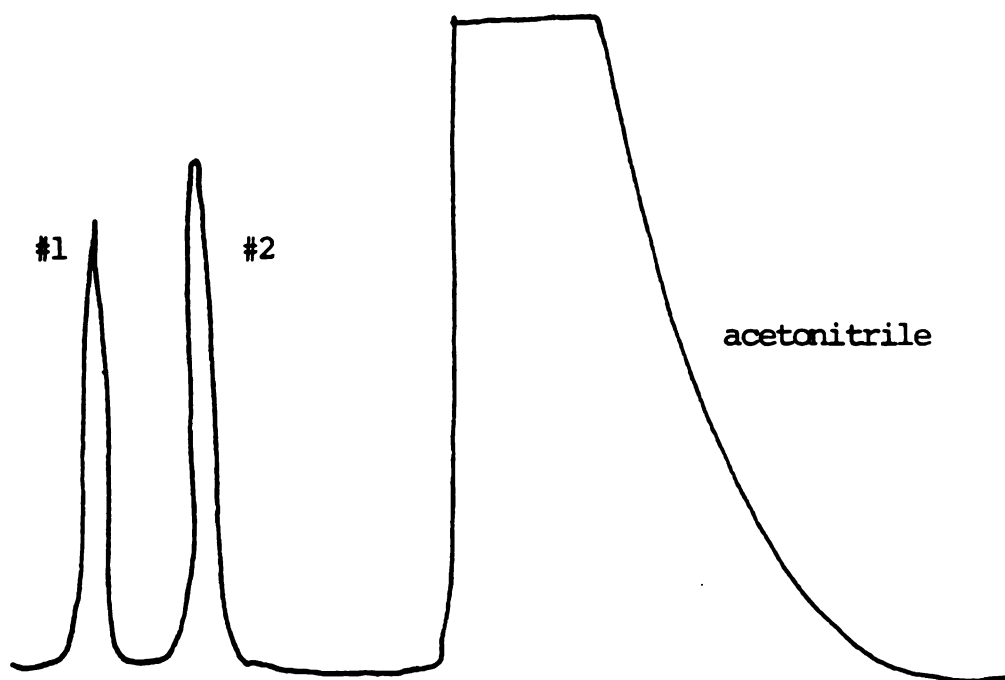
Degassing Procedure: A 5 ml syringe was used to fill the irradiation tubes with 2.8 ml of the appropriate solution. The tubes were attached to a vacuum line on a manifold fitted with 12 stopcocks using one hole rubber stoppers (size 00). All samples were degassed by four freeze-pump-thaw cycles; frozen by slow immersion into the liquid nitrogen, pumped for 10-20 minutes at 5×10^{-4} mm, then allowed to thaw by standing in air. On the final cycle, the tubes were frozen, then pumped and sealed with an oxygen torch under vacuum.

Irradiation Procedures: Photochemical studies involved the use of three different irradiation apparatus. Two of these involved the use of Hanovia 450 watt medium pressure mercury lamps cooled by quartz immersion wells which were placed inside a "merry-go-round" apparatus (7 mm slit width).¹⁹⁹ The entire apparatus was placed inside a large crock filled with distilled water held at 25°C. All tubes were irradiated in parallel to ensure that each received an equal amount of light. To isolate the 313 nm region, an aqueous filter solution of 0.002 M potassium chromate and 1% potassium carbonate was used. To

isolate the 366 nm region, a Corning No. 7-83 filter was employed. The third apparatus was an optical bench - a 1000 watt Xenon lamp in line with a Bausch and Lomb monochrometer held 8 cm from the quartz window of an ambient temperature lamp containing a merry-go-round apparatus.

Analysis of Samples

Identification of Photoproducts: The alkyl pyridyl ketones were identified by comparison with the gas chromatography (gc) retention times of authentic samples. The alkene photoproducts of the pentaammineruthenium(II) pyridyl ketone complexes were identified by comparison with the gc retention time of alkene generated by independent photolysis of the free pyridyl ketones (Peak #1 = alkene, Peak #2 = cyclohexane). Other photoproducts were identified by isolation



and comparison with authentic samples.

Ligand Fragmentation: Ligands were identified by comparison of the gc retention time with an authentic sample.

Gas Chromatography Procedures: On-column sample injections of 0.4 microliters were made into 1/8 inch diameter aluminum columns using nitrogen as the carrier gas. The following columns were employed:

Column A - 5% QF-1, 1.25% Carbowax 20M, Chromosorb G 60:80 DMSC acid washed, treated with $\text{Me}_3\text{SiNHSiMe}_3$; 25 ml/min (N_2 flow rate); 8' x 1/8"; 50°C column, 50°C injector, 200°C detector (propene analysis); 140°C column, 170°C injector, 200°C detector (acetophenone analysis).

Column B - 5% QF-1, 1.25% Carbowax 20M, 2% potassium hydroxide, Chromosorb G 60:80 DMSC acid washed, treated with $\text{Me}_3\text{SiNHSiMe}_3$; 25 ml/min (N_2 flow rate); 12' x 1/8"; Column temperature varied with analysis (see Appendix), 180°C injector, 200°C detector (pyridyl ketone analysis).

Column C - 25% 1,2,3-tris(2-cyanoethoxy)propane, Chromosorb W DMSC acid washed; 25' x 1/8"; 25 ml/min (N_2 flow rate); 50°C column, 40°C injector, (cis- and trans-1,3-pentadiene analysis).

Column D - 20% SE-30, Chromosorb W 60:80 DMSC acid washed; 25 ml/min (N_2 flow rate); 5' x 1/8"; 235°C column, 245°C injector, 250°C detector (cis- and trans-stilbene analysis).

Column E - 5% SE-30, Chromosorb W 60:80 DMSC acid washed; 25 ml/min (N_2 flow rate); 5' x 1/8"; 125°C column, 180°C injector, 200°C detector (bibenzyl analysis); 170°C column, 180°C injector, 200°C detector (1,2-di-p-toylyethane and 2,3-diphenyl-2,3-butanediol analysis).

Column F - 20% Carbowax 20M, Chromosorb G 60:80 DMSC acid washed; 25 ml/min (N_2 flow rate); 8' x 1/8"; 60°C column, 80°C injector, 200°C detector (acetone analysis).

Actinometry and Quantum Yield Determination

Internal standards were used for all analyses except for the photoreduction studies and Type II disappearance studies in acetonitrile where the standard was added after photolysis. The concentration of photoproduct was determined using the gc area product : internal(external) standard area ratio. A detector response factor (RF) was determined to account for the difference in molar response for each compound. The response factor is the reciprocal slope of the plot of concentration ratio of compound to standard versus area ratio of compound to standard. Response factors are listed in Table 31. Product concentrations were determined from (49).

$$[\text{Product}] = \text{RF} \times \frac{[\text{Internal Standard}] \times \text{Area of Product}}{\text{Area of Internal Standard}} \quad (49)$$

Valerophenone actinometry was used for all product quantum yield determinations. A 0.1 M solution of valerophenone in benzene containing a known concentration of cyclohexane and/or hexadecane was irradiated with the desired compound and analyzed on Column A. Photoproduct quantum yields were determined from (50). The quantum yield for 0.1 M valerophenone in benzene is 0.33

$$\phi_{\text{Product}} = \frac{[\text{Product}]}{[\text{Product}]_{\text{actinometer}}} \times 0.33 \quad (50)$$

When the ketone did not absorb all the light, an absorbance correction was made by multiplying ϕ_{product} by the following equation based on Beer's Law:

$$\text{Absorbance Correction} = \frac{1 - T_{\text{actinometer}}}{1 - T_{\text{ketone}}} \quad (51)$$

Table 31. Internal Standard : ketone response factors.

<u>Internal Standard : Ketone</u>	<u>RF</u>
hexadecane : acetophenone (AP)	2.20
octadecane : acetophenone (AP)	2.40
pentadecane : 1,2-di-p-tolyethane (DTE)	0.95
hexadecane : 2-acetylpyridine (2AP)	2.94
heptadecane : 2-acetylpyridine (2AP)	3.36
heptadecane : 3-acetylpyridine (3AP)	3.66
heptadecane : 4-acetylpyridine (4AP)	3.06
octadecane : 4-acetylpyridine (4AP)	3.09
octadecane : 2-butyrylpyridine (2BP)	2.37
nonadecane : 2-butyrylpyridine (2BP)	2.67
heptadecane : 3-butyrylpyridine (3BP)	2.55
eicosane : 3-butyrylpyridine (3BP)	2.76
heptadecane : 4-butyrylpyridine (4BP)	2.50
heptadecane : 2-valerylpyridine (2VP)	2.19
eicosane : 2-valerylpyridine (2VP)	2.26
heptadecane : 3-valerylpyridine (3VP)	2.21
nonadecane : 3-valerylpyridine (3VP)	2.24
heptadecane : 4-valerylpyridine (4VP)	2.74
heneicosane : 4-valerylpyridine (4VP)	2.62
heptadecane : 3-methyl-3-butyrylpyridine (β Me3BP)	2.52
heptadecane : 3-methyl-4-valerylpyridine (γ Me4VP)	2.26
octadecane : <u>trans</u> -stilbene	1.40
cyclohexane : propene (assumed)	2.00
cyclohexane : 2-methylpropene (assumed)	1.50
cyclohexane : acetone	3.01

Ketone disappearance quantum yields (ϕ_{-K}) were determined by two methods. When the internal(external) response factor was known, the quantum yields were calculated by the usual method. When the internal (external) response factor was not known, disappearance quantum yields

were determined by comparing the ketone : internal(external) standard area ratios of the solutions before and after irradiation. The factor R (52), when multiplied by the original ketone concentration and the result subtracted from the original ketone concentration, gives the change in ketone concentration (53) from which the disappearance quantum yield is calculated (54).

$$\left(\frac{\text{Area}_{\text{Ketone}}}{\text{Area}_{\text{Standard}}} \right)_{\text{after}} / \left(\frac{\text{Area}_{\text{Ketone}}}{\text{Area}_{\text{Standard}}} \right)_{\text{before}} = R \quad (52)$$

$$[\text{Ketone}]_{\text{original}} - R[\text{Ketone}]_{\text{original}} = \Delta[\text{Ketone}] \quad (53)$$

$$\phi_{-K} = \frac{[\text{Ketone}]}{[\text{Product}]_{\text{actinometer}}} \times 0.33 \quad (54)$$

Maximum Type II fragmentation quantum yields (ϕ_{max}): A constant aliquot of stock ketone solution was pipetted into several volumetric flasks. Varying aliquots of stock tert-butyl alcohol were added to give concentrations from 1.0-8.0 M after dilution. The tubes were prepared, irradiated and analyzed in the usual manner.

Type II quantum yields extrapolated to infinite dilution (ϕ_{O}^{∞}): Varying aliquots of stock ketone were pipetted into volumetric flasks to give concentrations up to 0.15 M after dilution. The tubes were prepared, irradiated in two sets to assure comparable percent conversion over the concentration range and analyzed in the usual manner. The y-axis intercept of the plot of ϕ_{II} versus [Ketone] is ϕ_{O}^{∞} .

Photoreduction quantum yields were determined by the irradiation of a constant aliquot of stock ketone solution in the presence of various hydrogen donors. The absolute quantum yield of photoproduct

formation were determined by adding various aliquots of stock donor solution to a constant aliquot of stock ketone solution and diluting to volume. The tubes were prepared, irradiated and analyzed in the usual manner. A plot of $(\phi_{\text{acetophenone}})^{-1}$ versus $[\text{hydrogen donor}]^{-1}$ yields a line in which the slope divided by the intercept equals k_d/k_r .

Intersystem crossing yields were determined from the ketone sensitization of the cis-trans isomerization of either cis-1,3-pentadiene or trans-stilbene. A constant aliquot of stock ketone solution was pipetted into several volumetric flasks. Varying aliquots of stock quencher solution were also pipetted into the flasks and diluted to volume. Actinometers were prepared by making a solution of the appropriate ketone (acetophenone for 313 nm, benzophenone for 366 nm) and adding enough quencher solution to quench more than 99% of the triplet state. Tubes were prepared, degassed, irradiated and analyzed in the usual manner. Results were analyzed using (55)-(57). For cis-1,3-pen-

$$\beta = \frac{\text{Area}_{\text{new isomer}}}{\text{Area}_{\text{new isomer}} + \text{Area}_{\text{original isomer}}} \quad (55)$$

$$\beta' = \ln \frac{\alpha}{\alpha + \beta} \quad (56)$$

$$\phi_{\text{isom}} = \frac{\beta'_{\text{ketone}} \times [\text{Quencher}]}{\beta'_{\text{actinometer}} \times [\text{Quencher}]} \times \alpha \quad (57)$$

tadiene, $\alpha = 0.55$, for trans-stilbene, $\alpha = 0.596$.¹⁹⁸ A plot of $\alpha/\phi_{\text{isom}}$ versus $[\text{Quencher}]^{-1}$ yields a line in which the reciprocal of the intercept equals ϕ_{isc} and the intercept divided by the slope equals $k_q\tau$.

Stern Volmer Studies

For the Norrish Type II fragmentation studies, samples of ketone solution were prepared in the same manner as for the intersystem crossing studies. For the intermolecular photoreduction studies, the samples of ketone solution contained in addition a constant aliquot of hydrogen donor. The slope of ϕ_0/ϕ versus [Quencher] gave $k_q\tau$.

Absorption Spectra

Spectra were taken using 10 mm matched quartz cells. A Beckman recording quartz spectrophotometer with Gilford accessories was used to determine the extinction coefficients at 313 and 366 nm. The spectra of the ruthenium complexes were taken immediately after the solutions were made. Extinction coefficients are reproducible to $\pm 10\%$.

Emission Spectra

Spectra were taken using 5 mm quartz tubes at room temperature, or at 77°K using a quartz dewar for liquid nitrogen. Ketone solution concentrations were approximately 1.5×10^{-4} M, ruthenium pyridyl ketone complex solutions were approximately 2.5×10^{-4} M. The chopper was used at high speed, to assure that only the long lived component of emission was seen (greater than 50 μ sec).

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APPENDIX

APPENDIX

This section contains the raw experimental data used to determine the photokinetic parameters by the methods given in the Experimental Section. The concentrations of reactants and standards, product to standard area ratios obtained from gas chromatography analysis and gas chromatograph column temperatures are listed.

The additional abbreviations used in this section are: cyc = cyclohexane; C16 = hexadecane; C17 = heptadecane; C18 = octadecane; C19 = nonadecane; C20 = eicosane; AP = acetophenone; BP = benzophenone; pr = propene; c-P = cis-1,3-pentadiene; t-P = trans-1,3-pentadiene; c-S = cis-stilbene; t-S = trans-stilbene; benpy = benzoylpyridine and act = actinometer.

$$[\text{VP}]_0 = 0.01 \text{ M in benzene.}$$

$$I_a = [\text{acetophenone}] / 0.33.$$

Table 32. Stern Volmer data for 1-(2-pyridyl)butanone.^a

<u>[Q], (M)</u>	<u>Area 2AP / Area C16</u>	<u>[2AP], (M)</u>	<u>ϕ_o/ϕ</u>
0.0 ^b	0.316	0.00129	-
0.00103	0.202	0.000826	1.5
0.00206	0.156	0.000638	2.2
0.00310	0.123	0.000503	2.5
0.00413	0.097	0.000396	3.2
0.00516	0.081	0.000331	3.8
0.0 ^c	0.273	0.000923	-
0.00058	0.203	0.000686	1.4
0.00116	0.170	0.000575	1.6
0.00175	0.135	0.000456	2.0
0.00233	0.118	0.000399	2.4
0.00291	0.102	0.000346	2.7

^a313 nm, gc Column B at 120°C, Q = 1,3-Pentadiene; ^bbenzene solvent, [2BP] = 0.0508 M, [C16] = 0.00139 M, [C16]_{act} = 0.00696 M, Area AP / Area C16 = 0.0169, I_a = 0.00078 El⁻¹; ^cacetonitrile solvent, [2BP] = 0.0501 M, [C16] = 0.00115 M, [C16]_{act} = 0.00765 M, Area AP / Area C16 = 0.0721, I_a = 0.0036 El⁻¹.

Table 33. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(2-pyridyl)butanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 2AP / Area C16</u>	<u>[2AP], (M)</u>	<u>ϕ</u>
0.0	0.299	0.00170	0.16
0.87	0.673	0.00382	0.35
3.49	0.699	0.00397	0.37
4.36	0.731	0.00415	0.38
5.23	0.754	0.00428	0.39
6.97	0.574	0.00326	0.30

^abenzene solvent; 313 nm; gc Column B at 115°C; [2BP] = 0.0534 M; [C16] = 0.00193 M; [C16]_{act} = 0.00967 M, Area AP / Area C16 = 0.174, I_a = 0.011 El⁻¹.

Table 34. Data for the effect of concentration of 1-(2-pyridyl)butanone on ϕ_{II}^a

<u>[2BP], (M)</u>	<u>[Cl6], (M)</u>	<u>Area 2AP / Area Cl6</u>	<u>[2AP], (M)</u>	<u>ϕ</u>
0.0404 ^b	0.00211	0.216	0.00314	0.16 ^c
0.0807	0.00423	0.134	0.00195	0.20 ^c
0.121	0.00634	0.226	0.00329	0.26 ^d
0.161	0.00845	0.160	0.00233	0.24 ^d
0.202	0.0106	0.119	0.00173	0.23 ^d
0.0402 ^e	0.00200	0.085	0.00151	0.22 ^f
0.0804	0.00399	0.053	0.00941	0.27 ^f
0.121	0.00599	0.108	0.00192	0.27 ^g
0.161	0.00798	0.090	0.00160	0.30 ^g
0.201	0.00998	0.059	0.00105	0.24 ^g

^a313 nm, gc Column B at 127°C; ^bbenzene solvent, [Cl6]_{act} = 0.00495 M,^cArea AP/ Area Cl6 = 0.0272, $I_a = 0.00089 \text{ El}^{-1}$; ^dArea AP/ Area Cl6 =0.0544 M, $I_a = 0.0019 \text{ El}^{-1}$; ^eacetonitrile solvent, [Cl6]_{act} = 0.00604 M;^fArea AP/ Area Cl6 = 0.0573, $I_a = 0.0071 \text{ El}^{-1}$; Area AP/ Area Cl6 = 0.178, $I_a = 0.0023 \text{ El}^{-1}$.**Table 35.** Data for ϕ_{-K} for 1-(2-pyridyl)butanone.^a

	<u>Run 1^{b,c}</u>	<u>Run 2^{b,d}</u>	<u>Run 3^e</u>
[2BP] _o	0.0544 M	0.0507 M	0.0753 M
[Cl6]	0.0050 M		0.0769 M
[Cl7]		0.0228 M	

Area 2BP / Area Standard:

Unirradiated			3.077
Irradiated	0.842	0.746	2.274
-[2BP]	0.00996 M	0.0104 M	0.0196 M

^a313 nm, gc Column B at 138°C; ^bbenzene solvent; ^c[Cl6]_{act} = 0.00499 M, Area AP/ Area Cl6 = 0.236, $I_a = 0.0079 \text{ El}^{-1}$; ^d[Cl6]_{act} = 0.00586 M, Area AP/ Area Cl6 = 0.273, $I_a = 0.10 \text{ El}^{-1}$; ^eacetonitrile solvent, [Cl6]_{act} = 0.00769 M, Area AP/ Area Cl6 = 0.462, $I_a = 0.024 \text{ El}^{-1}$.

Table

[C]

0

0

0

0

0

0

0

0

0

a₃₁

b_{[3}

Cl

[C]

Tal

a_{be}

[C]

I_a

Table 36. Stern Volmer data for 1-(3-pyridyl)butanone.^a

<u>[Q], (M)</u>	<u>Area 3AP / Area Cl7</u>	<u>[3AP], (M)</u>	<u>ϕ_o / ϕ</u>
0.0 ^b	0.594	0.00190	-
0.00175	0.301	0.000964	2.1
0.00350	0.180	0.000577	3.4
0.00527	0.140	0.000448	4.3
0.00701	0.121	0.000388	4.7
0.00876	0.092	0.000295	5.5
0.0 ^c	0.424	0.00138	-
0.00097	0.232	0.000754	1.2
0.00389	0.134	0.000436	3.2
0.00486	0.120	0.000390	3.6

^a313 nm, acetone solvent, gc Column B at 127°C, Q = 1,3-Pentadiene;

^b[3BP] = 0.0516 M, [Cl7] = 0.000875 M, [Cl6]_{act} = 0.0584 M, Area AP/Area Cl6 = 0.0755, $I_a = 0.029 \text{ El}^{-1}$; ^c[3BP] = 0.0499 M, [Cl7] = 0.00089 M, [Cl6]_{act} = 0.0561 M, Area AP/ Area Cl6 = 0.0517, $I_a = 0.019 \text{ El}^{-1}$.

Table 37. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(3-pyridyl)butanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 3AP/ Area Cl7</u>	<u>[3AP], (M)</u>	<u>ϕ</u>
0.0	0.478	0.00187	0.44
0.95	0.800	0.00313	0.74
1.90	0.940	0.00368	0.87
3.80	0.810	0.00317	0.75
4.75	0.806	0.00316	0.75
5.71	0.946	0.00370	0.87
7.61	0.705	0.00276	0.65

^abenzene solvent, 313 nm, gc Column B at 130°C, [3BP] = 0.0512 M, [Cl7] = 0.00107 M, [Cl6]_{act} = 0.00490 M, Area AP/ Area Cl6 = 0.127, $I_a = 0.0042 \text{ El}^{-1}$.

Table 38. Data for the effect of concentration of 1-(3-pyridyl) butanone on ϕ_{II} .^a

[3BP], (M)	[C17], (M)	Area 3AP/ Area C17	[3AP], (M)	ϕ
0.0295 ^b	0.00158	0.0877	0.000507	0.33 ^c
0.0590	0.00315	0.0569	0.000656	0.43 ^c
0.0885	0.00473	0.0653	0.00113	0.38 ^d
0.118	0.00630	0.0464	0.00110	0.36 ^d
0.148	0.00788	0.0369	0.00106	0.36 ^d
0.0388 ^e	0.00160	0.254	0.00255	0.66 ^f
0.0620	0.00255	0.307	0.00287	0.63 ^f
0.0776	0.00319	0.230	0.00269	0.60 ^g
0.0766	0.00319	0.220	0.00257	0.57 ^g
0.116	0.00479	0.149	0.00261	0.58 ^g
0.155	0.00638	0.098	0.00229	0.51 ^g
0.194	0.00798	0.080	0.00234	0.51 ^g

^a313 nm, gc Column B at 160°C; ^bbenzene solvent, [C16]_{act} = 0.00457 M; ^cArea AP/ Area C16 = 0.0499, $I_a = 0.0015 \text{ El}^{-1}$; ^dArea AP/ Area C16 = 0.0969, $I_a = 0.0029 \text{ El}^{-1}$; ^eacetonitrile solvent, [C16]_{act} = 0.00492 M; ^fArea AP/ Area C16 = 0.069, $I_a = 0.00074 \text{ El}^{-1}$; ^gArea AP/ Area C16 = 0.136, $I_a = 0.0014 \text{ El}^{-1}$.

Table 39. Data for ϕ_{-K} for 1-(3-pyridyl)butanone.^a

	Run 1 ^b	Run 2 ^c
[3BP] _o	0.0533 M	0.0577 M
[C17]		0.0358 M
[C20]	0.0251 M	
Area 3BP/ Area Standard:		
Unirradiated	0.746	0.684
Irradiated	0.697	0.629
-[3BP]	0.0035 M	0.0046 M

^a313 nm, gc Column B at 180°C; ^bbenzene solvent, [C16]_{act} = 0.00551 M, Area AP/ Area C16 = 0.234, $I_a = 0.0086 \text{ El}^{-1}$; ^cacetonitrile solvent, [C16]_{act} = 0.0474 M, Area AP/ Area C16 = 0.108, $I_a = 0.034 \text{ El}^{-1}$.

Table 40. Stern Volmer data for 1-(4-pyridyl)butanone.^a

<u>[Q], (M)</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ_o/ϕ</u>
0.0 ^b	0.598	0.00194	-
0.0038	0.349	0.00113	1.7
0.0076	0.239	0.000775	2.5
0.0114	0.185	0.000600	3.2
0.0152	0.164	0.000532	3.7
0.0190	0.132	0.000428	4.5
0.0 ^c	0.680	0.00182	-
0.00384	0.383	0.00103	1.8
0.00768	0.278	0.000746	2.4
0.0152	0.209	0.000561	3.3

^a313 nm, acetonitrile solvent, gc Column B at 125°C, Q = 1,3-Pentadiene.

^b[4BP] = 0.0502 M, [C17] = 0.00106 M, [C16]_{act} = 0.0057 M, Area AP/ Area C16 = 0.187, $I_a = 0.0071 \text{ El}^{-1}$. ^c[4BP] = 0.0504 M, [C17] = 0.00088 M, [C16]_{act} = 0.00488 M, Area AP/ Area C16 = 0.08, $I_a = 0.0026 \text{ El}^{-1}$.

Table 41. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(4-pyridyl)butanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ</u>
0.0	0.083	0.000274	0.20
0.97	0.177	0.000585	0.42
1.94	0.215	0.000711	0.50
3.89	0.236	0.000780	0.55
4.86	0.248	0.000820	0.58
5.83	0.258	0.000853	0.60
7.77	0.266	0.000879	0.63

^abenzene solvent, 313 nm, gc Column B at 170°C, [4BP] = 0.517 M, [C17] = 0.00108 M, [C16]_{act} = 0.00586 M, Area AP/ Area C16 = 0.361, $I_a = 0.014 \text{ El}^{-1}$.

Table 42. Data for the effect of concentration of 1-(4-pyridyl)butanone on ϕ_{II} .^a

[4BP], (M)	[Cl7], (M)	Area 4AP/ Area Cl7	[4AP], (M)	ϕ
0.0236 ^b	0.00154	0.0509	0.00024	0.15 ^c
0.0283	0.00185	0.0527	0.00030	0.17 ^c
0.0378	0.00246	0.0368	0.00028	0.15 ^c
0.0472	0.00308	0.0724	0.00068	0.18 ^d
0.0708	0.00461	0.0513	0.00072	0.20 ^d
0.0943	0.00615	0.0395	0.00074	0.20 ^d
0.118	0.00769	0.0389	0.00092	0.25 ^d
0.0222 ^e	0.00098	1.208	0.00362	0.57 ^f
0.0444	0.00196	0.614	0.00368	0.58 ^f
0.0666	0.00294	0.827	0.00744	0.58 ^g
0.110	0.00491	0.541	0.00813	0.63 ^g

^a313 nm, gc Column B at 172°C. ^bbenzene solvent, [Cl6]_{act} = 0.005 M. ^cArea AP/ Area Cl6 = 0.0543, $I_a = 0.0018 \text{ El}^{-1}$. ^dArea AP/ Area Cl6 = 0.110, $I_a = 0.0036 \text{ El}^{-1}$. ^eacetonitrile solvent, [Cl6]_{act} = 0.00466 M. ^fArea AP/ Area Cl6 = 0.211, $I_a = 0.0065 \text{ El}^{-1}$. ^gArea AP/ Area Cl6 = 0.657, $I_a = 0.020 \text{ El}^{-1}$.

Table 43. Data for ϕ_{-K} for 1-(4-pyridyl)butanone.^a

	Run 1 ^b	Run 2 ^c
[4BP] _o	0.0508 M	0.0647 M
[Cl7]	0.025 M	0.045 M
Area 4BP/ Area Cl7:		
Unirradiated	0.945	1.709
Irradiated	0.737	1.144
-[4BP]	0.0112 M	0.0214 M

^a313 nm, gc Column B at 175°C. ^bbenzene solvent, [Cl6]_{act} = 0.00573 M, Area AP/ Area Cl6 = 0.853, $I_a = 0.032 \text{ El}^{-1}$. ^cacetonitrile solvent, [Cl6]_{act} = 0.00612 M, Area AP/ Area Cl6 = 0.611, $I_a = 0.032 \text{ El}^{-1}$.

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Table 44. Stern Volmer data for 1-(2-pyridyl)pentanone.^a

[Q], (M)	Area 2AP/ Area Cl6	[2AP], (M)	ϕ_o/ϕ
0.0 ^b	0.767	0.00177	-
0.022	0.382	0.000879	2.1
0.044	0.274	0.000631	2.2
0.066	0.247	0.000569	2.6
0.088	0.196	0.000451	2.9
0.11	0.191	0.000440	3.1
0.0 ^c	0.620	0.00149	-
0.012	0.380	0.000912	1.7
0.024	0.274	0.000657	2.3
0.036	0.217	0.000521	2.9
0.048	0.163	0.000391	3.9
0.060	0.144	0.000346	4.4

^a313 nm. gc Column B at 120°C, Q = 1,3-Pentadiene. ^bbenzene solvent, [ZVP] = 0.0505 M, [Cl7] = 0.000783 M, [Cl6]_{act} = 0.00479 M, Area AP/ Area Cl6 = 0.300, $I_a = 0.0095 \text{ El}^{-1}$. ^cacetonitrile solvent, [ZVP] = 0.0489 M, [Cl7] = 0.000816 M, [Cl6]_{act} = 0.0056 M, Area AP/ Area Cl6 = 0.0663, $I_a = 0.0021 \text{ El}^{-1}$.

Table 45. Data for ϕ_{-K} for 1-(2-pyridyl)pentanone.^a

	Run 1 ^{b,c}	Run 2 ^{b,d}	Run 3 ^e
[ZVP] _o	0.0501 M	0.0614 M	0.0450 M
[Cl6]			0.0176 M
[C20]	0.0263	0.0424 M	
Area ZVP/ Area Standard:			
Unirradiated	0.740		0.632
Irradiated	0.707	0.608	0.570
-[ZVP]	0.0022 M	0.00314 M	0.00441 M

^a313 nm. gc Column B at 135°C. ^bbenzene solvent. ^c[Cl6]_{act} = 0.00586 M, Area AP/ Area Cl6 = 0.273, $I_a = 0.010 \text{ El}^{-1}$. ^d[Cl6]_{act} = 0.00542 M, Area AP/ Area Cl6 = 0.256, $I_a = 0.0092 \text{ El}^{-1}$. ^eacetonitrile solution, [Cl6]_{act} = 0.00769 M, Area AP/ Area Cl6 = 0.121, $I_a = 0.006 \text{ El}^{-1}$.

Table 46. Data for the effect of concentration of 1-(2-pyridyl) pentanone on ϕ_{II} .^a

<u>[ZVP], (M)</u>	<u>[C16], (M)</u>	<u>Area 2AP/ Area C16</u>	<u>[2AP], (M)</u>	<u>ϕ</u>
0.0243 ^b	0.00054	0.426	0.000679	0.17 ^c
0.0365	0.00081	0.663	0.00158	0.18 ^d
0.0402	0.00108	0.198	0.00126	0.11 ^e
0.0486	0.00216	0.584	0.00185	0.21 ^d
0.0804	0.00432	0.135	0.00171	0.29 ^f
0.161	0.00864	0.192	0.00488	0.42 ^f
0.043 ^g	0.00246	0.211	0.00153	0.68 ^h
0.0806	0.00491	0.107	0.00154	0.69 ^h
0.0161	0.00982	0.139	0.00398	0.70 ⁱ
0.0202	0.0123	0.112	0.00405	0.70 ⁱ

^a313 nm, gc Column B at 127°C. ^bbenzene solvent, [C16]_{act} = 0.0054 M, ^cArea AP/ Area C16 = 0.111, $I_a = 0.004 \text{ El}^{-1}$. ^dArea AP/ Area C16 = 0.241, $I_a = 0.0086 \text{ El}^{-1}$. ^eArea AP/ Area C16 = 0.165, $I_a = 0.0059$. ^fArea AP/ Area C16 = 0.322, $I_a = 0.011 \text{ El}^{-1}$. ^gacetonitrile solvent, [C16]_{act} = 0.0049 M. ^hArea AP/ Area C16 = 0.069, $I_a = 0.0023 \text{ El}^{-1}$. ⁱArea AP/ Area C16 = 0.175, $I_a = 0.0019 \text{ El}^{-1}$.

Table 47. Data for the effect of tert-butyl alcohol on ϕ_{II} for 1-(2-pyridyl)pentanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 2AP/ Area C16</u>	<u>[2AP], (M)</u>	<u>ϕ</u>
0.0	0.0768	0.000212	0.19
0.98	0.172	0.000474	0.41
1.96	0.185	0.000510	0.44
3.91	0.259	0.000714	0.62
4.90	0.260	0.000714	0.62
5.87	0.250	0.000689	0.60
7.82	0.281	0.000775	0.65

^abenzene solvent. 313 nm gc Column B at 127°C, [ZVP] = 0.0511 M, [C16] = 0.000983 M, [C16]_{act} = 0.00469 M, Area AP/ Area C16 = 0.0371, $I_a = 0.0011 \text{ El}^{-1}$.

Table 48. Stern Volmer data for 1-(3-pyridyl)pentanone.^a

<u>[Q], (M)</u>	<u>Area 3AP/ Area C17</u>	<u>[3AP], (M)</u>	<u>ϕ_o/ϕ</u>
0.0 ^b	0.717	0.0028	-
0.0322	0.463	0.00147	1.5
0.0665	0.321	0.00102	2.1
0.100	0.271	0.000863	2.7
0.133	0.203	0.000646	3.5
0.166	0.182	0.000580	3.9
0.0 ^c	0.722	0.00235	-
0.0203	0.442	0.00135	1.6
0.0407	0.308	0.000939	2.4
0.0601	0.258	0.000787	2.8
0.0813	0.204	0.000622	3.4
0.102	0.173	0.000527	4.2

^a313 nm, gc Column B at 125°C, Q= 1,3-Pentadiene. ^bbenzene solvent, [3VP] = 0.0498 M, [C17] = 0.00087 M, [C16]_{act} = 0.00491 M, Area AP/ Area C16 = 0.200, $I_a = 0.0066 \text{ El}^{-1}$. ^cacetonitrile solvent, [3VP] = 0.0505 M, [C17] = 0.000833 M, [C16]_{act} = 0.00601 M, Area AP/ Area C16 = 0.0642, $I_a = 0.0026 \text{ El}^{-1}$.

Table 49. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(3-pyridyl)pentanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 3AP/ Area C17</u>	<u>[3AP], (M)</u>	<u>ϕ</u>
0.0	0.313	0.00128	0.41
1.01	0.548	0.00225	0.71
2.02	0.562	0.00230	0.73
4.04	0.551	0.00226	0.71
5.05	0.601	0.00246	0.78
6.06	0.677	0.00278	0.87
8.08	0.680	0.00279	0.88

^a313 nm, gc Column B at 145°C, benzene solvent, [3VP] = 0.0483 M, [C17] = 0.00112 M, [C16]_{act} = 0.00605 M, Area AP/ Area C16 = 0.0975, $I_a = 0.0040 \text{ El}^{-1}$

Table 50. Data for the effect of concentration of 1-(3-pyridyl) pentanone on ϕ_{II}^a

<u>[3VP], (M)</u>	<u>[C17], (M)</u>	<u>Area 3AP/ Area C16</u>	<u>[3AP], (M)</u>	<u>ϕ</u>
0.0302 ^b	0.00174	0.0797	0.000508	0.33 ^c
0.0604	0.00348	0.0461	0.000587	0.39 ^c
0.0905	0.00522	0.0683	0.00131	0.42 ^d
0.121	0.00696	0.0554	0.00141	0.45 ^d
0.151	0.00870	0.0481	0.00153	0.50 ^d
0.0652 ^e	0.00392	0.0771	0.00111	0.85 ^f
0.0979	0.00588	0.1120	0.00241	0.84 ^f
0.130	0.00783	0.0899	0.00258	0.90 ^g

^a313 nm, gc Column B at 152°C. ^bbenzene solvent, [C16]_{act} = 0.00513 M.

^cArea AP/ Area C16 = 0.0435 $I_a = 0.0015 \text{ El}^{-1}$. ^dArea AP/ Area C16 = 0.083, $I_a = 0.0028 \text{ El}^{-1}$. ^eacetonitrile solution, [C16]_{act} = 0.00591 M.

^fArea AP/ Area C16 = 0.037, $I_a = 0.00146 \text{ El}^{-1}$. ^gArea AP/ Area C16 = 0.0817, $I_a = 0.0032 \text{ El}^{-1}$.

Table 51. Data for ϕ_{-K} for 1-(3-pyridyl)pentanone.^a

	<u>Run 1^{b,c}</u>	<u>Run 2^{b,d}</u>	<u>Run 3^e</u>
[3VP] _o	0.0472 M	0.05	0.0471 M
[C17]			0.0357
[C19]	0.0292 M	0.0226	
Area 3VP/ Area Standard:			
Unirradiated			0.0595
Irradiated	0.0698	0.0794	0.0564
-[3VP]	0.00457 M	0.00402 M	0.0046 M

^a313 nm, gc Column B at 165°C. ^bbenzene solvent. ^c[C16]_{act} = 0.00542 M, Area AP/ Area C16 = 0.159, $I_a = 0.0057 \text{ El}^{-1}$. ^d[C16] = 0.00551 M, Area AP/ Area C16 = 0.188, $I_a = 0.0069 \text{ El}^{-1}$. ^eacetonitrile solvent, [C16]_{act} = 0.00474 M, Area AP/ Area C16 = 0.108, $I_a = 0.0034 \text{ El}^{-1}$.

Table 52. Stern Volmer data for 1-(4-pyridyl)pentanone.^a

<u>[Q], (M)</u>	<u>Area 4AP/ Area Cl7</u>	<u>[4AP], (M)</u>	<u>ϕ_o/ϕ</u>
0.0 ^b	0.789	0.00212	-
0.08	0.544	0.00146	1.5
0.16	0.407	0.0010	2.0
0.24	0.307	0.000827	2.7
0.32	0.289	0.000778	2.9
0.40	0.254	0.000684	3.2
0.0 ^c	0.848	0.00201	-
0.060	0.515	0.00122	1.6
0.121	0.357	0.000848	2.3
0.181	0.258	0.000613	3.2
0.241	0.246	0.000584	3.4
0.301	0.203	0.000482	4.0

^a 313 nm, gc Column B at 125°C, Q = 1,3-Pentadiene. ^b benzene solvent, [4VP] = 0.0614 M, [Cl7] = 0.00088 M, [Cl6]_{act} = 0.0052 M, Area AP/ Area Cl6 = 0.269, $I_a = 0.0093 \text{ El}^{-1}$. ^c acetonitrile solvent, [4VP] = 0.0518 M, [Cl7] = 0.000776 M, [Cl6]_{act} = 0.00551 M, Area AP/ Area Cl6 = 0.0881, $I_a = 0.0032 \text{ El}^{-1}$.

Table 53. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(4-pyridyl)pentanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 4AP/ Area Cl7</u>	<u>[4AP], (M)</u>	<u>ϕ</u>
0.97	0.547	0.00127	0.50
1.95	0.462	0.00107	0.42
3.89	0.661	0.00154	0.60
4.87	0.527	0.00123	0.48
5.48	0.530	0.00125	0.48
7.79	0.537	0.00128	0.49

^a benzene solvent, 313 nm, gc Column B at 158°C, [4VP] = 0.0503 M, [Cl7] = 0.00076 M, [Cl6]_{act} = 0.00553 M, Area AP/ Area Cl6 = 0.0708, $I_a = 0.0026 \text{ El}^{-1}$.

Table 54. Data for the effect of concentration of 1-(4-pyridyl)pentanone on ϕ_{II} .^a

[4VP], (M)	[Cl7], (M)	Area 4AP/ Area Cl7	[4AP], (M)	ϕ
0.0313 ^b	0.00204	0.133	0.000830	0.20 ^c
0.0625	0.00409	0.072	0.000901	0.21 ^c
0.0938	0.00613	0.112	0.00210	0.25 ^d
0.125	0.00818	0.092	0.00230	0.27 ^d
0.156	0.0102	0.074	0.00231	0.27 ^d
0.0316 ^e	0.00550	0.169	0.00284	0.55 ^f
0.0422	0.00733	0.131	0.00295	0.57 ^f
0.0969	0.00478	0.186	0.00272	0.58 ^g
0.1290	0.00683	0.143	0.00299	0.59 ^g
0.1610	0.00708	0.145	0.00305	0.60 ^g

^agc Column B at 158°C, 313 nm. ^bbenzene solvent, [Cl6]_{act} = 0.00614 M.

^cArea AP/ Area Cl6 = 0.103, $I_a = 0.00422 \text{ El}^{-1}$. ^dArea AP/ Area Cl6 = 0.207, $I_a = 0.00847 \text{ El}^{-1}$. ^eacetonitrile solvent, [Cl6]_{act} = 0.00541. ^fArea AP/ Area Cl6 = 0.131, $I_a = 0.00472 \text{ El}^{-1}$. ^gArea AP/ Area Cl6 = 0.188, $I_a = 0.00472 \text{ El}^{-1}$.

Table 55. Data for ϕ_{-K} for 1-(4-pyridyl)pentanone.^a

	Run 1 ^b	Run 2 ^c
[4VP] _o	0.0458 M	0.0525 M
[Cl7]		0.0443 M
[C21]	0.0292 M	
Area 4VP/ Area Standard:		
Unirradiated	0.531	1.629
Irradiated	0.398	1.209
-[4VP]	0.0115 M	0.0135 M

^a313 nm, gc Column B at 175°C. ^bbenzene solvent, [Cl6]_{act} = 0.00583 M, Area AP/ Area Cl6 = 0.234, $I_a = 0.0091 \text{ El}^{-1}$. ^cacetonitrile solvent, [Cl6]_{act} = 0.00524 M, Area AP/ Area Cl6 = 0.644 M, $I_a = 0.0225 \text{ El}^{-1}$.

Table 56. Stern Volmer data for 4-methyl-1-(2-pyridyl)pentanone.^a

<u>[Q], (M)</u>	<u>Area 2AP/ Area C16</u>	<u>[2AP], (M)</u>	<u>ϕ_o/ϕ</u>
0.0 ^b	0.473	0.00117	-
0.044	0.356	0.000882	1.4
0.088	0.297	0.000736	1.6
0.132	0.262	0.000649	1.9
0.176	0.225	0.000558	2.2
0.220	0.208	0.000516	2.3
0.0 ^{c,d}	0.606	0.00143	-
0.045	0.398	0.000938	1.5
0.090	0.348	0.000821	1.8
0.136	0.281	0.000663	2.2
0.181	0.255	0.000601	2.4
0.226	0.214	0.000505	2.8
0.0 ^{c,e}	0.666	0.00150	-
0.074	0.408	0.000918	1.6
0.147	0.319	0.000718	2.1
0.221	0.250	0.000562	2.7
0.294	0.183	0.000412	3.6
0.368	0.175	0.000395	3.8

^aQ = 1,3-Pentadiene, 313 nm, gc Column B at 140°C. ^bbenzene solvent, $[\gamma\text{Me2VP}] = 0.0497 \text{ M}$, $[\text{C16}] = 0.000843 \text{ M}$, $[\text{C16}]_{\text{act}} = 0.00534 \text{ M}$, Area AP/ Area C16 = 0.207, $I_a = 0.0074 \text{ El}^{-1}$. ^cacetonitrile solvent. ^d $[\gamma\text{Me2VP}] = 0.0505 \text{ M}$, $[\text{C16}] = 0.000802 \text{ M}$, $[\text{C16}]_{\text{act}} = 0.00538 \text{ M}$, Area AP/ Area C16 = 0.0648, $I_a = 0.0023 \text{ El}^{-1}$. ^e $[\gamma\text{Me2VP}] = 0.0509 \text{ M}$, $[\text{C16}] = 0.000765 \text{ M}$, $[\text{C16}]_{\text{act}} = 0.00553 \text{ M}$, Area AP/ Area C16 = 0.0588, $I_a = 0.0022 \text{ El}^{-1}$.

Table 57. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 4-methyl-1-(2-pyridyl)pentanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 2AP/ Area C16</u>	<u>[2AP], (M)</u>	<u>ϕ</u>
0.0	0.274	0.00602	0.17
0.94	0.726	0.00159	0.45
1.98	0.869	0.00191	0.54
3.98	1.027	0.00226	0.66
4.97	1.116	0.00245	0.69
5.97	1.146	0.00252	0.70
7.95	1.210	0.00266	0.75

^abenzene solvent, 313 nm, gc Column B at 158°C, $[\gamma\text{Me2VP}] = 0.0398 \text{ M}$, $[\text{C16}] = 0.000747 \text{ M}$, $[\text{C16}]_{\text{act}} = 0.00543 \text{ M}$, Area AP/ Area C16 = 0.113, $I_a = 0.004 \text{ El}^{-1}$.

Table 58. Data for the effect of concentration of 4-methyl-1-(2-pyridyl)pentanone on ϕ_{II} .^a

$[\gamma\text{Me2VP}]$, (M)	$[\text{Cl6}]$, (M)	Area 2AP/ Area Cl6	$[\text{2AP}]$, (M)	
0.0235 ^b	0.00192	0.121	0.000683	0.16 ^c
0.0470	0.00383	0.0713	0.000803	0.19 ^c
0.0705	0.00575	0.0916	0.00155	0.21 ^d
0.0904	0.00766	0.0777	0.00175	0.23 ^d
0.1175	0.00957	0.0689	0.00193	0.24 ^d
0.0475 ^e	0.00327	0.498	0.00479	0.71 ^f
0.0713	0.00491	0.602	0.00869	0.74 ^g
0.095	0.00654	0.458	0.00659	0.76 ^g
0.117	0.00977	0.387	0.0111	0.80 ^g
0.119	0.00818	0.375	0.00902	0.77 ^g

^a313 nm, gc Column B at 130°C. ^bbenzene solvent, $[\text{Cl6}]_{\text{act}} = 0.00515 \text{ M}$.

^cArea AP/ Area Cl6 = 0.129, $I_a = 0.0044 \text{ El}^{-1}$. ^dArea AP/ Area Cl6 = 0.227, $I_a = 0.0080 \text{ El}^{-1}$. ^eacetonitrile solvent, $[\text{Cl6}]_{\text{act}} = 0.0057 \text{ M}$. ^fArea AP/ Area Cl6 = 0.184, $I_a = 0.007 \text{ El}^{-1}$. ^gArea AP/ Area Cl6 = 0.307, $I_a = 0.12 \text{ El}^{-1}$.

Table 59. Data for ϕ_K for 4-methyl-1-(2-pyridyl)pentanone.^a

	Run 1 ^b	Run 2 ^c
$[\gamma\text{Me2VP}]_0$	0.0421 M	0.0400 M
$[\text{Cl6}]$		0.00117 M
$[\text{C20}]$	0.0175 M	
Area γMe2VP / Area Standard:		
Unirradiated	1.030	6.134
Irradiated	0.942	3.459
$-\gamma\text{Me2VP}$	0.0036 M	0.0174

^a313 nm, gc Column B at 138°C. ^bbenzene solvent, $[\text{Cl6}]_{\text{act}} = 0.00441 \text{ M}$, Area AP/ Area Cl6 = 0.559. $I_a = 0.016 \text{ El}^{-1}$. ^cacetonitrile solvent, $[\text{Cl6}]_{\text{act}} = 0.0057 \text{ M}$, Area AP/ Area Cl6 = 0.58, $I_a = 0.22 \text{ El}^{-1}$.

Table 60. Stern Volmer data for 3-methyl-1-(3-pyridyl)butanone.^a

$[Q], (M)$	Area 3AP/ Area C17	$[3AP], (M)$	ϕ_o/ϕ
0.0 ^b	0.600	0.00176	-
0.0068	0.381	0.00112	1.6
0.0136	0.276	0.000810	2.2
0.0204	0.200	0.000587	3.0
0.0273	0.172	0.000505	3.5
0.0341	0.148	0.000434	4.1
0.0 ^{c,d}	0.483	0.00160	-
0.0039	0.330	0.00110	1.5
0.0077	0.255	0.000847	1.9
0.0116	0.204	0.000677	2.4
0.0155	0.177	0.000588	2.7
0.0194	0.146	0.000485	3.3
0.0 ^{c,e}	0.612	0.00187	-
0.0053	0.414	0.00126	1.5
0.0107	0.307	0.000936	2.0
0.0159	0.242	0.000738	2.5
0.0213	0.128	0.000665	2.8
0.0266	0.169	0.000512	3.6

^a313 nm, gc Column B at 140°C, Q = 1,3-Pentadiene. ^bbenzene solvent, $[\beta\text{Me3BP}] = 0.0503 \text{ M}$, $[\text{C17}] = 0.000802 \text{ M}$, $[\text{C16}]_{\text{act}} = 0.00547 \text{ M}$, Area AP/ Area C16 = 0.152, $I_a = 0.0055 \text{ El}^{-1}$. ^cacetonitrile solvent. ^d $[\beta\text{Me3BP}] = 0.0518 \text{ M}$, $[\text{C17}] = 0.00091 \text{ M}$, $[\text{C16}]_{\text{act}} = 0.00563 \text{ M}$, Area AP/ Area C16 = 0.055, $I_a = 0.0021 \text{ El}^{-1}$. ^e $[\beta\text{Me3BP}] = 0.0407 \text{ M}$, $[\text{C17}] = 0.000833 \text{ M}$, $[\text{C16}]_{\text{act}} = 0.0055 \text{ M}$, Area AP/ Area C16 = 0.0554, $I_a = 0.0020 \text{ El}^{-1}$.

Table 61. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 3-methyl-1-(3-pyridyl)butanone.^a

$[\text{t-BuOH}], (M)$	Area 3AP/ Area C17	$[3AP], (M)$	ϕ
0.0	0.218	0.00070	0.33
1.0	0.463	0.00148	0.70
2.0	0.476	0.00152	0.72
4.0	0.470	0.00151	0.71
5.0	0.486	0.00156	0.74
6.0	0.455	0.00146	0.70
8.0	0.371	0.00119	0.56

^abenzene solvent, 313 nm, gc Column B at 142°C, $[\beta\text{Me3BP}] = 0.0495 \text{ M}$, $[\text{C17}] = 0.0088 \text{ M}$, $[\text{C16}]_{\text{act}} = 0.00562 \text{ M}$, Area AP/ Area C16 = 0.574, $I_a = 0.0022 \text{ El}^{-1}$.

Table 62. Data for the effect of concentration of 3-methyl-1-(3-pyridyl)butanone on ϕ_{II}^a

$[\beta\text{Me3BP}]$, (M)	$[\text{C17}]$, (M)	Area 3AP/ Area C17	$[\text{3AP}]$, (M)	ϕ
0.0230 ^b	0.00167	0.274	0.00167	0.25 ^c
0.0461	0.00333	0.162	0.00197	0.28 ^c
0.0691	0.00500	0.252	0.00461	0.31 ^d
0.0921	0.00667	0.199	0.00486	0.33 ^d
0.1150	0.00833	0.157	0.00479	0.33 ^d
0.0267 ^e	0.00180	0.493	0.00325	0.67 ^f
0.0400	0.00269	0.702	0.00691	0.77 ^g
0.0534	0.00359	0.594	0.00780	0.87 ^g
0.0667	0.00449	0.447	0.00735	0.85 ^g

^a313 nm, gc Column B at 170°C. ^bbenzene solvent. ^c $[\text{C16}]_{\text{act}} = 0.00577 \text{ M}$, Area AP/ Area C16 = 0.174, $I_a = 0.0067 \text{ El}^{-1}$. ^d $[\text{C16}]_{\text{act}} = 0.00681 \text{ M}$, Area AP/ Area C16 = 0.321, $I_a = 0.015 \text{ El}^{-1}$. ^eacetonitrile solvent, $[\text{C16}]_{\text{act}} = 0.00519 \text{ M}$. ^fArea AP/ Area C16 = 0.138, $I_a = 0.0048 \text{ El}^{-1}$. ^gArea AP/ Area C16 = 0.254, $I_a = 0.0047 \text{ El}^{-1}$.

Table 63. Data for ϕ_{-K} for 3-methyl-1-(3-pyridyl)butanone.^a

	<u>Run 1^b</u>	<u>Run 2^c</u>
$[\beta\text{Me3BP}]_0$	0.0691 M	0.0534 M
$[\text{C17}]$	0.03 M	0.03 M
Area βMe3BP / Area C17		
Unirradiated	0.945	0.786
Irradiated	0.886	0.706
$-\beta\text{Me3BP}$	0.0043 M	0.0544 M

^a313 nm, gc Column B at 170°C. ^bbenzene solvent, $[\text{C16}]_{\text{act}} = 0.00481 \text{ M}$, Area AP/ Area C16 = 0.307, $I_a = 0.0089 \text{ El}^{-1}$. ^cacetonitrile solvent, $[\text{C16}]_{\text{act}} = 0.00555 \text{ M}$, Area AP/ Area C16 = 0.118, $I_a = 0.0044 \text{ El}^{-1}$.

Table 64. Stern Volmer data for 3-methyl-1-(4-pyridyl)butanone.^a

<u>[Q], (M)</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ_O/ϕ</u>
0.0 ^b	3.635	0.00444	-
0.0208	2.106	0.00257	1.7
0.0417	1.318	0.00161	2.8
0.0 ^c	2.335	0.00572	-
0.0180	1.296	0.00317	1.8
0.0361	0.942	0.00231	2.5
0.0541	0.683	0.00167	3.4
0.0722	0.530	0.00130	4.4
0.0902	0.460	0.00113	5.1

^a313 nm, gc Column B at 165°C, acetonitrile solvent, Q = Ethyl sorbate.

^b[β Me4BP] = 0.0508 M, [C17] = 0.000399 M, [C16]_{act} = 0.00501 M, Area AP/ Area C16 = 0.283, $I_a = 0.0095 \text{ El}^{-1}$. ^c[β Me4BP] = 0.0499 M, [C17] = 0.008 M, [C16]_{act} = 0.00606 M, Area AP/ Area C16 = 0.236, $I_a = 0.0095 \text{ El}^{-1}$

Table 65. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 3-methyl-1-(4-pyridyl)butanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ</u>
0.0	0.769	0.00199	0.16
0.96	1.428	0.00357	0.29
3.85	1.647	0.00412	0.33
4.81	2.441	0.00611	0.51
5.77	2.471	0.00619	0.50
7.69	2.219	0.00555	0.49

^abenzene solvent, 313 nm, gc Column B at 165°C, [β Me4BP] = 0.0494 M, [C17] = 0.000818 M, [C16]_{act} = 0.046 M, Area AP/ Area C16 = 0.0406 M, $I_a = 0.013 \text{ El}^{-1}$.

Table 66 Data for ϕ_K for 3-methyl-1-(4-pyridyl)butanone.^a

	<u>Run 1^b</u>	<u>Run 2^c</u>
[β Me4BP] ₀	0.0495 M	0.0498 M
[C17]	0.0400 M	0.0400 M
Area β Me4BP/ Area C17:		
Unirradiated	0.974	1.037
Irradiated	0.877	0.748
-[β Me4BP]	0.0094 M	0.0139 M

^a313 nm, gc Column B at 165°C. ^bbenzene solvent, [C16]_{act} = 0.0046 M, Area AP/ Area C16 = 1.148, $I_a = 0.018 \text{ El}^{-1}$. ^cacetonitrile solvent, [C16]_{act} = 0.0061 M, Area AP/ Area C16 = 0.442, $I_a = 0.035 \text{ El}^{-1}$.

Table 67. Stern Volmer data for 4-methyl-1-(4-pyridyl)pentanone.^a

<u>[Q], (M)</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ_o/ϕ</u>
0.0 ^b	0.703	0.00165	-
0.26	0.473	0.00111	1.5
0.52	0.344	0.00081	2.0
0.78	0.295	0.00069	2.4
1.04	0.255	0.00060	2.8
1.31	0.216	0.00051	3.3
0.0 ^c	0.913	0.00275	-
0.171	0.615	0.00185	1.5
0.342	0.476	0.00143	1.9
0.514	0.370	0.00111	2.4
0.645	0.334	0.00101	2.7
0.856	0.285	0.00086	3.2

^a313 nm, gc Column B at 140°C, Q = 1,3-Pentadiene. ^bbenzene solvent, [γ Me4VP] = 0.0538 M, [C17] = 0.000768 M, [C16]_{act} = 0.00571 M, Area AP/ Area C16 = 0.233, $I_a = 0.0089 \text{ El}^{-1}$. ^cacetonitrile solvent, [γ Me4VP] = 0.0503 M, [C17] = 0.000984 M, [C16]_{act} = 0.00505 M, Area AP/ Area C16 = 0.134, $I_a = 0.0045 \text{ El}^{-1}$.

Table 68. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 4-methyl-1-(4-pyridyl)pentanone.^a

<u>[t-BuOH], (M)</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ</u>
0.0	0.344	0.00083	0.18
1.0	0.860	0.00207	0.44
2.0	0.950	0.00229	0.49
4.0	0.994	0.00240	0.51
6.0	0.980	0.00236	0.50
8.0	0.694	0.00167	0.36

^a313 nm, gc Column B at 140°C, benzene solvent, [γMe4VP] = 0.0504 M, [C17] = 0.000788 M, [C16]_{act} = 0.00577 M, Area AP/ Area C16 = 0.127, I_a = 0.0016 El⁻¹.

Table 69. Data for the effect of concentration of 4-methyl-1-(4-pyridyl)pentanone on ϕ_{II} .^a

<u>[γMe4VP], (M)</u>	<u>[C17], (M)</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ</u>
0.0283 ^b	0.00190	0.0896	0.000521	0.15 ^c
0.0378	0.00253	0.0787	0.000609	0.18 ^c
0.0473	0.00317	0.0597	0.000579	0.17 ^c
0.0709	0.00475	0.1120	0.00174	0.19 ^d
0.0946	0.00633	0.0880	0.00170	0.19 ^d
0.118	0.00792	0.0773	0.00187	0.21 ^d
0.0234 ^c	0.00115	0.366	0.00129	0.52 ^f
0.0279	0.00139	0.317	0.00135	0.55 ^f
0.0465	0.00231	0.177	0.00125	0.57 ^f
0.0698	0.00346	0.458	0.00485	0.57 ^g
0.0931	0.00462	0.341	0.00482	0.56 ^g
0.116	0.00577	0.282	0.00498	0.58 ^g

^a313 nm, gc Column B at 167°C. ^bbenzene solvent, [C16]_{act} = 0.00575 M. ^cArea AP/ Area C16 = 0.0918, I_a = 0.0034 El⁻¹. ^dArea AP/ Area C16 = 0.238, I_a = 0.0088 El⁻¹. ^eacetonitrile solvent, [C16]_{act} = 0.0045 M, I_a = 0.0024 El⁻¹. ^gArea AP/ Area C16 = 0.0086 El⁻¹.

Table 70. Data for ϕ_{-K} for 4-methyl-1-(4-pyridyl)pentanone.^a

	Run 1 ^b	Run 2 ^c
[γ Me4VP] ₀	0.0459 M	0.0455 M
[C17]		0.045 M
[C21]	0.0246 M	
Area γ Me4VP/ Area Standard:		
Unirradiated	0.696	1.558
Irradiated	0.630	1.146
-[γ Me4VP]	0.0043 M	0.012 M

^a313 nm, gc Column B at 165°C. ^bbenzene solvent, [C16]_{act} = 0.00559 M, Area AP/ Area C16 = 0.268, $I_a = 0.010 \text{ El}^{-1}$. ^cacetonitrile solvent, [C16]_{act} = 0.0057 M, Area AP/ Area C16 = 0.58, $I_a = 0.22 \text{ El}^{-1}$.

Table 71. Stern Volmer data for 1-(2-pyridyl)butanone hydrochloride.^a

[Q], (M)	Area 2APHC1/ Area C16	[2APHC1], (M)	ϕ_0/ϕ
0.0 ^b	0.216	0.000613	-
0.0063	0.198	0.000562	1.2
0.0126	0.195	0.000554	1.2
0.0189	0.178	0.000506	1.3
0.0252	0.153	0.000435	1.4
0.0315	0.164	0.000466	1.4
0.0 ^c	0.271	0.000782	-
0.046	0.149	0.000430	1.9
0.093	0.117	0.000337	2.5
0.139	0.110	0.000317	2.6
0.186	0.088	0.000254	3.2
0.234	0.081	0.000234	3.6

^a313 nm, gc Column B at 108°C, acetonitrile solvent, Q = 1,3-Pentadiene. ^b[2BPHCl] = 0.0251 M, [C16] = 0.000966 M, [C16]_{act} = 0.0055 M, Area AP/ Area C16 = 0.164, $I_a = 0.006 \text{ El}^{-1}$. ^c[2BPHCl] = 0.0284 M, [C16] = 0.00981 M, [C16]_{act} = 0.00504 M, Area AP/ Area C16 = 0.208, $I_a = 0.007 \text{ El}^{-1}$.

Table 72. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(2-pyridyl)pentanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 2APHC1/ Area C16</u>	<u>[2APHC1], (M)</u>	<u>ϕ</u>
0.0	0.145	0.000431	0.14
0.99	0.188	0.000558	0.082
1.98	0.202	0.000600	0.12
3.97	0.235	0.000698	0.14
4.95	0.242	0.000719	0.14
5.94	0.237	0.000704	0.14
7.93	0.236	0.000701	0.14

^abenzene solvent, 313 nm, gc Column B at 111°C. [2BPHCl] = 0.0509 M, [C16] = 0.00101 M, [C16]_{act} = 0.00458 M, Area AP/ Area C16 = 0.0165, $I_a = 0.0050 \text{ El}^{-1}$.

Table 73. Data for the effect of concentration of 1-(2-pyridyl) butanone hydrochloride on ϕ_{II} .^a

<u>[2BPHCl], (M)</u>	<u>[C16], (M)</u>	<u>Area 2APHC1/ Area C16</u>	<u>[2APHC1], (M)</u>	<u>ϕ</u>
0.0231	0.00173	0.0529	0.000269	0.097 ^b
0.0461	0.00345	0.0202	0.000305	0.14 ^b
0.0692	0.00518	0.0207	0.000315	0.12 ^c
0.0922	0.00690	0.0148	0.000300	0.11 ^c
0.1150	0.00863	0.0118	0.000299	0.11 ^c

^a313 nm, acetonitrile solvent, gc Column B at 138°C, [C16]_{act} = 0.00498 M. ^bArea AP/ Area C16 = 0.0405, $I_a = 0.0013 \text{ El}^{-1}$. ^cArea AP/ Area C16 = 0.0808, $I_a = 0.0027 \text{ El}^{-1}$.

Table 74. Data for ϕ_{-K} for 1-(2-pyridyl)butanone hydrochloride.^a

[2BPHCl]	0.0496 M
[C16]	0.0337 M
Area 2BPHCl/ Area C16:	
Unirradiated	0.659
Irradiated	0.633
-[2BPHCl]	0.0020 M



Table 74. Continued.

^a_{313 nm}, acetonitrile solvent, gc Column B at 135°C, [C16]_{act} = 0.0511 M, Area AP/ Area C16 = 0.187, I_a = 0.0064 El⁻¹.

Table 75. Data for ϕ_{-K} for 1-(3-pyridyl)butanone hydrochloride.^a

[3BPHCl] _o	0.0552 M
[C17]	0.0395 M

Area 3BPHCl/ Area C17:

Unirradiated	0.456
Irradiated	0.408
-[3BPHCl]	0.0058 M

^a_{313 nm}, acetonitrile solvent, gc Column B at 170°C, [C16]_{act} = 0.0056 M, Area AP/ Area C16 = 0.456, I_a = 0.17 El⁻¹.

Table 76. Data for ϕ_{-K} for 1-(4-pyridyl)butanone hydrochloride.^a

[4BPHCl] _o	0.0504 M
[C17]	0.0375 M

Area 4BPHCl/ Area C17:

Unirradiated	0.533
Irradiated	0.481
-[4BPHCl]	0.0049 M

^a_{313 nm}, acetonitrile solvent, gc Column B at 170°C, [C16]_{act} = 0.00532 M, Area AP/ Area C16 = 0.711, I_a = 0.025 El⁻¹.

Table 77. Data for the effect of concentration of 1-(3-pyridyl)butanone hydrochloride on ϕ_{II} .^a

[3BPHCl], (M)	[Cl7], (M)	Area 3APHC1/ Area Cl7	[3APHC1], (M)	ϕ
0.023 ^b	0.00179	0.0984	0.000645	0.20 ^c
0.045	0.00358	0.0527	0.000691	0.21 ^c
0.091	0.00176	0.0403	0.000260	0.27 ^d
0.114	0.00896	0.0311	0.000109	0.26 ^d
0.023 ^c	0.00167	0.159	0.000972	0.18 ^f
0.046	0.00336	0.0993	0.00122	0.23 ^f
0.078	0.00569	0.123	0.00256	0.22 ^g
0.092	0.00669	0.112	0.00274	0.23 ^g

^aacetonitrile solvent, 313 nm, gc Column B at 170°C. ^b[Cl6]_{act} = 0.00859 M. ^cArea AP/ Area Cl6 = 0.033, $I_a = 0.0019 \text{ El}^{-1}$. ^dArea AP/ Area Cl6 = 0.108, $I_a = 0.0062 \text{ El}^{-1}$. ^e[Cl6]_{act} = 0.00555 M. ^fArea AP/ Area Cl6 = 0.311, $I_a = 0.012 \text{ El}^{-1}$. ^gArea AP/ Area Cl6 = 0.611, $I_a = 0.023 \text{ El}^{-1}$.

Table 78. Stern Volmer data for 1-(4-pyridyl)butanone hydrochloride.^a

[Q], (M)	Area 4APHC1/ Area Cl7	[4APHC1], (M)	ϕ_o/ϕ
0.0 ^b	0.389	0.000458	-
0.0053	0.316	0.000372	1.2
0.0106	0.289	0.000341	1.4
0.0158	0.269	0.000317	1.5
0.0211	0.255	0.000300	1.5
0.0264	0.233	0.000275	1.7
0.0 ^c	0.489	0.000625	-
0.027	0.284	0.000363	1.8
0.081	0.165	0.000211	3.0
0.108	0.138	0.000177	3.6
0.136	0.119	0.000152	4.2

^a313 nm, gc Column B at 140°C, acetonitrile solvent, Q = 1,3-Pentadiene,

^b[4BPHCl] = 0.0233 M, [Cl7] = 0.000385 M, [Cl6]_{act} = 0.00524 M, Area AP/ Area Cl6 = 0.157, $I_a = 0.0055 \text{ El}^{-1}$. ^c[4BPHCl] = 0.0228 M, [Cl7] = 0.000418 M, [Cl6]_{act} = 0.00476 M, Area AP/ Area Cl6 = 0.199, $I_a = 0.0063 \text{ El}^{-1}$.

Table 79. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(3-pyridyl)butanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 3APHC1/ Area C17</u>	<u>[3APHC1], (M)</u>	<u>ϕ</u>
0.0	0.141	0.000469	0.23
0.95	0.190	0.000639	0.31
1.90	0.201	0.000668	0.33
3.90	0.256	0.000851	0.42
5.70	0.249	0.000828	0.41
7.60	0.211	0.000701	0.34

^abenzene solvent, 313 nm, gc Column B at 178°C, [3BPHCl] = 0.0463 M, [C17] = 0.000908 M, [C16]_{act} = 0.00859 M, Area AP/ Area C16 = 0.272, $I_a = 0.016 \text{ El}^{-1}$.

Table 80. Stern Volmer data for 1-(3-pyridyl)butanone hydrochloride.^a

<u>[Q], (M)</u>	<u>Area 3APHC1/ Area C17</u>	<u>[3APHC1], (M)</u>	<u>ϕ_o/ϕ</u>
0.0 ^b	0.993	0.00137	-
0.071	0.781	0.00108	1.3
0.106	0.703	0.00097	1.4
0.141	0.633	0.00087	1.6
0.0 ^c	0.411	0.000662	-
0.035	0.331	0.000533	1.2
0.071	0.300	0.000483	1.4
0.108	0.268	0.000432	1.5
0.141	0.250	0.000403	1.6
0.176	0.224	0.000361	1.8

^a313 nm, gc Column B at 140°C, acetonitrile solvent, Q = 1,3-Pentadiene. ^b[3BPHCl] = 0.0252 M, [C17] = 0.000377 M, [C16]_{act} = 0.00535 M, Area AP/ Area C16 = 0.132, $I_a = 0.0047 \text{ El}^{-1}$. ^c[3BPHCl] = 0.0169 M, [C17] = 0.00044 M, [C16]_{act} = 0.00613 M, Area AP/ Area C16 = 0.065, $I_a = 0.0026 \text{ El}^{-1}$.

Table 81. Data for the effect of concentration of 1-(4-pyridyl) butanone hydrochloride on ϕ_{II} .^a

<u>[4BPHCl], (M)</u>	<u>[Cl7], (M)</u>	<u>Area 4APHC1/ Area Cl7</u>	<u>[4APHC1], (M)</u>	<u>ϕ</u>
0.020	0.00143	0.0516	0.000226	0.094 ^b
0.041	0.00285	0.0258	0.000225	0.094 ^b
0.061	0.00428	0.0254	0.000332	0.14 ^c
0.081	0.00571	0.0162	0.000283	0.12 ^c
0.101	0.00713	0.0124	0.000271	0.11 ^c
0.121	0.00856	0.0081	0.000212	0.08 ^c

^a313 nm, gc Column B at 160°C, acetonitrile solvent, [Cl6]_{act} = 0.00573 M. ^bArea AP/ Area Cl6 = 0.053, $I_a = 0.0020 \text{ El}^{-1}$. ^cArea AP/Area Cl6 = 0.132, $I_a = 0.0051 \text{ El}^{-1}$.

Table 82. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(4-pyridyl)butanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 4APHC1/ Area Cl7</u>	<u>[4APHC1], (M)</u>	<u>ϕ</u>
1.85	0.069	0.000164	0.063
3.71	0.129	0.000307	0.11
4.65	0.159	0.000379	0.14
5.56	0.139	0.000331	0.12
7.41	0.136	0.000324	0.12

^a313 nm, gc Column B at 160°C, benzene solvent, [4BPHCl] = 0.0424 M, [Cl7] = 0.000778 M, [Cl6]_{act} = 0.0045 M, Area AP/ Area Cl6 = 0.0897, $I_a = 0.0027 \text{ El}^{-1}$.

Table 83. Stern Volmer data for 1-(2-pyridyl)pentanone hydrochloride.^a

<u>[Q], (M)</u>	<u>Area 2APHC1/ Area C16</u>	<u>[2APHC1], (M)</u>	<u>ϕ_o/ϕ</u>
0.0	0.290	0.00580	-
0.086	0.199	0.00398	1.5
0.188	0.169	0.00338	1.8
0.257	0.135	0.00270	2.2
0.342	0.110	0.00220	2.7
0.428	0.105	0.00210	2.8

^a313 nm, gc Column B at 135°C, acetonitrile solvent, Q = 1,3-Pentadiene, [2VPHC1] = 0.0259 M, [C16] = 0.0068, [C16]_{act} = 0.00604 M, Area AP/ Area C16 = 0.154, I_a = 0.0062 El⁻¹.

Table 84. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(2-pyridyl)pentanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 2APHC1/ Area C16</u>	<u>[2APHC1], (M)</u>	<u>ϕ</u>
0.0	0.108	0.00155	0.14
0.91	0.120	0.00173	0.15
1.82	0.143	0.00206	0.18
3.65	0.171	0.00246	0.21
4.56	0.193	0.00277	0.24
7.29	0.218	0.00312	0.27

^abenzene solvent, 313 nm, gc Column B at 135°C, [2VPHC1] = 0.0495 M, [C16] = 0.00489 M, Area AP/ Area C16 = 0.707, I_a = 0.023 El⁻¹.

Table 85. Data for the effect of concentration of 1-(2-pyridyl)pentanone hydrochloride on ϕ_{II} .^a

<u>[2VPHC1], (M)</u>	<u>[C16], (M)</u>	<u>Area 2APHC1/ Area C16</u>	<u>[2APHC1], (M)</u>	<u>ϕ</u>
0.024	0.00159	0.0927	0.000437	0.12 ^b
0.049	0.00319	0.0486	0.000456	0.12 ^b
0.073	0.00478	0.0734	0.000313	0.12 ^c
0.097	0.00637	0.0442	0.0000828	0.11 ^c
0.121	0.00796	0.0321	0.0000751	0.088 ^c

^a313 nm, gc Column B at 138°C, acetonitrile solvent, [C16]_{act} = 0.0058 M,
^bArea AP/ Area C16 = 0.0971, I_a = 0.0037 El⁻¹. ^cArea AP/ Area C16 = 0.221, I_a = 0.0055 El⁻¹.

Table 86. Data for ϕ_{-K} for 1-(2-pyridyl)pentanone hydrochloride.^a

$[2VPHCl]_O$	0.0498 M
$[Cl6]$	0.0365 M
Area 2VPHCl/ Area Cl6:	
Unirradiated	0.566
Irradiated	0.512
$-[2VPHCl]$	0.0048 M

^a313 nm, acetonitrile solvent, $[Cl6]_{act} = 0.00511$ M, Area AP/ Area Cl6 = 0.388, $I_a = 0.013$ El^{-1} , gc Column B at 135°C.

Table 87. Stern Volmer data for 1-(3-pyridyl)pentanone hydrochloride.^a

$[Q], (M)$	Area 3APHCl/ Area Cl7	$[3APHCl], (M)$	ϕ_O/ϕ
0.0 ^b	0.470	0.000676	-
0.10	0.354	0.000509	1.3
0.20	0.285	0.000410	1.7
0.30	0.182	0.000262	2.6
0.40	0.172	0.000247	2.8
0.50	0.139	0.000200	3.5
0.0 ^c	0.328	0.000826	-
0.099	0.253	0.000637	1.5
0.199	0.211	0.000531	1.8
0.298	0.151	0.000380	2.5
0.397	0.123	0.000310	3.0
0.496	0.101	0.000254	3.7

^aacetonitrile solvent, 313 nm, gc Column B at 135°C. ^b $Q = 1,3$ -Pentadiene, $[3VPHCl] = 0.0268$ M, $[Cl7] = 0.000393$ M, $[Cl6] = 0.00592$ M, Area AP/ Area Cl6 = 0.628, $I_a = 0.025$ El^{-1} . ^c $Q =$ Ethyl sorbate, $[3VPHCl] = 0.0497$ M, $[Cl7] = 0.000688$ M, $[Cl6]_{act} = 0.00538$ M, Area AP/ Area Cl6 = 0.235, $I_a = 0.0084$ El^{-1} .

Table 88. Data for the effect of concentration of 1-(3-pyridyl) pentanone hydrochloride on ϕ_{II} .^a

<u>[3VPHC1], (M)</u>	<u>[C17], (M)</u>	<u>Area 3APHC1/ Area C17</u>	<u>[3APHC1], (M)</u>	<u>ϕ</u>
0.0467	0.00321	0.178	0.00209	0.26 ^b
0.0701	0.00481	0.179	0.00315	0.29 ^c
0.0934	0.00642	0.148	0.00348	0.30 ^c
0.1170	0.00802	0.115	0.00358	0.31 ^c

^a313 nm, gc Column B at 170°C, acetonitrile solvent. ^b[C16]_{act} = 0.00525 M, Area AP/ Area C16 = 0.238, $I_a = 0.0083 \text{ El}^{-1}$. ^c[C16]_{act} = 0.00613 M, Area AP/ Area C16 = 0.254, $I_a = 0.010 \text{ El}^{-1}$.

Table 89. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(3-pyridyl)pentanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 3APHC1/ Area C17</u>	<u>[3APHC1], (M)</u>	<u>ϕ</u>
0.0	0.655	0.00221	0.21
1.05	0.704	0.00238	0.23
1.85	0.743	0.00251	0.24
3.71	0.800	0.00270	0.26
4.99	0.789	0.00265	0.26
5.56	0.818	0.00275	0.27
7.41	0.744	0.00251	0.24

^a313 nm, gc Column B at 176°C, benzene solvent, [3VPHC1] = 0.0497 M, [C17] = 0.000922 M, [C16]_{act} = 0.00504 M, Area AP/ Area C16 = 0.302, $I_a = 0.010 \text{ El}^{-1}$.

Table 90. Data for ϕ_{-K} for 1-(3-pyridyl)pentanone hydrochloride.^a

<u>[3VPHC1]_o</u>	0.0409 M
<u>[C17]</u>	0.0367 M
<u>Area 3VPHC1/ Area C17:</u>	
Unirradiated	0.618
Irradiated	0.500
-[3VPHC1]	0.0095 M

^a313 nm, acetonitrile solvent, [C16]_{act} = 0.00504 M, Area AP/ Area C16 = 0.235, $I_a = 0.0079 \text{ El}^{-1}$, gc Column B at 180°C.

Table 91. Stern Volmer data for 1-(4-pyridyl)pentanone hydrochloride.^a

[Q], (M)	Area 4APHC1/ Area C17	[4APHC1], (M)	ϕ_o/ϕ
0.0 ^b	0.359	0.000816	-
0.172	0.216	0.000491	1.7
0.343	0.164	0.000373	2.2
0.515	0.134	0.000305	2.7
0.859	0.101	0.000230	3.7
0.0 ^c	0.487	0.00123	-
0.173	0.406	0.00103	1.2
0.346	0.282	0.000715	1.9
0.520	0.216	0.000547	2.3
0.693	0.193	0.000489	2.6
0.866	0.149	0.000378	3.3
0.0 ^d	0.380	0.000806	-
0.172	0.263	0.000558	1.5
0.344	0.192	0.000407	2.1
0.517	0.147	0.000312	2.7
0.689	0.125	0.000265	3.2
0.861	0.106	0.000225	3.7
0.0 ^e	0.921	0.00148	-
0.228	0.591	0.000951	1.5
0.456	0.521	0.000839	1.8
0.684	0.417	0.000671	2.2
0.911	0.353	0.000568	2.6
1.139	0.310	0.000499	2.9
0.0 ^f	0.770	0.000835	-
0.00690	0.752	0.000815	1.0
0.0104	0.749	0.000811	1.0
0.0138	0.742	0.000804	1.0
0.0173	0.671	0.000727	1.0

^aacetonitrile solution, gc Column B at 140°C. ^bQ = 1,3-Pentadiene, 313 nm, [4VPHCl] = 0.0444M, [C17] = 0.000743 M, [C16]_{act} = 0.00618 M, Area AP/ Area C16 = 0.149, $I_a = 0.0061 \text{ #l}^{-1}$. ^cQ = 1,3-Pentadiene, 313 nm, [4VPHCl] = 0.0477 M, [C17] = 0.000828 M, [C16]_{act} = 0.00541 M, Area AP/ Area C16 = 0.226, $I_a = 0.0082 \text{ El}^{-1}$. ^dQ = Ethyl sorbate, 313 nm, [4VPHCl] = 0.0497 M, [C17] = 0.000693 M, [C16]_{act} = 0.00433 M, Area AP/ Area C16 = 0.277, $I_a = 0.0080 \text{ El}^{-1}$. ^eQ = p-xylene, 313 nm, [4VPHCl] = 0.0103 M, [C17] = 0.000526 M. ^fQ = Naphthalene, 366 nm, [4VPHCl] = 0.0102 M, [C17] = 0.000354 M.

Table 92. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 1-(4-pyridyl)pentanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 4APHC1/ Area C17</u>	<u>[4APHC1], (M)</u>	<u>ϕ</u>
0.0	0.150	0.000500	0.11
0.97	0.136	0.000454	0.10
1.92	0.141	0.000470	0.10
3.87	0.129	0.000430	0.094
4.83	0.128	0.000427	0.094
5.80	0.125	0.000417	0.091

^abenzene solvent, 313 nm, gc Column B at 165°C, [4VPHCl] = 0.0502 M, [C17] = 0.00109 M, [C16]_{act} = 0.00481, Area AP/ Area C16 = 0.142, $I_a = 0.0046 \text{ El}^{-1}$.

Table 93. Data for the effect of concentration of 1-(4-pyridyl)pentanone hydrochloride on ϕ_{II} .^a

<u>[4VPHCl], (M)</u>	<u>[C17], (M)</u>	<u>Area 4APHC1/ Area C17</u>	<u>[4APHC1], (M)</u>	<u>ϕ</u>
0.0235	0.00175	0.0824	0.000442	0.099 ^b
0.0470	0.00350	0.0423	0.000453	0.10 ^b
0.0705	0.00525	0.0506	0.000813	0.10 ^c
0.094	0.00700	0.0455	0.000975	0.12 ^c
0.117	0.00875	0.0382	0.00102	0.13 ^c

^aacetonitrile solvent, 313 nm, gc Column B at 165°C, [C16]_{act} = 0.00436 M.

^bArea AP/ Area C16 = 0.116, $I_a = 0.0033 \text{ El}^{-1}$. ^cArea AP/ Area C16 = 0.205, $I_a = 0.0060 \text{ El}^{-1}$.

Table 94. Data for ϕ_{-K} for 1-(4-pyridyl)pentanone hydrochloride.^a

[4VPHCl] _o	0.0472 M ^a	0.0489 M ^b
[C17]	0.0283 M	0.0378 M
Area 4VPHCl/ Area C17:		
Unirradiated	0.692	0.544
Irradiated	0.634	0.500
-[4VPHCl]	0.0037 M	0.0040 M

^aacetonitrile solution, gc Column B at 178°C, 313 nm. ^b[C16]_{act} = 0.0051 M, Area AP/ Area C16 = 0.789, $I_a = 0.027 \text{ El}^{-1}$. ^c[C16]_{act} = 0.00511 M, Area AP/ Area C16 = 0.388, $I_a = 0.132 \text{ El}^{-1}$.

Table 95. Stern Volmer data for 4-methyl-1-(2-pyridyl)pentanone hydrochloride.^a

<u>[Q], (M)</u>	<u>Area 2APHC1/ Area C16</u>	<u>[2APHC1], (M)</u>	<u>ϕ_o/ϕ</u>
0.0	0.723	0.00232	-
0.06	0.555	0.00178	1.4
0.12	0.453	0.00145	1.6
0.24	0.352	0.00113	2.1

^a313 nm, gc Column B at 135°C, acetonitrile solvent, Q = 1,3-Pentadiene, [γ Me2VPHCl] = 0.0479 M, [C16] = 0.00109 M, [C16]_{act} = 0.00511 M, Area AP/ Area C16 = 0.352, $I_a = 0.012 \text{ El}^{-1}$.

Table 96. Data for the effect of concentration of 4-methyl-1-(2-pyridyl)pentanone hydrochloride on ϕ_{II} .^a

<u>[γMe2VPHCl], (M)</u>	<u>[C16], (M)</u>	<u>Area 2APHC1/Area C16</u>	<u>[2APHC1], (M)</u>	<u>ϕ</u>
0.0235	0.00129	0.184	0.000698	0.16 ^b
0.0470	0.00257	0.113	0.000854	0.19 ^b
0.0705	0.00386	0.108	0.00123	0.15 ^c
0.0940	0.00514	0.078	0.00118	0.073 ^c
0.118	0.00643	0.036	0.000681	0.083 ^c

^a313 nm, gc Column B at 135°C, acetonitrile solvent, [C16]_{act} = 0.00546 M. ^bArea AP/ Area C16 = 0.123, $I_a = 0.0045 \text{ El}^{-1}$. ^cArea AP/ Area C16 = 0.222, $I_a = 0.0081 \text{ El}^{-1}$.

Table 97. Data for ϕ_K for 4-methyl-1-(2-pyridyl)pentanone hydrochloride.^a

[γ Me2VPHCl] _o	0.0698 M
[C16]	0.0555 M
Area γ Me2VPHCl/ Area C16:	
Unirradiated	0.826
Irradiated	0.744
- [γ Me2VPHCl]	0.0069 M

^aacetonitrile solvent, gc Column B at 135°C, 313 nm, [C16]_{act} = 0.0055 M, Area AP/ Area C16 = 0.753, $I_a = 0.028 \text{ El}^{-1}$.

Table 98. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 4-methyl-1-(2-pyridyl)pentanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 2APHC1/ Area C16</u>	<u>[2APHC1], (M)</u>	<u>ϕ</u>
0.0	0.136	0.000272	0.13
0.98	0.192	0.000384	0.18
1.95	0.205	0.000410	0.19
3.90	0.252	0.000505	0.24
4.88	0.296	0.000593	0.28
5.85	0.250	0.000501	0.24
7.80	0.302	0.000605	0.28

^abenzene solvent, 313 nm, gc Column B at 135°C, [γ Me2VPHCl] = 0.0488 M, [C16] = 0.000681 M, [C16]_{act} = 0.00681 M, Area AP/ Area C16 = 0.0681, $I_a = 0.00309 \text{ El}^{-1}$.

Table 99. Stern Volmer data for 3-methyl-1-(3-pyridyl)butanone hydrochloride.^a

<u>[Q], (M)</u>	<u>Area 3APHC1/ Area C17</u>	<u>[3APHC1], (M)</u>	<u>ϕ_o/ϕ</u>
0.0	0.795	0.00162	-
0.061	0.404	0.000826	2.0
0.121	0.339	0.000692	2.4
0.242	0.193	0.000394	4.2
0.303	0.159	0.000325	5.0

^aacetonitrile solvent, 313 nm, gc Column B at 170°C, Q = Ethyl sorbate, [β Me3BPHCl] = 0.0274 M, [C17] = 0.000558 M, [C16]_{act} = 0.00532 M, Area AP/ Area C16 = 0.272, $I_a = 0.0097 \text{ El}^{-1}$

Table 100. Data for ϕ_{-K} for 3-methyl-1-(3-pyridyl)butanone hydrochloride.^a

[β Me3BPHCl]_o

[C17]

Area β Me3BPHCl/ Area C17:

Unirradiated

Irradiated

-[β Me3BPHCl]

^aacetonitrile solvent, 313 nm, gc Column B at 170°C, [C16]_{act} = 0.00555 M, Area AP/ Area C16 = 0.754, $I_a = 0.028 \text{ El}^{-1}$.

Table 101. Data for the effect of concentration of 3-methyl-1-(3-pyridyl)butanone hydrochloride on ϕ_{II} .^a

<u>[βMe3BPHCl], (M)</u>	<u>[C17], (M)</u>	<u>Area 3APHC1/ Area C17</u>	<u>[3APHC1], (M)</u>	<u>ϕ</u>
0.0224	0.00149	0.277	0.00151	0.15 ^b
0.0449	0.00298	0.135	0.00147	0.17 ^b
0.0673	0.00446	0.202	0.00100	0.18 ^c
0.0896	0.00595	0.172	0.000875	0.21 ^c
0.1120	0.00744	0.155	0.000422	0.23 ^c

^aacetonitrile solvent, 313 nm, gc Column B at 170°C, [C16]_{act} = 0.00506 M. ^bArea AP/ Area C16 = 0.257, $I_a = 0.0087 \text{ El}^{-1}$. ^cArea AP/ Area C16 = 0.533, $I_a = 0.018 \text{ El}^{-1}$.

Table 102. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 3-methyl-1-(3-pyridyl)butanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 3APHC1/ Area C17</u>	<u>[3APHC1], (M)</u>	<u>ϕ</u>
0.0	0.857	0.00182	0.18
1.02	0.998	0.00212	0.21
2.05	1.063	0.00226	0.22
4.10	1.347	0.00286	0.29
5.12	1.037	0.00220	0.21
6.14	1.233	0.00262	0.25
8.19	1.171	0.00249	0.24

^abenzene solvent, 313 nm, gc Column B at 170°C, [β Me3BPHCl] = 0.0513 M, [C17] = 0.00058 M, [C16]_{act} = 0.00507 M, Area AP/ Area C16 = 0.541, $I_a = 0.018 \text{ El}^{-1}$.

Table 103. Data for the effect of concentration of 4-methyl-1-(4-pyridyl)pentanone hydrochloride on ϕ_{II} .^a

$[\gamma\text{Me4VPHCl}]$, (M)	$[\text{Cl7}]$, (M)	Area 4APHC1/Area Cl7	$[\text{4APHC1}]$, (M)	ϕ
0.0230	0.00148	0.0740	0.000328	0.13 ^b
0.0459	0.00295	0.0387	0.000349	0.13 ^b
0.0689	0.00443	0.0539	0.000731	0.14 ^c
0.0919	0.00591	0.0409	0.000740	0.14 ^c
0.115	0.00739	0.0334	0.000755	0.14 ^c

^aacetonitrile solvent, 313 nm, gc Column B at 170°C, $[\text{Cl6}]_{\text{act}} = 0.00637$ M. ^bArea AP/ Area Cl6 = 0.0632, $I_a = 0.0030 \text{ El}^{-1}$. ^cArea AP/ Area Cl6 = 0.127, $I_a = 0.0054 \text{ El}^{-1}$.

Table 104. Stern Volmer data for 3-methyl-1-(4-pyridyl)butanone hydrochloride.^a

$[\text{Q}]$, (M)	Area 4APHC1/ Area Cl7	$[\text{4APHC1}]$, (M)	ϕ_o/ϕ
0.0	0.697	0.00152	-
0.061	0.216	0.000471	1.4
0.120	0.143	0.000321	2.1
0.180	0.122	0.000266	2.4
0.240	0.103	0.000225	2.8
0.300	0.094	0.000205	3.3

^aacetonitrile solvent, 313 nm, gc Column B at 170°C, Q = Ethyl sorbate, $[\beta\text{Me4BPHCl}] = 0.0501$ M, $[\text{Cl7}] = 0.000713$ M, $[\text{Cl6}]_{\text{act}} = 0.00533$ M, Area AP/ Area Cl6 = 0.274, $I_a = 0.0097 \text{ El}^{-1}$.

Table 105. Data for ϕ_{-K} for 3-methyl-1-(4-pyridyl)butanone hydrochloride.^a

$[\beta\text{Me4BPHCl}]_o$	0.0501 M
$[\text{Cl7}]$	0.0228 M
Area $\beta\text{Me4BPHCl}$ / Area Cl7:	
Unirradiated	0.986
Irradiated	0.910
$-\beta\text{Me4BPHCl}$	0.0039 M

^aacetonitrile solvent, gc Column B at 165°C, $[\text{Cl6}]_{\text{act}} = 0.00533$ M, Area AP/ Area Cl6 = 0.183, $I_a = 0.0065 \text{ El}^{-1}$.

Table 106. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 3-methyl-1-(4-pyridyl)butanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 4APHC1/ Area C17</u>	<u>[4APHC1], (M)</u>	<u>ϕ</u>
0.0	0.436	0.00137	0.16
0.92	0.293	0.000924	0.12
1.84	0.305	0.000961	0.12
3.67	0.366	0.00115	0.099
4.59	0.344	0.00108	0.14
5.51	0.345	0.00109	0.15
7.35	0.299	0.000942	0.12

^abenzene solvent, 313 nm, gc Column B at 165°C, [Me4BPHCl] = 0.0513 M, [C17] = 0.00103 M, [C16]_{act} = 0.00533 M, Area AP/ Area C16 = 0.347, I_a = 0.0123.

Table 107. Data for the effect of concentration of 3-methyl-1-(4-pyridyl)butanone hydrochloride on ϕ_{II} .^a

<u>[gMe4BPHCl], (M)</u>	<u>[C17], (M)</u>	<u>Area 4APHC1/ Area C17</u>	<u>[4APHC1], (M)</u>	<u>ϕ</u>
0.0166	0.0033	0.262	0.00265	0.19 ^b
0.0331	0.0066	0.139	0.00281	0.21 ^b
0.0497	0.0099	0.083	0.00251	0.18 ^b
0.0662	0.0132	0.119	0.00481	0.20 ^c
0.0828	0.0165	0.0782	0.00394	0.16 ^c
0.0993	0.0198	0.067	0.00406	0.17 ^c

^aacetonitrile solvent, 313 nm, gc Column B at 165°C, [C16]_{act} = 0.00661 M.

^bArea AP/ Area C16 = 0.204, I_a = 0.0090 El⁻¹. ^cArea AP/ Area C16 = 0.55, I_a = 0.024 El⁻¹.

Table 108. Data for ϕ_{-K} for 4-methyl-1-(4-pyridyl)pentanone hydrochloride.^a

$[\gamma\text{Me4VPHCl}]_0$	0.0787 M
[C17]	0.0355 M
Area $\gamma\text{Me4VPHCl}$ / Area C17:	
Unirradiated	0.896
Irradiated	0.816
$-\gamma\text{Me4VPHCl}$	0.0070 M

^aacetonitrile solvent, gc Column B at 170°C, 313 nm, [C16]_{act} = 0.00555 M, Area AP/ Area C16 = 0.820, I_a = 0.030 El⁻¹.

Table 109. Stern Volmer data for 4-methyl-1-(4-pyridyl)pentanone hydrochloride.^a

<u>[Q], (M)</u>	<u>Area 4APHC1/ Area C17</u>	<u>[4APHC1], (M)</u>	<u>ϕ_o/ϕ</u>
0.0 ^b	0.177	0.000473	-
0.121	0.141	0.000377	1.3
0.241	0.114	0.000305	1.6
0.362	0.106	0.000283	1.7
0.482	0.094	0.000251	2.3
0.0 ^c	1.409	0.00352	-
0.223	0.821	0.00205	1.7
0.445	0.760	0.00190	1.9
0.668	0.609	0.00152	2.3
0.890	0.506	0.00125	2.8
1.113	0.443	0.00111	3.2

^aacetonitrile solvent, 313 nm, gc Column B at 170°C. ^b_Q = 1,3-Pentadiene, [γ Me4VPHCl] = 0.0505 M, [C17] = 0.00083 M, [C16]_{act} = 0.0048 M, Area AP/ Area C16 = 0.11, $I_a = 0.0035 \text{ El}^{-1}$. ^c_Q = Ethyl sorbate, [γ Me4VPHCl] = 0.0645 M, [C17] = 0.000816 M, [C16]_{act} = 0.00481 M, Area AP/ Area C16 = 0.895, $I_a = 0.029 \text{ El}^{-1}$.

Table 110. Data for the effect of concentration of tert-butyl alcohol on ϕ_{II} for 4-methyl-1-(4-pyridyl)pentanone hydrochloride.^a

<u>[t-BuOH], (M)</u>	<u>Area 4APHC1/ Area C17</u>	<u>[4APHC1], (M)</u>	<u>ϕ</u>
0.0	0.362	0.000651	0.12
0.91	0.366	0.000659	0.13
1.82	0.358	0.000644	0.11
4.00	0.375	0.000675	0.12
5.47	0.323	0.000581	0.10
7.29	0.278	0.000500	0.86

^abenzene solvent, 313 nm, gc Column B at 170°C, [Me4VPHCl] = 0.0504 M, [C17] = 0.000588 M, [C16]_{act} = 0.00681 M, Area AP/ Area C16 = 0.137, $I_a = 0.00622$.

Table 111. Data for the effect of additives on ϕ_{II} for
1-(4-pyridyl)pentanone.^a

<u>[ZnCl₂], (M)^b</u>	<u>[4VP], (M)</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ</u>
0.0157	0.0496	0.294	0.000695	0.16
0.0297	0.0496	0.264	0.000624	0.14
0.0517	0.0496	0.257	0.000607	0.14
<u>[Ru4VP], (M)^b</u>				
0.0101	0.0496	0.216	0.000510	0.12
<u>[Rupy], (M)^b</u>				
0.0061	0.0496	0.210	0.000496	0.11
<u>[BrRe(CO)₅], (M)^c</u>				
0.00320	0.0188	0.0781	0.000185	0.042
<u>[Re4VP], (M)^c</u>				
0.000137	0.0188	0.114	0.000331	0.061

^a313 nm, gc Column B at 170°C, [C16]_{act} = 0.00572 M, Area AP/ Area C16 = 0.116, I_a = 0.0044 El⁻¹, [C17] = 0.000772 M. ^bacetonitrile solvent.

^c benzene solvent.

Table 112. Data for output of the optical bench.^a

<u>t_{irr}, (hr.)</u>	<u>Area pr/ Area cyclohexane</u>	<u>% conversion</u>
18 ^b	0.0171	0.17
24 ^b	0.0239	0.24
32 ^b	0.0139	0.32
12 ^c	0.0563	0.63
44 ^c	0.218	2.4

^aacetonitrile solvent, 313 nm, gc Column A at 50°C ^a[VP] = 0.0564 M, [cyc] = 0.00256 M. ^b[VP] = 0.0503 M, [cyc] = 0.00281 M.

Table 113. Quantum yield data for 4-acetylpyridine hydrochloride and p-xylene (BH) in acetonitrile.^a

<u>[BH], (M)</u>	<u>Area DTE/ Area C15</u>	<u>I_a, El⁻¹</u>	<u>φ^{corr}_{DTE}</u>
0.313	0.103	0.295	0.00531
0.625	0.119	0.295	0.00633
0.938	0.114	0.295	0.00608
1.251	0.130	0.295	0.00691
1.563	0.162	0.295	0.00868
1.896	0.136	0.210	0.0102
2.189	0.174	0.210	0.0130
2.501	0.175	0.210	0.0130

^a_{313 nm}, [4APHC1] = 0.0102 M, [C15] = 0.0123 M, gc Column E.

Table 114. Quantum yield data for 4-acetylpyridine hydrochloride and 1-phenylethanol (BH) in acetonitrile.^a

<u>[BH], (M)</u>	<u>Area AP/ Area C18</u>	<u>[C18], (M)</u>	<u>I_a, El⁻¹</u>	<u>φ^{corr}_{AP}</u>
0.100	0.300	0.00737	0.431	0.0169
0.201	0.253	0.01020	0.267	0.0319
0.301	0.553	0.00488	0.217	0.0427
0.401	0.217	0.01704	0.187	0.0655
0.502	0.253	0.01704	0.187	0.0719

^a_{313 nm}, [4APHC1] = 0.01 M, Absorbance correction = 1.34, gc Column A.

Table 115. Quantum yield data for 3-acetylpyridine hydrochloride and 1-phenylethanol (BH) in acetonitrile.^a

<u>[BH], (M)</u>	<u>Area AP/ Area C18</u>	<u>[C18], (M)</u>	<u>I_a, El⁻¹</u>	<u>φ^{corr}_{AP}</u>
0.106	0.544	0.00488	0.623	0.0166
0.106	0.189	0.01020	0.431	0.0174
0.212	0.805	0.00488	0.267	0.0322
0.318	1.022	0.00488	0.417	0.0466
0.318	0.197	0.01704	0.267	0.0489
0.502	0.129	0.03660	0.203	0.0908

^a_{313 nm}, [3APHC1] = 0.01 M, Absorbance correction = 1.623, gc Column A.

Table 116. Data for the sensitized irradiation of cis-1,3-pentadiene by the pyridyl ketones.^a

<u>[c-P], (M)</u>	<u>[t-P], (M)</u>	<u>β</u>	<u>ϕ_{c-t}</u>
0.499 ^b	0.0273	0.0708	0.50
0.661	0.0353	0.0641	0.50
0.998	0.0308	0.0534	0.47
1.001	0.0374	0.0374	0.52
1.0 (AP)	0.0397	0.0416	-
0.399 ^c	0.0256	0.0637	0.43
0.499	0.0268	0.0538	0.44
0.588	0.0303	0.0460	0.50
0.997	0.0316	0.0316	0.51
0.997 (AP)	0.0331	0.0337	-
0.401 ^d	0.0203	0.0507	0.36
0.501	0.0219	0.0440	0.39
0.661	0.0240	0.0364	0.42
1.002	0.0250	0.0255	0.45
1.002 (AP)	0.0317	0.0314	-

^abenzene solvent, 313 nm, gc Column C. ^a[ZVP] = 0.0492 M, [AP] = 0.1 M. ^b[3VP] = 0.0495 M, [AP] = 0.0943 M. ^c[4VP] = 0.0532 M, [AP] = 0.0938 M.

Table 117. Data for the effect of water on ϕ_{II} for 1-(4-pyridyl) pentanone.^a

<u>[4VP], (M)</u>	<u>% water</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>	<u>ϕ</u>
0.052 ^b	1	0.730	0.00306	0.57
0.055	2	0.754	0.00316	0.58
0.063	3	0.591	0.00248	0.47
0.061 ^c	0	0.413	0.00118	0.45
0.056	2	0.489	0.00140	0.58
0.055	3	0.455	0.00130	0.54
0.057	4	0.420	0.00120	0.50

^aacetonitrile solvent, 313 nm, gc Column B at 125°C. ^b[C17] = 0.0014 M, [C16]_{act} = 0.00539 M, Area AP/ Area C16 = 0.160, $I_a = 0.0058 \text{ El}^{-1}$. ^c[C17] = 0.000933 M, [C16]_{act} = 0.00525 M, Area AP/ Area C16 = 0.111, $I_a = 0.0039 \text{ El}^{-1}$.

Table 118. Quantum yield data for 4-acetylpyridine hydrochloride and 2-propanol (BH) in acetonitrile.^a

[BH], (M)	Area acetone/ Area cyc	[acetone], (M)	I_a, El^{-1}	$\phi_{\text{acetone}}^{\text{corr}}$
0.126 ^b	0.0595	0.00121	0.012	0.10
0.251	0.0818	0.00166	0.012	0.15
0.377	0.115	0.00230	0.012	0.20
0.502	0.0864	0.00175	0.0075	0.23
0.753	0.112	0.00227	0.0075	0.30
0.879	0.122	0.00247	0.0075	0.32
1.004	0.126	0.00255	0.0075	0.33
0.126 ^c	0.0320	0.00532	0.0059	0.057
0.251	0.0519	0.00862	0.0059	0.093
0.378	0.0693	0.0115	0.0059	0.12
0.504	0.0798	0.0133	0.0059	0.14
0.630	0.0533	0.00886	0.0092	0.15
0.756	0.0595	0.00989	0.0092	0.16
0.882	0.0645	0.0103	0.0092	0.18
1.008	0.0695	0.0115	0.0092	0.20

^a313 nm, gc Column F. ^b[4APHC1] = 0.0113 M, [cyc] = 0.00662 M. ^c[4APHC1] = 0.0103 M, [cyc] = 0.0543 M.

Table 119. Quantum yield data for 3-acetylpyridine hydrochloride and 2-propanol (BH) in acetonitrile.^a

[BH], (M)	Area acetone/ Area cyc	[acetone], (M)	I_a, El^{-1}	$\phi_{\text{acetone}}^{\text{corr}}$
0.501 ^b	0.0314	0.000623	0.014	0.044
0.626	0.0210	0.000416	0.0084	0.049
0.752	0.0295	0.000585	0.0084	0.069
0.877	0.0319	0.000633	0.0084	0.074
1.00	0.0409	0.000811	0.0084	0.081
0.125 ^c	0.0513	0.000837	0.018	0.047
0.250	0.0490	0.000799	0.018	0.044
0.366	0.0426	0.000711	0.018	0.039
0.501	0.0321	0.000765	0.018	0.043
0.626	0.0459	0.000763	0.0094	0.049
0.751	0.0398	0.000653	0.0094	0.069
0.870	0.0326	0.000708	0.0094	0.075
1.00	0.0244	0.000752	0.0094	0.080

^a313 nm, gc Column F. ^b[3APHC1] = 0.00973 M, [cyc] = 0.00648 M.

^c[3APHC1] = 0.00992 M, [cyc] = 0.00533 M.

Table 120. Data for the effect of concentration of 4-acetylpyridine hydrochloride on ϕ_{DTE} in acetonitrile.^a

<u>[4APHC1], (M)</u>	<u>Area DTE/ Area C15</u>	<u>[DTE], (M)</u>	<u>ϕ_{DTE}</u>
0.0124	0.297	0.000167	0.0074
0.0220	0.359	0.000195	0.0077
0.0376	0.395	0.000214	0.0080
0.0470	0.411	0.000223	0.0083
0.0746	0.453	0.000246	0.0091
0.0809	0.455	0.000247	0.0091

^a313 nm, [C15] = 0.00571 M, $I_a = 0.027 \text{ El}^{-1}$, gc Column E.

Table 121. Stern Volmer data for 4-acetylpyridine hydrochloride in acetonitrile.^a

<u>[Q], (M)</u>	<u>Area acetone/ Area cyc</u>	<u>[acetone], (M)</u>	<u>ϕ_o/ϕ</u>
0.00142 ^b	0.0348	0.000679	1.0
0.00427	0.0328	0.000640	1.1
0.00569	0.0304	0.000593	1.2
0.00711	0.0290	0.000566	1.2
0.0107	0.0265	0.000517	1.4
0.0142	0.0239	0.000466	1.5
0.00161 ^c	0.0428	0.000700	2.0
0.00807	0.0413	0.000675	2.1
0.0121	0.0391	0.000639	2.1
0.0161	0.0376	0.000615	2.2
0.0202	0.0334	0.000546	2.4

^agc Column F, [2-propanol] = 0.377 M. ^bQ = Naphthalene, 366 nm, [4APHC1] = 0.0101 M, [cyc] = 0.00648 M. ^cQ = Ethyl sorbate, 313 nm, [4APHC1] = 0.0105 M, [cyc] = 0.00543 M.

Table 122. Stern Volmer data for 3-acetylpyridine hydrochloride in acetonitrile.^a

<u>[Q], (M)</u>	<u>Area acetone/ Area cyc</u>	<u>[acetone], (M)</u>	<u>ϕ_o/ϕ</u>
0.00166 ^b	0.0304	0.000475	1.1
0.00333	0.0280	0.000437	1.2
0.00498	0.0251	0.000392	1.3
0.00664	0.0242	0.000378	1.4
0.00830	0.0216	0.000337	1.5
0.0124	0.0198	0.000309	1.7
0.00408 ^c	0.0323	0.000528	2.7
0.00816	0.0348	0.000569	2.5
0.0122	0.0316	0.000517	2.8
0.0163	0.0279	0.000456	3.2
0.0204	0.0250	0.000409	3.5

^agc Column F, [2-propanol] = 0.0670 M. ^bQ = Naphthalene, 366 nm, [3APHC1] = 0.0103 M, [cyc] = 0.00519 M. ^cQ = Ethyl sorbate, 313 nm, [3APHC1] = 0.0125 M, [cyc] = 0.00543 M.

Table 121. Fragmentation data for the pyridyl ketone ruthenium(II) complexes.^a

<u>[Ru4AP], (M)</u>	<u>[C18], (M)</u>	<u>Inj T</u>	<u>Area 4VP/ Area C18</u>	<u>[4AP], (M)</u>
0.005	0.0005	250°C	0.0	0.0
0.005	0.0005	280°C	0.059	0.000092
0.005	0.0005	320°C	0.057	0.000088
0.005	0.0005	320°C	0.0804	0.0013
<u>[Ru4VP], (M)</u>	<u>[C17], (M)</u>	<u>Area 4VP/ Area C17</u>	<u>[4VP], (M)</u>	
0.0105 ^{b,c}	0.0106	0.0058	0.00011	
0.0105 ^{b,d}	0.0106	0.0051	0.00012	
0.0105 ^{b,e}	0.0106	0.0046	0.00011	
0.00454 ^f	0.00158	0.0126	0.000044	
0.0102 ^g	0.00156	0.0248	0.00011	

^aacetonitrile solvent, gc Column B at 140°C. ^b[triphenylphosphine] = 0.115 M. ^croom temperature, dark. ^dreflux 24 hr. ^ereflux 48 hr. ^fbutyronitrile solvent, [triphenylphosphine] = 0.058 M. ^gCH₃CN solvent, [LiCl] = 1.16 M.

Table 124. Stern Volmer data for $[\text{Ru}(\text{NH}_3)_5(1-(4\text{-pyridyl})\text{pentanone})][\text{BF}_4]_2$.^a

$[\text{Ru4VP}], (\text{M})$	$[\text{Q}], (\text{M})$	Area pr/ Area cyc	$[\text{pr}], (\text{M})$	ϕ_0/ϕ
0.0105 ^b	0.0	0.181	0.000395	-
0.0102	0.187	0.104	0.000297	2.2
0.0103	0.562	0.0746	0.000163	3.1
0.0103	0.937	0.0367	0.000080	6.6
0.0103 ^c	0.0	0.108	0.000238	-
0.0101	0.099	0.0558	0.000123	2.0
0.0107	0.197	0.0406	0.0000893	2.7
0.0097	0.296	0.0395	0.0000867	3.1
0.0103	0.394	0.0304	0.0000669	3.5
0.0099	0.493	0.0251	0.0000552	4.6

^aQ = Ethyl sorbate, acetonitrile solvent, 313 nm, gc Column A at 50°C.

^b[cyc] = 0.00190 M, [C17] = 0.0017 M, [cyc]_{act} = 0.0057 M, Area pr /Area cyc = 0.484, [C16]_{act} = 0.00549 M, Area AP/ Area C16 = 0.577, $I_a = 0.019 \text{ El}^{-1}$. ^c[cyc] = 0.0011 M, Area pr/ Area cyc = 0.389, [C16]_{act} = 0.0048 M, Area AP/ Area C16 = 0.480, $I_a = 0.014 \text{ El}^{-1}$.

Table 125. Stern Volmer data for $[\text{Ru}(\text{NH}_3)_5(1-(3\text{-pyridyl})\text{pentanone})][\text{BF}_4]_2$.^a

$[\text{Ru3VP}], (\text{M})$	$[\text{Q}], (\text{M})$	Area pr/ Area cyc ^b	$[\text{pr}], (\text{M})$	ϕ_0/ϕ
0.0101 ^c	0.0	0.0997 (0.0)	0.00109	-
0.0098	0.060	0.0586 (0.379)	0.000642	1.7
0.0104	0.181	0.0336 (0.669)	0.000368	2.9
0.0094	0.302	0.0225 (0.570)	0.000247	4.4
0.0098 ^d	0.0	0.0666 (0.0)	0.000128	-
0.0091	0.061	0.0372 (0.473)	0.0000716	1.8
0.0103	0.123	0.0272 (0.474)	0.0000524	2.4
0.0096	0.184	0.0243 (0.479)	0.0000468	2.7
0.0105	0.245	0.0198 (0.478)	0.0000381	3.4

^aQ = Ethyl sorbate, acetonitrile solvent, 313 nm. ^bNumbers in parenthesis are Area 3VP/ Area C17. ^c[cyc] = 0.00172 M, [C17] = 0.000978 M, [cyc]_{act} = 0.00548 M, Area pr/ Area cyc = 0.446, [C16]_{act} = 0.0048 M, Area AP/ Area C16 = 0.566, $I_a = 0.013 \text{ El}^{-1}$. ^d[cyc] = 0.000963 M, [C17] = 0.001 M, [cyc]_{act} = 0.00548 M, Area pr/ Area cyc = 0.297, [C16]_{act} = 0.0048 M, Area AP/ Area C16 = 0.356, $I_a = 0.010 \text{ El}^{-1}$.

Table 126. Stern Volmer data for $[\text{Ru}(\text{NH}_3)_5(4\text{-methyl-1-(4-pyridyl)pentanone})][\text{BF}_4]_2$.^a

$[\text{Ru} \gamma\text{Me4VP}], (\text{M})$	$[\text{Q}], (\text{M})$	Area pr/ Area cyc	$[\text{pr}], (\text{M})$	ϕ_o/ϕ
0.00976 ^b	0.0	0.256	0.000558	-
0.00953	0.201	0.129	0.000281	2.0
0.00957	0.602	0.0611	0.000133	4.2
0.0103	1.003	0.0346	0.0000754	7.4
0.00981 ^c	0.0	0.313	0.000669	-
0.0102	0.085	0.223	0.000467	1.4
0.0105	0.169	0.159	0.000340	2.0
0.0102	0.254	0.128	0.000274	2.5
0.0102	0.339	0.118	0.000229	2.9
0.0102	0.423	0.107	0.000253	3.3

^aQ = Ethyl sorbate, acetonitrile solvent, gc Column A at 50°C. ^b[cyc] = 0.00109 M, [Cl7] = 0.0017 M, [cyc]_{act} = 0.00571 M, [Cl6]_{act} = 0.00594 M, Area pr/ Area Cl6 = 0.504. Area AP/ Area Cl6 = 0.575, $I_a = 0.019 \text{ El}^{-1}$.

^c[cyc] = 0.00107 M, [Cl7] = 0.0017 M, [cyc]_{act} = 0.00548 M, Area pr/ Area cyc = 0.434, [Cl6]_{act} = 0.0048 M, Area AP/ Area Cl6 = 0.539, $I_a = 0.16 \text{ El}^{-1}$.

Table 127. Stern Volmer data for $[\text{Ru}(\text{NH}_3)_5(3\text{-methyl-1-(3-pyridyl)butanone})][\text{BF}_4]_2$.^a

$[\text{Ru} \beta\text{Me3BP}], (\text{M})$	$[\text{Q}], (\text{M})$	Area pr/ Area cyc ^b	$[\text{pr}], (\text{M})$	ϕ_o/ϕ
0.0103	0.0	0.1180 (0.0778)	0.00260	-
0.0094	0.96	0.0341 (0.175)	0.000750	3.2
0.0101	0.191	0.0252 (0.206)	0.000554	5.1
0.0102	0.242	0.0263 (0.225)	0.000578	5.3
0.0102	0.287	0.0172 (0.240)	0.000378	7.2
0.0098	0.382	0.0130 (0.329)	0.000286	9.8

^aQ = Ethyl sorbate, acetonitrile solvent, 313 nm. ^bNumbers in parenthesis are Area 3VP/ Area Cl7, gc Column A at 50°C, gc Column B at 140°C. ^a[cyc] = 0.0011 M, [Cl7] = 0.00192 M, [cyc]_{act} = 0.00548 M, Area pr/ Area cyc = 0.378, [Cl6]_{act} = 0.0048 M, Area AP/ Area Cl6 = 0.498, $I_a = 0.14 \text{ El}^{-1}$.

Table 128. Stern Volmer data for $[\text{Ru}(\text{NH}_3)_5(3\text{-methyl-1-(4-pyridyl)butanone})][\text{BF}_4]_2$.^a

$[\text{RuMe4BP}], (\text{M})$	$[\text{Q}], (\text{M})$	Area pr/ Area cyc	$[\text{pr}], (\text{M})$	ϕ_{O}/ϕ
0.0106	0.0	0.333	0.000946	-
0.0093	0.0577	0.192	0.000545	1.7
0.0097	0.115	0.141	0.000400	2.5
0.0090	0.173	0.102	0.000290	3.2
0.0100	0.231	0.086	0.000244	3.7
0.0101	0.289	0.067	0.000190	4.6

^aQ = Ethyl sorbate, acetonitrile solvent, 313 nm, gc Column A at 50°C, [cyc] = 0.00142 M, [Cl7] = 0.00233 M, [cyc]_{act} = 0.00988 M, Area pr/ Area cyc = 0.491, [Cl6]_{act} = 0.00608 M, $I_a = 0.030 \text{ El}^{-1}$.

Table 129. Quantum yield data for $[\text{Ru}(\text{NH}_3)_5(4\text{-acetylpyridine})][\text{BF}_4]_2$ with 2-propanol (BH) in acetonitrile.^a

$[\text{BH}], (\text{M})$	Area acetone/ Area cyc	I_a, El^{-1}	ϕ_{acetone}
0.201 ^b	0.0304	0.015	0.033
0.402 ^c	0.0323	0.015	0.035
0.602 ^d	0.0337	0.0062	0.086
0.805 ^e	0.0426	0.0062	0.11
1.00 ^f	0.0484	0.0062	0.13

^a313 nm, gc Column F, [cyc] = 0.00519 M. ^b[Ru4AP] = 0.0099 M. ^c[Ru4AP] = 0.0099 M. ^d[Ru4AP] = 0.00961 M. ^e[Ru4AP] = 0.00998 M. ^f[Ru4AP] = 0.011 M.

Table 130. Quantum yield data for $[\text{Ru}(\text{NH}_3)_5(3\text{-acetylpyridine})][\text{BF}_4]_2$ with 2-propanol (BH) in acetonitrile.^a

$[\text{BH}], (\text{M})$	Area acetone/ Area cyc	I_a, El^{-1}	ϕ_{acetone}
0.199 ^b	0.0166	0.015	0.018
0.400 ^c	0.0236	0.015	0.034
0.599 ^d	0.0209	0.0062	0.054
0.799 ^d	0.0281	0.0062	0.069
0.999 ^e	0.0327	0.0062	0.084

^a313 nm, gc Column F, [cyc] = 0.00519 M. ^b[Ru3AP] = 0.00949 M. ^c[Ru3AP] = 0.00937 M. ^{d,e}[Ru3AP] = 0.0104 M. ^e[Ru3AP] = 0.010 M.

Table 131. Stern Volmer data for $[\text{Ru}(\text{NH}_3)_5(4\text{-acetylpyridine})][\text{BF}_4]_2$.^a

<u>[Ru4AP], (M)</u>	<u>[Q], (M)</u>	<u>Area acetone/ Area cyc</u>	<u>[acetone], (M)</u>
0.0096 ^b	0.0	0.0338	0.00061
0.0101	0.00231	0.0318	0.00057
0.0099	0.00462	0.0325	0.00059
0.0128	0.00770	0.0456	0.00082
0.0104	0.0116	0.0306	0.00055
0.0111	0.0154	0.0333	0.00060
0.0109	0.0	0.0332	0.00060
0.00848 ^c	0.0756	0.0319	0.00058
0.00986 ^d	0.05	0.0328	0.00060
0.0107 ^e	0.0595	0.0340	0.00061
0.0101 ^f	0.05	0.0337	0.00061
0.00876	0.0	0.0319	0.00058
0.00994 ^g	0.0503	0.0340	0.00061
0.00901 ^h	0.00924	0.0332	0.00060
0.00799 ^h	0.0274	0.0335	0.00061
0.0104 ^h	0.0510	0.0329	0.00059

^aacetonitrile solvent, gc Column F, [cyc] = 0.0060 M, [2-propanol] = 0.599 M. ^bQ = naphthalene, 366 nm. ^cQ = fumaronitrile, 313 nm. ^dQ = 1,3-cyclooctadiene, 313 nm. ^eQ = 2,3-dimethylbut-2-ene, 313 nm. ^fQ = 2,4-hexadieneol, 313 nm. ^gQ = 1-naphthylacetic acid, 366 nm. ^hQ = 2-chloronaphthalene, 366 nm.

Table 132. Stern Volmer data for $[\text{Ru}(\text{NH}_3)_5(3\text{-acetylpyridine})][\text{BF}_4]_2$.^a

<u>[Ru3AP], (M)</u>	<u>[Q], (M)</u>	<u>Area acetone / Area cyc</u>	<u>[acetone], (M)</u>
0.0101	0.0	0.0250	0.00044
0.00994	0.00231	0.0163	0.00028
0.0108	0.00462	0.0241	0.00042
0.0103	0.00770	0.0245	0.00043
0.0098	0.0116	0.0257	0.00045
0.0113	0.0154	0.0236	0.00041

^aacetonitrile solvent, 366 nm, gc Column F, [cyc] = 0.0058 M, [2-propanol] = 0.609 M.

Table 133. Fragmentation data for the rhenium(I) pyridyl ketone complexes.^a

<u>[Re2AP], (M)</u>	<u>[C17], (M)</u>	<u>Inj T.</u>	<u>Area 2AP/ Area C17</u>	<u>[2AP], (M)</u>
0.00101	0.0115	235	0.00627	0.0020
0.00101	0.0134	259	0.0225	0.0010
<u>[Re3AP], (M)</u>	<u>[C17], (M)</u>	<u>Inj T.</u>	<u>Area 3AP/ Area C17</u>	<u>[3AP], (M)</u>
0.0076	0.0166	230	0.153	0.0091
0.00135	0.0115	235	0.0352	0.0015
0.00104	0.0134	250	0.0286	0.0014
<u>[Re4AP], (M)</u>	<u>[C17], (M)</u>	<u>Inj T.</u>	<u>Area 4AP/ Area C17</u>	<u>[4AP], (M)</u>
0.00997	0.00525	145	0.234	0.0038
0.00997	0.00525	190	0.450	0.0072
0.00997	0.00525	200	0.984	0.016
0.00997	0.00525	210	1.019	0.016
0.01820	0.0115	235	0.063	0.022
<u>[Re2BP], (M)</u>	<u>[C16], (M)</u>	<u>Inj T.</u>	<u>Area 2BP/ Area C16</u>	<u>[2BP], (M)</u>
0.00124	0.0111	235	0.0347	0.00092
<u>[Re3BP], (M)</u>	<u>[C17], (M)</u>	<u>Inj T.</u>	<u>Area 3BP/ Area C17</u>	<u>[3BP], (M)</u>
0.00139	0.0104	235	0.0449	0.0012
<u>[Re4BP], (M)</u>	<u>[C17], (M)</u>	<u>Inj T.</u>	<u>Area 4BP/ Area C17</u>	<u>[4BP], (M)</u>
0.000386	0.0104	249	0.0125	0.00033
<u>[Re2VP], (M)</u>	<u>[C17], (M)</u>	<u>Inj T.</u>	<u>Area 2VP/ Area C17</u>	<u>[2VP], (M)</u>
0.00547	0.0166	230	0.0818	0.0030
0.00118	0.0115	235	0.0299	0.00075
0.00089	0.0134	250	0.0399	0.0010
<u>[Re3VP], (M)</u>	<u>[C17], (M)</u>	<u>Inj T.</u>	<u>Area 3VP/ Area C17</u>	<u>[3VP], (M)</u>
0.00429	0.0166	230	0.233	0.0085
<u>[Re4VP], (M)</u>	<u>[C17], (M)</u>	<u>Inj T.</u>	<u>Area 4VP/ Area C17</u>	<u>[4VP], (M)</u>
0.0093	0.0124	140	0.388	0.0096
0.0113	0.0093	140	0.363	0.0093
0.0093	0.0124	180	0.545	0.013
0.0093	0.0124	195	0.868	0.021
0.0113	0.0093	195	0.852	0.022
0.0124	0.0093	208	1.043	0.025
0.0124	0.0093	223	0.983	0.024
0.0124	0.0093	230	1.005	0.024

^aTemperature in °C, benzene solvent, gc Column B at 130°C.

Table 134. Quantum yield data for the ruthenium(II) acetylpyridine complexes.^a

	<u>[RuAP], (M)</u>	<u>[C17], (M)</u>	<u>Area AP/ Area C17</u>
Ru4AP	0.0103	0.0158	0.0
Ru3AP	0.00917	0.0013	0.11
Ru2AP	0.00846	0.00034	0.0

^aacetonitrile solvent, 313 nm, gc Column B at 125°C, [C16]_{act} = 0.00508 M, Area AP/ Area C16 = 0.541, $I_a = 0.018 \text{ El}^{-1}$.

Table 135. Photochemical data for $\text{BrRe}(\text{CO})_3(2\text{VP})_2$.^a

	<u>Area 2AP/ Area C17</u>	<u>Area 2VP/ Area C17</u>	<u>[2VP], (M)</u>	<u>ϕ_{-K}</u>
Re2VP-1	0	1.366	0.00341	0.51 ^b
Re2VP-2	0	1.745	0.00436	0.051 ^c
sensRe2VP-1	0	1.681	0.00420	0.31 ^b
sensRe2VP-2	0	1.163	0.00290	0.075 ^c

^abenzene solvent, 313 nm, gc Column B at 125°C, sens = acetophenone @ 0.0494 M, [Re2VP] = 0.00697 M, [Re2VP]_{sens} = 0.00586 M, [C17] = 0.00114 M, [C16]_{act} = 0.00538 M. ^bArea AP/ Area C16 = 0.475, $I_a = 0.017 \text{ El}^{-1}$. ^cArea AP/ Area C16 = 3.63, $I_a = 0.13 \text{ El}^{-1}$. UV(benzene) 465 nm (ϵ 3945 $\text{M}^{-1}\text{cm}^{-1}$) 277 nm (ϵ 15208 $\text{M}^{-1}\text{cm}^{-1}$), $\epsilon_{313\text{nm}} = 6126 \text{ M}^{-1}\text{cm}^{-1}$.

Table 136. Photochemical data for $\text{BrRe}(\text{CO})_3(3\text{VP})_2$.^a

	<u>Area 3AP/ Area C17</u>	<u>Area 3VP/ Area C17</u>	<u>[3VP], (M)</u>	<u>ϕ_{-K}</u>
Re3VP-1	0	2.19	0.00823	0.072 ^b
Re3VP-2	0	4.51	0.0169	0.14 ^c
sensRe3VP-1	0	3.23	0.0121	0.046 ^b
sensRe3VP-2	0	4.27	0.0160	0.18 ^c

^abenzene solvent, 313 nm, gc Column B at 130°C, sens = acetophenone @ 0.0488 M, [Re3VP] = 0.00936 M, [Re3VP]_{sens} = 0.00938 M, [C17] = 0.00170 M, [C16]_{act} = 0.00567. ^bArea AP/ Area C16 = 0.36, $I_a = 0.14 \text{ El}^{-1}$. ^cArea AP/ Area C16 = 3.901. UV(benzene) sh ~ 300 nm (ϵ 7999 $\text{M}^{-1}\text{cm}^{-1}$) 276 nm (ϵ 10250 $\text{M}^{-1}\text{cm}^{-1}$), $\epsilon_{313\text{nm}} = 7422 \text{ M}^{-1}\text{cm}^{-1}$.

Table 137. Photochemical data for $\text{BrRe}(\text{CO})_3(4\text{VP})_2$ and $\text{BrRe}(\text{CO})_3(4\text{AP})_2$.^a

	Area 4AP/ Area C17	Area 4VP/ Area C21	ϕ_{-K}
Re4AP ^b	4.58	-	0.0725
Re4VP	0.0	1.22	0.0101

	Area 4AP/ Area C17	Area 4VP/ Area C21	[4VP], (M)	ϕ_{-K}
Re4VP-1 ^c	0	7.40	0.020	0.0 ^d
Re4VP-2	0	5.59	0.015	0.029 ^e
sensRe4VP-1	0	7.50	0.020	0.0 ^d
sensRe4VP-2	0	4.89	0.013	0.035 ^e

^abenzene solvent, 313 nm, gc Column B at 120°C. ^b[Re4AP] = 0.0108 M, [Re4VP] = 0.0100 M, [C17] = 0.00115 M, [C21] = 0.006; M, [C16]_{act} = 0.00523 M, Area AP/ Area C16 = 2.154, $I_a = 0.075 \text{ El}^{-1}$, UV analysis: Re4VP prior to $h\nu$ (benzene) 272 nm ($\epsilon 14060 \text{ M}^{-1}\text{cm}^{-1}$) 342 nm ($\epsilon 9726 \text{ M}^{-1}\text{cm}^{-1}$); Re4VP after 8 hr. $h\nu$ (benzene) 272 nm ($\epsilon 14590 \text{ M}^{-1}\text{cm}^{-1}$) 340 nm broad ($\epsilon 8030 \text{ M}^{-1}\text{cm}^{-1}$). ^csens = acetophenone @ 0.0431 M, [Re4VP] = 0.00997 M, [Re4VP]_{sens} = 0.0101 M, [C17] = 0.000975 M, [C21] = 0.00103 M, [C16]_{act} = 0.00543 M. ^dArea AP/ Area C16 = 0.683, $I_a = 0.0243 \text{ El}^{-1}$. ^eArea AP/ Area C16 = 4.93, $I_a = 0.18 \text{ El}^{-1}$ UV after $h\nu$ 276 nm ($\epsilon 9550 \text{ M}^{-1}\text{cm}^{-1}$) 343 nm ($\epsilon 8335 \text{ M}^{-1}\text{cm}^{-1}$).

Table 138. Data for the sensitized isomerization of cis-1,3-pentadiene by $\text{BrRe}(\text{CO})_3(\text{pyridine})_2$.^a

<u>[c-P], (M)</u>	<u>[t-P], (M)</u>	<u>β</u>	<u>$\phi_{c \rightarrow t}$</u>
0.4027	0.0024	0.00574	0.025
0.5033	0.0022	0.00439	0.023
0.6644	0.0030	0.00458	0.032
1.007	0.0027	0.00276	0.029
0.755 (AP)	0.0491	0.0660	-

^abenzene solvent, 313 nm, [Repy] = 0.000488 M, [AP] = 0.103 M, gc Column C at 50°C.

Table 139. Data for the sensitized isomerization of trans-stilbene by $\text{BrRe}(\text{CO})_3(\text{pyridine})_2$.^a

<u>[t-S], (M)</u>	<u>[c-S], (M)</u>	<u>Area t-S/ Area Cl8^b</u>	<u>Area c-S/ Area Cl8</u>	<u>t c</u>
0.0080	0.0000599	1.532 (0.0035)	0.0175	0.0058
0.0100	0.0000972	1.565 (0.0044)	0.0156	0.0092
0.0199	0.0001655	1.562 (0.0088)	0.0134	0.016
0.0399	0.000360	1.604 (0.0177)	0.0146	0.086
1.0155 (BP)	0.0753	-	-	-

^abenzene solvent, 366 nm, [Repy] = 0.000488 M, [BP] = 0.103 M, gc Column C. ^bNumbers in parenthesis are [Cl8].

Table 140. Data for the sensitized isomerization of cis-1,3-pentadiene by $\text{BrRe}(\text{CO})_3[1-(3\text{-pyridyl})\text{pentanone}]_2$.^a

<u>[c-P], (M)</u>	<u>[t-P], (M)</u>	<u>β</u>	<u>$\phi_{c \rightarrow t}$</u>
0.410 ^b	0.0095	0.0238	0.36
0.501	0.0111	0.0220	0.42
0.661	0.0136	0.0206	0.51
1.00	0.0107	0.0107	0.40
0.751 (AP)	0.0165	0.0195	-
0.402	0.0073	0.0181	0.32
0.503	0.0073	0.0145	0.32
0.664	0.0078	0.0118	0.34
1.00	0.0097	0.00964	0.42
c: 1.01 (AP)	0.0143	0.0121	-

^abenzene solvent, 313 nm, gc Column C. ^b[Re3VP] = 0.000254 M, [AP] = 0.0973 M. ^c[Re3VP] = 0.00026 M, [AP] = 0.105 M.

Table 141. Data for the sensitized isomerization of cis-1,3-pentadiene by $\text{BrRe}(\text{CO})_3[1-(2\text{-pyridyl})\text{pentanone}]_2$.^a

<u>[c-P], (M)</u>	<u>[t-P], (M)</u>	<u>β</u>	<u>$\phi_{c \rightarrow t}$</u>
0.492	0.0011	0.00275	0.0044
0.504	0.0013	0.00253	0.0061
0.684	0.0025	0.00310	0.0085
1.01	0.0027	0.00260	0.011
0.805 (BP)	0.531	0.148	-

^abenzene solvent, 313 nm, [Re2VP] = 0.00278 M, [BP] = 0.120, gc Column C.

Table 142. Data for the sensitized isomerization of trans-stilbene by $\text{BrRe}(\text{CO})_3[1-(3\text{-pyridyl})\text{pentanone}]_2$.^a

$[\underline{t}\text{-S}], (\text{M})$	$[\underline{c}\text{-S}], (\text{M})$	Area $\underline{t}\text{-S}/$ Area C18	Area $\underline{c}\text{-S}/$ Area C18	$\phi_{\underline{t} \rightarrow \underline{c}}$
0.0083	0.000236	1.445 (0.0039)	0.0471	1.99
0.0104	0.000273	1.492 (0.0049)	0.0403	1.72
0.0207	0.000335	1.505 (0.0097)	0.0246	1.42
0.0414	0.000463	1.515 (0.0194)	0.0170	1.04

^abenzene solvent, 366 nm, $[\text{Re3VP}] = 0.00165 \text{ M}$, $[\text{BP}] = 1.1016 \text{ M}$,
gc Column D. ^bNumbers in parenthesis are [C18].

Table 143. Data for the sensitized isomerization of cis-1,3-pentadiene by $\text{BrRe}(\text{CO})_3[1-(4\text{-pyridyl})\text{pentanone}]_2$.^a

$[\underline{c}\text{-P}], (\text{M})$	$[\underline{t}\text{-P}], (\text{M})$	β	$\phi_{\underline{t} \rightarrow \underline{c}}$
0.401 ^b	0.0086	0.0214	0.77
0.501	0.0088	0.0176	0.78
1.002	0.0099	0.00987	0.88
0.751 (AP)	0.0062	0.00822	-
0.401 ^c	0.0046	0.0116	0.58
0.501	0.0050	0.0100	0.62
0.661	0.0064	0.00963	0.80
1.002	0.0090	0.00904	1.1
1.002 (AP)	0.0039	0.00440	-
0.0080 ^d	0.001	0.0547	0.0016
0.0160	0.0005	0.0429	0.0025
0.0240	0.0009	0.0367	0.0032
0.0399	0.0017	0.0265	0.0041
0.998	0.0546	0.00981	0.028
0.09669 (AP1)	0.0129	0.153	-
0.998 (AP2)	0.0054	0.00561	-

^abenzene solvent, 313 nm, gc Column C. ^b $[\text{Re4VP}] = 0.000385 \text{ M}$, $[\text{AP}] = 0.104 \text{ M}$. ^c $[\text{Re4VP}] = 0.000361 \text{ M}$, $[\text{AP}] = 0.0978 \text{ M}$. ^d $[\text{Re4VP}] = 0.000266 \text{ M}$, $[\text{AP1}] = 0.104 \text{ M}$, $[\text{AP2}] = 0.0969 \text{ M}$.

Table 144. Data for the sensitized isomerization of trans-stilbene by $\text{BrRe}(\text{CO})_3[1-(4\text{-pyridyl})\text{pentanone}]_2$.^a

$[\underline{t}\text{-S}], (\text{M})$	$[\underline{c}\text{-S}], (\text{M})$	Area $\underline{t}\text{-S}/\text{Area Cl8}$ ^b	Area $\underline{c}\text{-S}/\text{Area Cl8}$	$\phi_{\underline{t}\rightarrow\underline{c}}$
0.00799 ^c	0.000388	-	-	0.66
0.00999	0.000411	-	-	0.70
0.0199	0.000682	-	-	1.16
0.0399	0.000197	-	-	1.26
0.202 (BP)	0.000249	-	-	-
0.008 ^d	0.000357	1.644 (0.0034)	0.0768	0.67
0.020	0.000390	1.68 (0.0085)	0.0334	0.68
0.040	0.000482	1.73 (0.0169)	0.0212	0.84
0.0507 (BP)	0.000531	-	-	-

^abenzene solvent, 366 nm, gc Column D. ^b() = [Cl8]. ^c[Re4VP] = 0.00361 M, [BP] = 0.995 M. ^d[Re4VP] = 0.0038 M, [BP] = 1.003 M.

Table 145. Data for the sensitized isomerization of cis-1,3-pentadiene by $\text{BrRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$.^a

$[\underline{c}\text{-P}], (\text{M})$	$[\underline{t}\text{-P}], (\text{M})$	β	$\phi_{\underline{c}\rightarrow\underline{t}}$
0.399	0.0080	0.0203	0.41
0.499	0.0091	0.0182	0.47
0.993	0.0111	0.0139	0.69
0.749 (AP)	0.0111	0.0148	-

^abenzene solvent, 313 nm, gc Column C, [Re3benzpy] = 0.000346 M, [AP] = 0.111 M.

Table 146. Data for the sensitized isomerization of trans-stilbene by $\text{BrRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$.^a

$[\underline{t}\text{-S}], (\text{M})$	$[\underline{c}\text{-S}], (\text{M})$	Area $\underline{t}\text{-S}/\text{Area Cl8}$	Area $\underline{c}\text{-S}/\text{Area Cl8}$	$\phi_{\underline{t}\rightarrow\underline{c}}$
0.0081	0.000243	1.634 (0.0038)	0.0487	0.33
0.0102	0.000247	1.622 (0.0047)	0.0373	0.35
0.0203	0.000284	1.589 (0.0095)	0.0214	0.41
0.0406	0.000356	1.592 (0.0135)	0.0135	0.51
0.0504 (BP)	0.000273	-	-	-

^abenzene solvent, 366 nm, [Rebenzpy] = 0.0122 M, [BP] = 1.002 M, gc Column D. ^bNumbers in parenthesis refer to [Cl8].