ABSTRACT

PART I

THE EFFICIENCY OF TRIPLET ENERGY TRANSFER FROM KETONES TO RARE EARTH IONS

By

Herbert Nick Schott

The Norrish Type II reaction of p-methoxyvalerophenone, which is known to react only from its triplet state, has been used as a monitoring tool to determine whether the rate of energy transfer from ketone triplets to rare earth ions in solution is really diffusion controlled as had been assumed previously.

Samples, made from methanol solutions containing p-methoxyvalerophenone and various concentrations of the following rare earth ions, Eu^{+3}, Sm^{+3}, Dy^{+3}, Er^{+3}, and Tb^{+3}, were irradiated at 3130 Å. The rate constants, k_q, for quenching of product formation, as determined by Stern-Volmer kinetics, for the lanthanide ions, were compared to the rate constant for quenching by naphthalene. Since naphthalene is known to quench triplet state reactions at near the diffusion controlled rate, the comparison between the quenching constant for each individual rare earth ion and the quenching constant for naphthalene was a good indicator of the efficiency of ketone-rare earth ion energy transfer. The results

indicated that energy transfer from ketone triplets to rare earth ions is approximately two orders of magnitude slower than the diffusion controlled rate.

PART II

THE NATURE OF THE PHOTOREACTIVE STATE IN P-METHOXYPHENYL ALKYL KETONES

Ketones possessing lowest π-π^* triplet states are generally unreactive in hydrogen abstraction reactions. However, the p-methoxyphenyl alkyl ketones, whose two triplet states are very close together, with the π-π^* state just below the n-π^* one, do undergo the Norrish Type II reaction, although the reactivity of these ketones is less than that of the unsubstituted phenyl alkyl ketones which possess a lowest n-π^* triplet state.

There are two possibilities as to what the nature of the reactive state in the p-methoxy ketones is. It can be either the lowest π-π^* state with enough n-π^* character mixed in it due to vibronic coupling to make it reactive, or it can be the upper n-π^* triplet, which is known to be the reactive state in the phenyl alkyl ketones.

In order to distinguish between these two possibilities, several anisyl ketones with electron-withdrawing groups near the γ carbon atom were synthesized. It was expected that the behavior of the two types of triplets towards the hydrogens on the γ carbon of these ketones should be quite different.

The n-π* triplet of ketones was known to be an electrophilic species and therefore its reactivity in abstracting a hydrogen from a carbon near an electron-withdrawing group should be subject to quite strong inductive effects. The π-π* triplet, on the other hand, was expected to be quite nucleophilic, and should be subject to opposite inductive effects. A comparison of the data for the anisyl ketones, as obtained from Stern-Volmer kinetics and quantum yield determinations, with the data for the analogous phenyl alkyl ketones, indicated that the reactive state in these two types of ketones was subject to identical inductive effects. This led to the conclusion that hydrogen abstraction in the p-methoxy ketones was occurring from the upper n-π* triplet state, which is in thermal equilibrium with the lower π-π* state.

If this conclusion is true, the only difference between the observed rate constant, k_r^{obs}, for hydrogen abstraction by the anisyl ketones, and k_r^n, the rate constant for hydrogen abstraction by benzoyl triplets, is due to the lower concentration of reactive n-π* triplets in the p-methoxy ketones. From the magnitude of X_n, the mole fraction of reactive n-π* triplets present in the anisyl ketones, it was calculated that the energy separation between the reactive upper n-π* state and the lower π-π* state is about three kilocalories per mole. This energy separation was found to be dependent on the nature of the solvent, since it increases in going from a non-polar to a polar solvent.

PART I

THE EFFICIENCY OF TRIPLET ENERGY TRANSFER FROM KETONES TO RARE EARTH IONS

PART II

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This thesis is dedicated to my wife, Marie, for her inspiration and encouragement, and to my parents, for their assistance and guidance, during my studies.

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TABLE OF CONTENTS

Page

PART I

THE EFFICIENCY OF TRIPLET ENERGY TRANSFER FROM KETONES TO RARE EARTH IONS

PART II

THE NATURE OF THE PHOTOREACTIVE STATE IN P-METHOXYPHENYL ALKYL KETONES

TABLE OF CONTENTS (Continued)

LIST OF TABLES

TABLE Page

TABLE Page

LIST OF FIGURES

PART I

THE EFFICIENCY OF TRIPLET ENERGY TRANSFER FROM KETONES TO RARE EARTH IONS

I. INTRODUCTION

In 1942 S. I. Weissman[1] published his classic paper on the transfer of excitation energy from the ligands of several europium chelates to the metal ion with subsequent emission from the ion. At that time it was known that the solvated lanthanide ions in solution usually exist in the tripositive state and absorb and emit light only weakly. However, since the ions readily coordinate with many chelating agents whose ligands strongly absorb light above 3000 Å, this provided a convenient means of introducing energy into the ion.

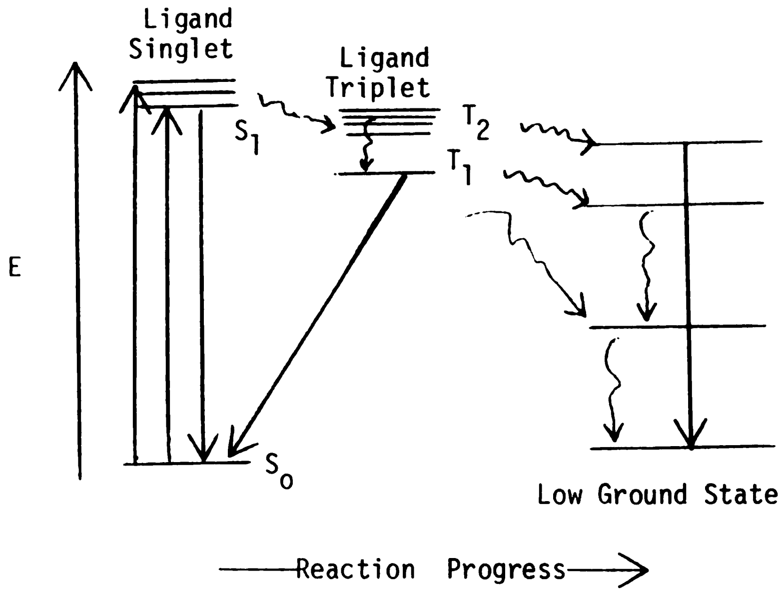
Weissman's initial work and Sevchenko[2] et al.'s later investigation of these systems did not cause any real waves in the sea of chemistry for about twenty years until the renaissance of rare earth ion photochemistry occurred. This period of rediscovery was stimulated by a growing interest in the use of rare earth ions and chelates as possible laser materials and the subsequent willingness of several government agencies and private corporations to fund research in this area.

The rare earth ions[3] owe their possible lasing action to their position in the periodic table. They comprise a group of 15 elements that form a f-type inner transition series in which the 4f level falls below that of the 5d level in energy and is consequently filled first.

The $4f^7$ and $4f^{14}$ electron arrangement in this series is reached as soon as possible due to the stability associated with the complete single ($4f^7$) or complete double ($4f^{14}$) occupancy of any set of orbitals. This entails the transfer of the single $5d^1$ electron that is present at the beginning (Lanthanum, Z = 58, $4f^0$, $5d^1$), middle (Gadolinium, Z = 64, $4f^7$, $5d^1$, $6s^2$) and end (Lutetium, Z = 71, $4f^{14}$, $5d^1$, $6s^2$) of the series into a lower f-orbital during the buildup of the series. According to Hund's Rule then, a maximum of seven unpaired electrons is reached in europium (Z = 63, $4f^7$, $6s^2$) which in the tripositive state will have 6 unpaired electrons[3].

As expected, the ions which have the closed f-orbital configurations, La^{+3} and Lu^{+3} ($4f^0$ and $4f^{14}$ respectively), and Gd^{+3} with its $4f^7$ complete single occupancy configuration, have no electronic transition in the visible or infrared and on excitation of their chelates, show predominantly ligand phosphorescence only[4,5]. However, the ions which have unfilled 4f orbitals can have a lower lying electron excited to a higher level, and if this happens to be a resonance level, line emission corresponding to a transition from that level to a lower 4f level occurs. This process is represented schematically below, where solid lines represent radiative transitions and wavy lines represent radiationless transitions.

FIGURE 1. Schematic Energy Level Diagram for a Rare Earth Chelate Possessing Low-lying 4f Electronic States.

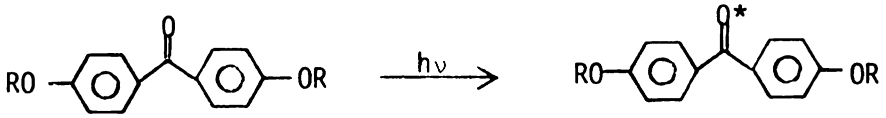


Early work by Crosby and Whan[6] and Bhaumik and El-Sayed[7] demonstrated clearly that triplet energy transfer occurs from the excited ligand to the metal ion. Crosby, Whan and Alire[8] found that the lowest triplet state energy level of the complex must equal or lie above the resonance energy level of the rare earth ion for emission to occur. In particular, for Eu^{+3} ions, which fluoresce strongly from two well-established resonance levels[7], selective excitation of the lower level occurs in chelates whose ligand triplet states lie between the two Eu^{+3} resonance levels. El-Sayed and Bhaumik[10] showed that the ligand-induced rare earth ion fluorescence could be sensitized by such triplet sensitizers as benzophenone, and quenched by piperylene or naphthalene[11]. They assumed that such energy transfer occurred at the diffusion controlled rate. Furthermore, Matsuda and coworkers[12] have shown that the phosphorescence of lanthanum dibenzoylmethide can be quenched by europium dibenzoylmethide but not by europium ions. In this case the phosphorescence of the lanthanum chelate is due solely to the ligand triplet to ligand ground state transition and thus involves only triplet energy.

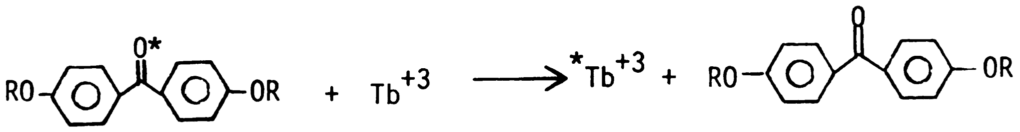
Despite various attempts to enhance the fluorescence yields of chelated rare earth ions by the addition of Lewis bases[13], change of ligands[14,15] use of substituted ligands[14,15], having two different ions bound to the same ligand[17], and addition of extraneous inorganic ions[18], energy transfer from ligand to ion has several disadvantages. Notable among these are photodisassociation of the chelate to produce ligand negative ions which can phosphoresce[19], the inability to choose the most efficient solvent and sensitizer combination, and the inherent inefficiency of energy transfer between ligand and ion, as manifested in ligand phosphorescence in many instances[20].

This inefficiency, and the possible utility of energy transfer to rare earth ions as an analytical tool[21] has led to the investigation of intermolecular energy transfer to unchelated rare earth ions. Matovich and Suzuki[22] reported the initial triplet energy transfer from excited ketones to rare earth ions. Irradiation of $EuCl_3$ in neat acetophenone, propiophenone and molten benzophenone at 3660 Å where only the ketones absorb produced the characteristic red emission of europium. Heller and Wasserman[23] have measured energy transfer from simple aromatic aldehydes and ketones to europium and terbium ions by monitoring the intensity of emission of the ions. They noted a decrease in fluorescence intensity in going from acetic to decanoic acid and attributed this to a lower rate of diffusion in the more viscous solvent. Ballard and Edwards[24], in measuring triplet energy transfer from acetophenone to various lanthanide nitrates as a function of lanthanide concentration assumed a diffusion limited value as the rate constant for energy transfer. Filipescu and Mushrush[25] tried to sensitize Eu^{+3} and Tb^{+3} emission with a large series of organic compounds in dimethylformamide. This series included compounds having triplet energies both above and below the rare earth ion acceptors. However, sensitization occurred only with donors having both a higher triplet energy than the ions and a large $S^* \rightarrow T^*$ intersystem crossing yield. From viscosity measurements they assumed that diffusion controlled energy transfer occurred and suggested that oxygen impurity quenching was responsible for the short ketone lifetimes obtained by using these diffusion rate constants.

The transfer of energy between ketones and rare earth ions can also be realized by utilizing other lanthanide ions as intermediates in the transferring process. Terbium is particularly useful and has been used to transfer energy from 4,4'-dimethoxybenzophenone to Eu^{+3} in acetic anhydride[26].



(1)



(2)

$$^{*}Tb^{+3} + Eu^{+3} \rightarrow {}^{*}Eu^{+3} + Tb^{+3} \qquad (3)$$

$$^{*}Eu^{+3} \rightarrow Eu^{+3} + h\nu \qquad (4)$$

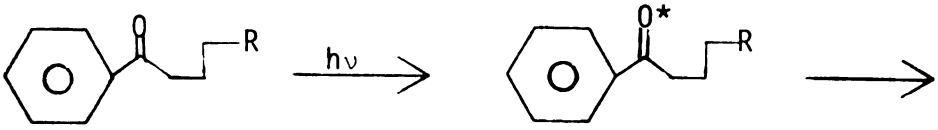
Since different ketone triplets show remarkable selectivity in energy transfer efficiency to lanthanide ions, even though such transfer may be highly exothermic, this can be used as a means of sensitizing ions which are not sensitized directly by certain ketones.

In all the above cases of ketone - rare earth ion energy transfer, it was assumed that the rate constant for energy transfer was diffusion controlled. This assumption is not altogether unreasonable since most reported cases of exothermic energy transfer between two organic molecules proceed at nearly the diffusion controlled rate in solution[27]. However, in the studies with the lanthanide ions, the competing chemical reactions of donor triplets, the effect of changing solvents, and the inability to measure emission intensities accurately have been largely ignored. Consequently the factors influencing energy transfer rates are not well known and it still remains to be determined whether energy transfer does actually occur at a diffusion controlled rate.

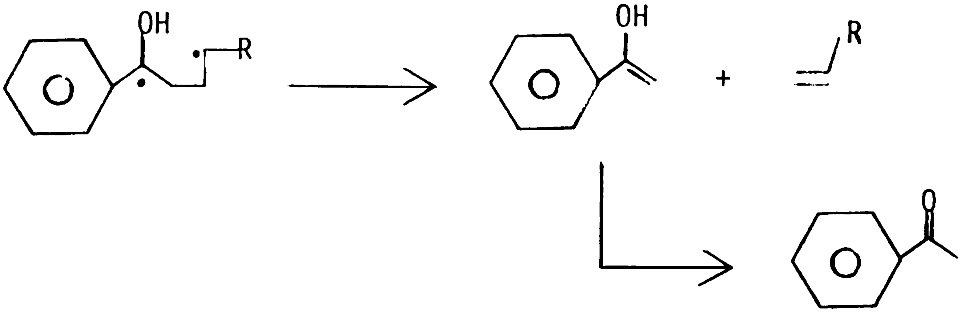
The method chosen to determine the actual efficiency of the energy transfer process was to simply monitor the quantum yields of some photochemical reaction of triplet ketones as a function of rare earth ion concentration. Standard Stern-Volmer plots of quantum yield ratios versus rare earth ion concentration will yield the ratio of rates for energy transfer to chemical reaction. By comparing the slopes, $k_q \tau$, obtained by the addition of the various lanthanide salts, to the slope

$k'_q\,\tau$, obtained by using a known diffusion controlled quencher such as a 2,4-hexadiene or naphthalene, it is possible to obtain a direct comparison of the energy transfer efficiency of ketones to rare earth ions versus ketones to other organic triplet quenchers. This method has been used successfully by Hammond and Foss to measure quenching rates of triplet benzophenone by transition metal chelates[28].

The reaction chosen in this case was the Norrish Type II elimination of phenyl alkyl ketones which is known to proceed strictly from the triplet state[29].



(5)



(6)

However, other photochemical monitors such as photoreduction or photocycloaddition to olefins could also have been used.

II. RESULTS AND DISCUSSION

The Type II reaction[30] of a phenyl alkyl ketone, K, is initiated by the absorption of light of suitable wavelength resulting in excitation to higher singlet levels. After rapid internal conversion to the lowest excited singlet state (10^{12} sec.$^{-1}$ in solution), intersystem crossing to the triplet manifold occurs with unit efficiency. The triplet ketone that is formed has three possible modes of reaction available to it:

a) It can abstract a hydrogen from the gamma carbon to form a biradical intermediate, BR.

b) It may undergo radiationless decay to the ground state, and

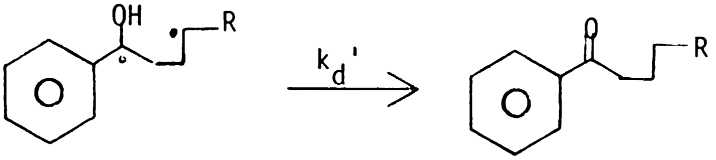
c) A transfer of triplet energy to an acceptor molecule may occur. This yields ground state ketone and an excited triplet quencher molecule.

The reaction sequence under consideration and the rate for each of the various processes is the following:

$$\begin{array}{lll r}
 & & \text{Rate} & \\
K + h\nu & \longrightarrow \ {}^{1}K^{*} & I_a & (7) \\
{}^{1}K^{*} & \xrightarrow{k_{isc}} \ {}^{3}K^{*} & k_{isc}\,({}^{1}K^{*}) & (8) \\
{}^{3}K^{*} & \xrightarrow{k_r} \ BR & k_r\,({}^{3}K^{*}) & (9) \\
{}^{3}K^{*} & \xrightarrow{k_d} \ K & k_d\,({}^{3}K^{*}) & (10) \\
{}^{3}K^{*} + Q & \xrightarrow{k_q} \ K + {}^{3}Q^{*} & k_q\,(Q)({}^{3}K^{*}) & (11)
\end{array}$$

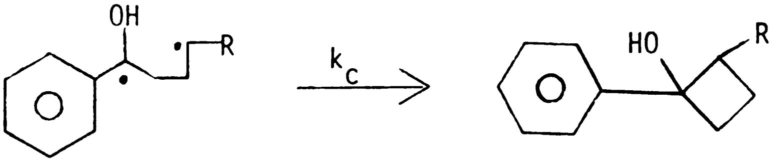
The biradical intermediate that is formed has three reaction pathways available to it also:

a) It can disproportionate back to ground state ketone by retransferring the hydrogen on the oxygen to the gamma carbon.



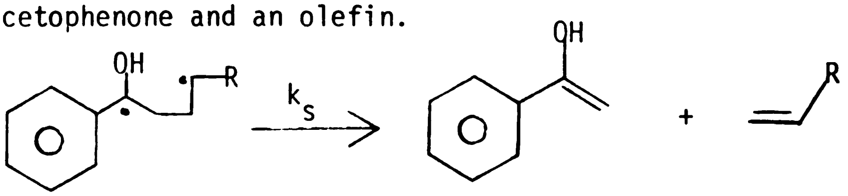
(12)

b) Coupling can occur between the two radical sites to form a cyclobutanol.



(13)

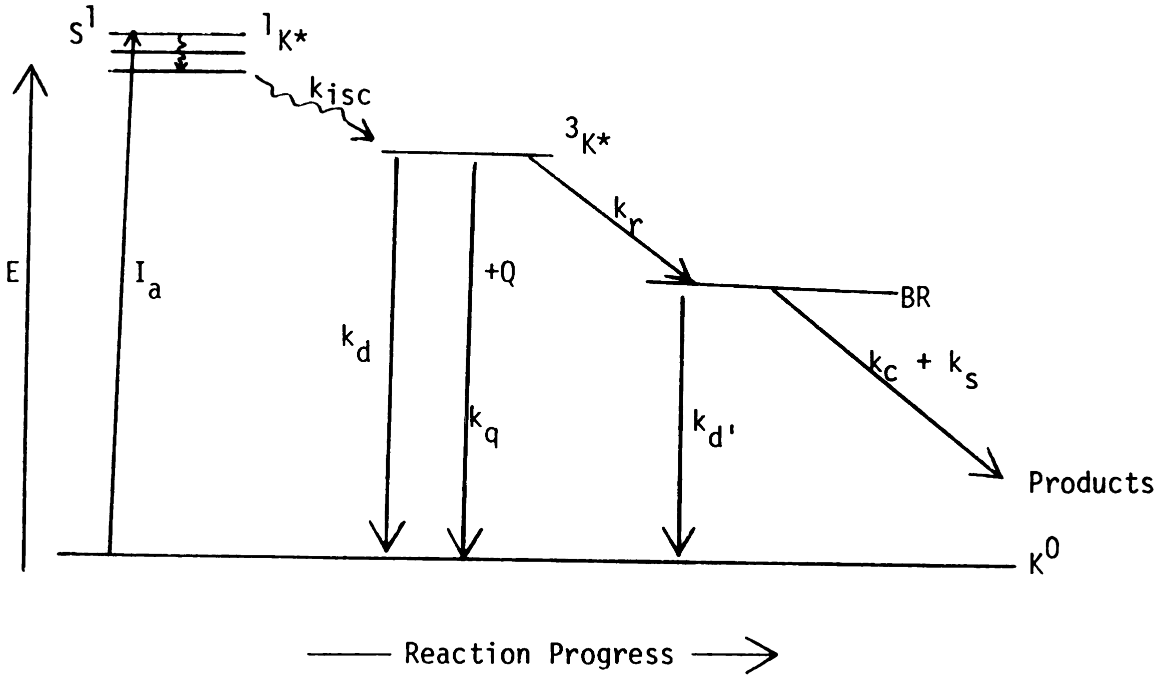
c) The biradical can cleave to yield the enol form of an acetophenone and an olefin.



(14)

Schematically, the whole process may represented as follows:

FIGURE 2. Modified Jablonski Diagram
for Phenyl Alkyl Ketones



The quantum yield of acetophenone formation, Φ_A, is defined[31] as

$$\Phi_A = \frac{\text{The number of molecules of acetophenone formed}}{\text{The number of quanta absorbed by the reacting ketone}}$$

This quantum yield is the mathematical product of the probabilities of each of the individual steps in the reaction sequence occuring[32]. Hence for the Type II reaction,

$$\Phi_A = \phi_{isc}\Phi_{BR}\Phi_P \tag{16}$$

Where ϕ_{isc} is the probability of intersystem crossing from singlet to triplet ketone, (which equals unity in these ketones[29]), Φ_{BR} is the probability of biradical formation from triplet ketone, and Φ_P is the probability that the biradical once formed will go on to desired product. The quantum yield can also be expressed in terms of the various rate constants of the overall process by assuming that steady state conditions exist during the course of the photolysis. The steady-state assumption simply implies that the triplets and the biradical intermediates that are formed are highly transient species and do not remain in solution long enough to build up to any appreciable concentration. The expressions obtained for Φ_A either in the presence and absence of quencher are:

$$\Phi_A = \frac{k_r k_s \Phi_{isc}}{(k_d + k_q(Q) + k_r)(k_c + k_s + k_d')} \quad \text{(with quencher)} \qquad (17)$$

and

$$\Phi_A^o = \frac{k_r k_s \Phi_{isc}}{(k_d + k_r)(k_s + k_c + k_d')} \quad \text{(without quencher)} \qquad (18)$$

If the ratio of the quantum yield without quencher to the quantum yield with quencher is taken, the familiar Stern-Volmer expression is obtained.

$$\frac{\Phi_A^o}{\Phi_A} = \frac{k_d + k_q(Q) + k_r}{k_d + k_r} \qquad (19)$$

$$= 1 + \frac{k_q(Q)}{k_d + k_r} \qquad (20)$$

which can be rewritten as

$$\frac{\Phi_A^o}{\Phi_A} = 1 + k_q(Q)\,\tau \qquad (21)$$

where τ, the lifetime of the triplet state is defined as

$$\tau = \frac{1}{k_d + k_r} \qquad (22)$$

A plot of Φ_A^o/Φ_A versus quencher concentration will have an intercept of one and a slope of $k_q\,\tau$. The numerical value of τ is obtained by substituting the values of the diffusion controlled rate constant and the slope of the plot (using naphthalene or diene as a quencher) into the expression

$$\tau = \frac{\text{slope}}{k_q^{\text{diff}}} \qquad (23)$$

Once the value of τ is known and the quenching slopes for the various lanthanide ions are obtained, it will be simple to calculate the bimolecular quenching constants for each ion from the expression

$$k_q = \frac{\text{slope}}{\tau} \qquad (24)$$

which will be a direct indication of the efficiency of the energy transfer process.

The ketone chosen for this study was p-methoxyvalerophenone (E_T = 73 kcal/mole)[32]. Initial work with p-methoxybutyrophenone in methanol showed that several side reactions occurred with the solvent during the photolysis which prevented quantitative analysis of the p-methoxyacetophenone that is formed. It was desirable to utilize a methoxy ketone since it is known that their triplet states have long lifetimes compared to unsubstituted ketones[29]. Less error should occur in the quenching slopes of long lived ketone triplets since they are more sensitive to a relatively inefficient quencher than ketones whose triplets are short-lived and quenched only with difficulty. The diffusion controlled quencher that was used for comparison with the lanthanide ions was naphthalene, whose $k_q = 4.7 \pm .4 \times 10^9 M^{-1} sec^{-1}$ for quenching ketone triplets in benzene[33], since it was found that 2,4-dimethyl-2,5-hexadiene is somewhat photolabile in alcoholic solution.

A. Quenching Studies

Degassed methanol solutions containing .1 M ketone, 4×10^{-3} M octadecane and various concentrations of quenchers were photolyzed at 3130 Å or at 3660 Å and the amount of p-methoxyacetophenone formed was determined by vapor phase chromatography.

Table I gives the $k_q \tau$ values obtained from quenching runs with naphthalene and several representative rare earth ions. The τ and k_q values were calculated from equations (23) and (24) respectively.

The k_q value assumed for the bimolecular quenching rate constant of a triplet ketone by naphthalene in methanol is $7.5 \times 10^9 M^{-1} sec^{-1}$ which is near the diffusion controlled limit[27]. The rare earth ions, however, are only 1/30 to 1/200 as effective as energy acceptors and their k_q values are two orders of magnitude smaller than those for organic quenchers. Similar results have been obtained in quenching the

TABLE 1. Quenching of Triplet p-Methoxyacetophenone by Naphthalene and Lanthanide Chlorides.

Quencher	$k_q\tau$, M^{-1}[a]	τ ($\times 10^6$) sec	k_q (M^{-1} sec^{-1})
Naphthalene	13,050 ± 50	1.73	7.5×10^9
$EuCl_3$	325 ± 75	1.73	1.9×10^8
$SmCl_3 \cdot 6H_2O$[b]	48 ± 3	1.73	2.9×10^7
$TbCl_3 \cdot 6H_2O$	56 ± 6	1.73	3.2×10^7
$DyCl_3 \cdot 6H_2O$	53 ± 4	1.73	3.1×10^7
$ErCl_3 \cdot 6H_2O$	90 ± 20	1.73	5.2×10^7

[a] The $k_q\tau$ values given are the average of two runs, the precision shown is that between the two runs; [b] Only one run, precision shown is that for drawing slope.

photoreduction of benzophenone (E_T = 69 kcal/mole) in aqueous acetic acid - dimethoxyethane solution[34].

These results indicate that other factors, aside from the requirement that it be exothermic, influence the rate of energy transfer from ketone triplets to the lanthanide ions. Nuclear magnetic resonance studies by Heller and Wasserman, and the fact that no shift in ion emission occurs while donors are being varied, have shown that no long-lived ground state complex forms between the ion and the ketone[23]. However, this does not exclude the possibility that the ion and the carbonyl group of the ketone must exist in a special configuration for energy transfer to take place. If this is the case, the actual process of energy transfer may have a significant activation energy or entropy[22]. The bare ions are strongly solvated in protic solvents, and it is very possible that the solvation shell of the ion prevents a close enough approach of the ion and the triplet carbonyl so that the orbital overlap which is necessary for effective exchange interaction to occur never develops sufficiently[35]. It is also possible that the poor or varying spectral overlap between ketone and ions may cause energy transfer to be less than maximum efficient. Heller and Wasserman found that high energy carbonyl compounds such as acetophenone and benzaldehyde, which have their most intense peak below 4500 Å sensitize europium ions much more efficiently than terbium ions, possibly because the high $^5D_2$ (4640 Å) level of europium is more easily populated than the $^5D_4$ level of terbium (5460 Å) due to better spectral overlap[23].

Although this work shows that energy transfer between ketone triplets and lanthanide ions is definitely slower than the diffusion controlled rate, the factors responsible for the inefficieny have not been determined. A systematic study using the anhydrous lanthanide salts in various aprotic solvents with different carbonyl compounds may further elucidate the chemistry of the energy transfer process.

Also of interest is the fact that some of the lanthanide ions undergo chemical reactions during the course of the photolysis. Solutions with relatively high (greater than 10^{-2} M) concentrations of $EuCl_3$ turned yellow and the solutions of erbium and dysprosium deposited pink mirrors on the wall of the photolysis tubes.

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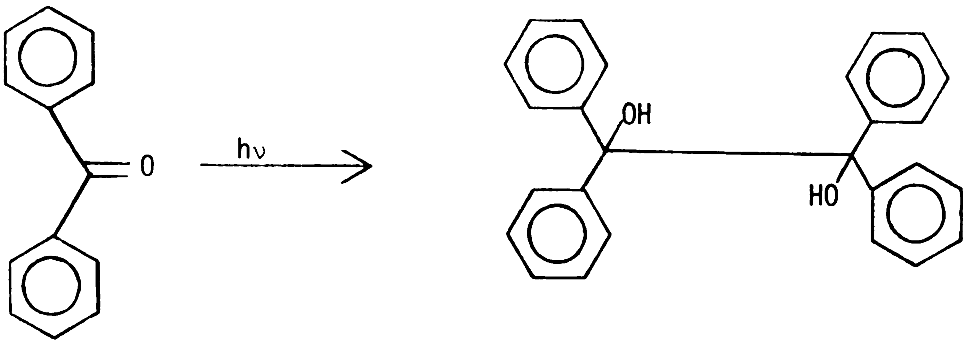
PART II

THE NATURE OF THE PHOTOREACTIVE STATE IN P-METHOXYPHENYL ALKYL KETONES

I. INTRODUCTION

The ability of a photoexcited ketone or aldehyde to abstract a hydrogen atom from good hydrogen donors in the solution phase was first discovered by Ciamician and Silber[1] in 1900 when they found that the action of sunlight on a solution of benzophenone in ethanol produced a good yield of benzpinacol.



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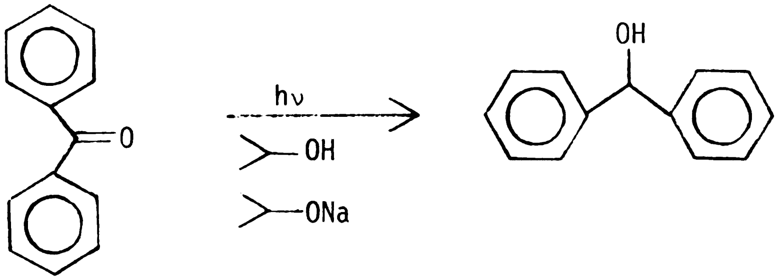
Ciamician and Silber[2,3] found that both aromatic carbonyls and dialkyl ones, such as acetone, could be photoreduced in the presence of alcohol. Cohen[4] extended the work of Ciamician and Silber and found that certain ketones would not photoreduce. These included phenyl-α-naphthyl ketone, Michler's ketone (p,p'-dimethylaminobenzophenone) and p-phenylbenzophenone. These findings were corroberated by the results of Hirshberg and coworkers[5,6] who studied both naphthyl and substituted phenyl ketones and found that neither the naphthyl ketones nor p-methoxypropiophenone or p-phenylbenzophenone yielded pinacols. Pinacol formation is also inhibited if the reaction is carried out in the presence of alkoxides, and hydrols are formed instead[7].



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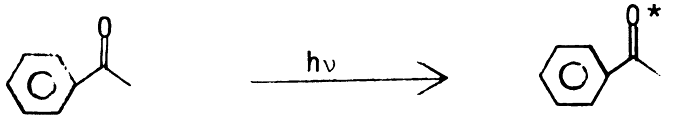
Early mechanistic work on photoreduction dealt mostly with the elucidation of the chemical processes following light absorption rather than the nature of the excited state. Hirshberg[5] found that if acetophenone is photolyzed in the presence of optically active α-phenylethanol, the pinacols formed are optically inactive, but the residual carbinol essentially retains its optical activity. This result implied that very little disproportionation occurred between two donor molecules after initial hydrogen abstraction. Pitts[8], in more quantitative studies twenty years later, confirmed these results by photolyzing benzophenone in the presence of optically active 2-butanol and also found no loss of optical activity in the remaining alcohol. Thus the photoreduction of acetophenone by α-phenylethanol may be represented as:



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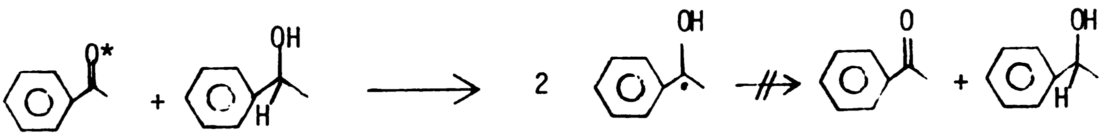

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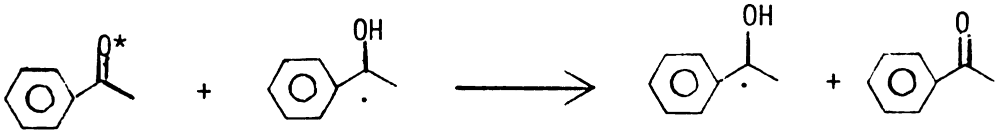
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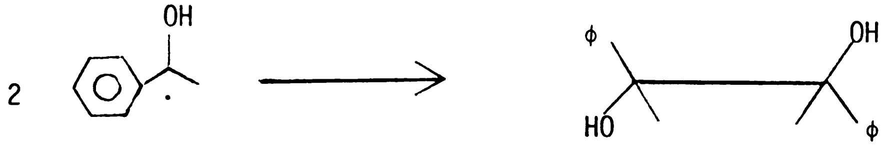
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Credit for the proposal that the excited state of benzophenone can be represented as a biradical in the hydrogen abstraction process should be given to Bäckström[9] who suggested this in 1934, and later indicated that these biradical states could be considered equivalent to triplet states[10]. However, it was not until the late fifties and early sixties that work in several laboratories indicated that the photoreduction of benzophenone did occur exclusively from the triplet state. Bäckström and Sandros[11] were the first to study the transfer of energy from the excited state of benzophenone to various acceptors in solution. Of particular importance was the quenching of excited benzophenone by biacetyl with the concommitant formation of biacetyl phosphorescence[12]. Hammond and coworkers[13] studied the photoreduction of benzophenone by benzhydrol in detail. Analysis of their data indicated that the lifetime of the chemically active state must be so long as to preclude the possibility that it is the singlet state. Quenching by added paramagnetic species supported the assignment of the triplet state as the reactive species. Finally, several groups have quenched the photoreduction of benzophenone with naphthalene which has a higher singlet and a lower triplet energy than benzophenone[14,15,16] and shortly thereafter, the triplets of benzophenone[17] and 2-acetonaphthone[18], among others, were observed and their lifetimes measured directly by flash photolysis.

Since it has been shown that the quantum yield of intersystem crossing for most aromatic carbonyls is unity[19,20], and that the rate of intersystem crossing is extremely rapid ($>10^{10}$ sec^{-1})[21,22] it can be safely assumed that in general aryl ketones will yield only products that are derived from their excited triplet states.

One of the major problems, which has stymied research workers for almost a decade now, arises from the fact that, *a priori* , there are two triplets that can react in aryl ketones. These are the n,π^* triplet of the carbonyl group, which is known to be the reactive state in dialkyl ketones, and the π,π^* triplet state that arises from the π electrons of the aryl ring, and which is generally believed to be unreactive. Which triplet state is lowest can be determined from the phosphorescence lifetime at 77°K. If the lifetime is long (on the order of 10^{-1} to one second) the lowest state is π-π^* in nature, and if the lifetime is short (less than 10^{-2} second), the lowest triplet is of the n-π^* type[23]. Most of the early work dealt with the relationship between photochemical reactivity and the nature of the lowest triplet.

As mentioned above, reports in the early literature[5,6,7] indicated that naphthyl ketones and ketones possessing electron donating ring substituents usually fail to photopinacolize. Pitts and coworkers[24,25] reinvestigated the photoreduction of several p-amino benzophenones in isopropanol and found that no product formation occurred after twenty-four hours of irradiation, while p-phenylbenzophenone reacted only one tenth as efficiently as benzophenone. Similar results were reported by Beckett and Porter[26] in their study of p-hydroxybenzophenones.

Hammond and Leermakers[27] reinvestigated the photoreduction of 1-naphthaldehyde and 2-acetonaphthone and found that these compounds, unlike benzophenone, were not photoreduced by secondary alcohols. Photoreduction occurred only in the presence of strong hydrogen donors like tributylstannane. The above investigators, citing spectroscopic data as supporting evidence, suggested that the loss of photoreactivity in each case was due to a reversal of the order of the two triplet states as compared to benzophenone, with the π,π^* level being the lowest state in these ketones. Porter later changed his mind concerning this explanation[28], and along with Suppan[29], has become strong advocate for the existence of a charge transfer state which is responsible for the lack of reactivity in ketones substituted with electron donating groups.

This CT state, rather than a reversal of the two triplet levels, is used by them to explain the fact that the quantum yields for photoreduction of p-hydroxy- and p-aminobenzophenones is quite substantial in cyclohexane, but drops to less than 10^{-4} in alcohol. Suppan[30] has reinvestigated the photoreduction of 2-acetonaphthone and has found that it does photoreduce somewhat in ethanol, the quantum yield of ketone disappearance going from 2.8×10^{-3} at 20°C to 12×10^{-3} at 90°C on irradiation at 3650 Å.

The π-π^* triplets in the above mentioned unreactive compounds are quite a bit lower in energy than the n-π^* triplets. Yang and coworkers[31,32], in an attempt to make the transition from a n,π^* state to a π,π^* state a gradual one, introduced successive methyl and methoxy groups onto the ring of acetophenone and then studied the ability of these ketones to be photoreduced. They found that a direct relationship existed between the decrease in reactivity, measured as the lowering of the quantum yield, and the increase in phosphorescence lifetime in going from parent ketone to ketones with several methoxy groups.

In an analogous investigation of the photoreduction of benzophenone, however, Yang and Dusenberry[33] found that the introduction of methyl substituents had a much smaller effect on the reactivity of the benzophenones as compared to the acetophenones. This difference in the effect of substituents on the two types of ketones was attributed to a smaller interaction between the two states in the diaryl ketones as compared to the aryl alkyl ketones. Wagner and Capen[34] have carried out a detailed investigation into the photochemistry of pyridyl ketones and have correlated the photochemical reactivity of these compounds with the position of the aza substituent in the ring. Their results indicated that the triplet states of pyridyl ketones are 2-3 times more photoreactive than the analogous phenyl ketones. This increased reactivity is attributed to an inductive effect on the lowest n,π^* triplet. Finally, both Wagner[35] and Yang[32] have attempted the disentanglement of the various factors that affect the quantum yields of ring substituted aceto- and valerophenones by performing quenching studies on these compounds. Although these experiments show that electron-donating substituents, which produce π,π^* lowest triplets, also decrease triplet state reactivity, they did not tell unequivocally what the nature of the reactive state is.

The aryl alkyl ketones are an excellent example where divergent tools of chemistry can be brought to bear on the same problem. Thus the study of the spectroscopy of these ketones has been closely related to the elucidation of their photochemical behavior and there has been a determined effort to interpret photochemical reactivity on the basis of spectroscopic findings.

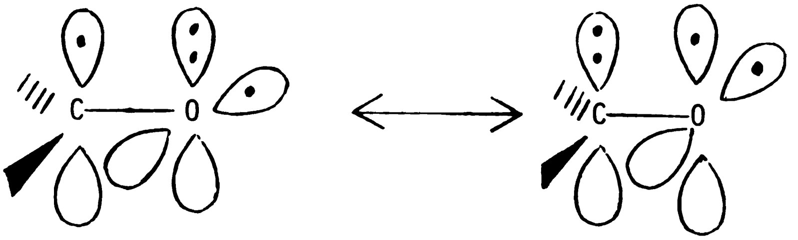
Yang and Murov[36], in one of the earlier papers on this topic, reported that 1-indanone and other phenyl alkyl ketones exhibit two groups of emission in their phosphorescence spectra at low temperatures. These two groups could be resolved and the individual lifetime of each measured. They assigned the short-lived component to a n,π^* state, while the longer lived emission displayed mixed n,π^* and π,π^* properties. Kearns and Case[23], using the technique of phosphorescence excitation, found that all acetophenones substituted with electron donating substituents seemed to possess lowest lying π,π^* triplet states, with the n,π^* state lying slightly above it. Similar results were found for various butyrophenones. The two triplets in these ketones are extremely close together, so that it has been very difficult to establish which state is actually the lowest one.

It is well known that the energetic disposition of the two triplet levels, aside from being substituent sensitive, is also strongly solvent dependent[37]. In general, n,π^* transitions are shifted towards higher energy (shorter wavelength) in going from nonpolar to polar solvents whereas the π,π^* transitions are shifted to lower energy (red shift). The blue shift of the n,π^* transitions is attributed, at least in part, to solvation (or hydrogen bonding in the case of protic solvents) of the lone pair of electrons on the oxygen in the ground state. In the n,π^* transition a n electron is removed from the oxygen, and the remaining n electron is not adequate to sustain the hydrogen bond in the excited state. Thus the breaking of the hydrogen bond in going from ground to excited state increases the energy required for the promotion of an electron from a n to a π^* orbital. The shift to lower energy for the π,π^* states, on the other hand, in going from non-polar to polar solvents is due to the fact the π,π^* excited states are quite polarizable and can become strongly solvated in the excited state.

Lamola[38] has been able to invert the lowest triplet states in acetophenone by going to very polar solvents. In hydrocarbon solvents the n,π^* state is lowest, while in phosphoric acid the ^3L_a π,π^* state (vide infra) predominates.

The observation of two components in the emission spectra of butyrophenones[39] and other aryl ketones[40,41] seems to be a general phenomena. These two components are observed when the ketones are in polar glasses[39] or absorbed on silica[42]. The general interpretation of the nature of the two components in aryl alkyl ketone phosphorescence spectra is that the shorter lived one is due to the n,π^* state and the longer lived one predominantly to the π,π^* state. Both Wagner[43] and Lim[44] disagree with this interpretation since it implies that the two states are not in equilibrium and that the rate of internal conversion between the two states is slower than phosphorescence. Lim postulates that the long lived component may be due to emission from an excited enolate ion since 2,2-dimethyl-1-indanone, which has no α hydrogens, has only a short lived component in its spectrum.

Since neither quantum yield and quenching studies, nor spectroscopic work have so far given a clear-cut indication as to the nature of the reactive excited state in these ketones, it was decided to exploit the inherent difference in reactivity of the $^3n,\pi^*$ and $^3\pi,\pi^*$ states towards hydrogen abstraction in order to solve this problem. The n,π^* excitation of ketones involves the promotion of a non-bonding electron belonging to the carbonyl oxygen to an antibonding orbital of the carbon oxygen bond. Thus a n,π^* triplet can be visualized as a system that contains two π electrons, one n electron and one π^* electron. Both molecular orbital (a) and valence bond (b) representation indicate that the excited carbonyl group should be a partially bipolar species.



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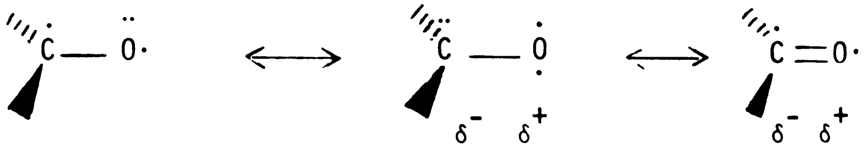
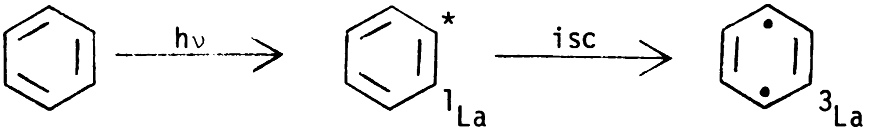


(b)

The oxygen with its seven electrons around it becomes a radical-like electrophilic species whose electron deficiency is present as a half vacant orbital in the plane of the carbonyl function. Walling and Gibian[45] as well as Padwa[46] found that the behavior of benzophenone, whose lowest triplet possesses essentially pure n,π^* character[47], paralleled very closely that of t-butoxy radicals in the abstraction of hydrogen from various donors. The excited benzophenone triplet did however show a somewhat greater selectivity and also a somewhat greater sensitivity toward electron availability, which is in accord with the notion that it is an electrophilic species.

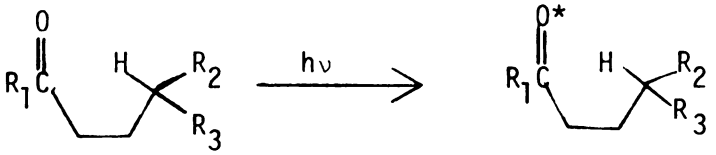
On the other hand, promotion of an electron of a π bonding orbital to a π^* antibonding orbital results in a π,π^* state. As mentioned, the position of the $^3\pi,\pi^*$ state with respect to the $^3n,\pi^*$ state is strongly solvent and substituent dependent[48]. Lamola[38], in an elegant piece of work, demonstrated that the so called $^3\pi,\pi^*$ state of phenyl alkyl ketones corresponds to the ^3L_a, or lowest triplet state, of benzene. One of the proposed canonical structures for this state is a 1,4 biradical[49] in which the inductive effect of the electron donating ring substituents can be transmitted to the carbonyl group. Porter[28] and Suppan[29] have proposed that a CT state exists in ketones where strong electron donating substituents are present. Whether or not this is actually the case, it is fairly certain that in ketones having lowest $^3\pi,\pi^*$ states, the carbonyl oxygen of the excited molecule should be at least as electron-rich as it is in the ground state. This leads to the expectation that, in the π,π^* triplets of ketones having electron donating ring substituents, the carbonyl oxygen should be a nucleophilic species possessing a minimum of alkoxy radical-like properties. Thus the behavior of ketones reacting from a $^3\pi,\pi^*$ state can be expected to be radically different from those that react from a $^3n,\pi^*$ state.



(7)

We have focused our attention on the photochemistry of the p-methoxyphenyl alkyl ketones. The two triplets in these ketones are close together[23,31] with the π-π^* triplet only a few kilocalories lower than the n-π^* triplet. Furthermore, Wagner[35] and Yang[32] have also shown that the reactivity of these compounds is less than that of ketones possessing lowest n-π^* states, such as simple phenyl alkyl ketones. The work of Wagner and Kemppainen[35] indicated that the lowering of the reactivity in these ketones, although significant, was not of such great magnitude as to preclude the use of these compounds in hydrogen abstraction studies.

The reaction system chosen as the most suitable one for the determination of the nature of the reactive states in the p-methoxy ketones was the Norrish Type II elimination[50]. This process has been one of the most actively studied photochemical reactions of the last few years[51]. The major reaction products are an olefin and the enol of a smaller carbonyl compound[52], although in most instances cyclobutanols are also formed in substantial amounts[53]. Yang[53], who was the first to observe the cyclobutanol formation, hypothesized that a 1,4 biradical intermediate is formed during the course of the reaction.



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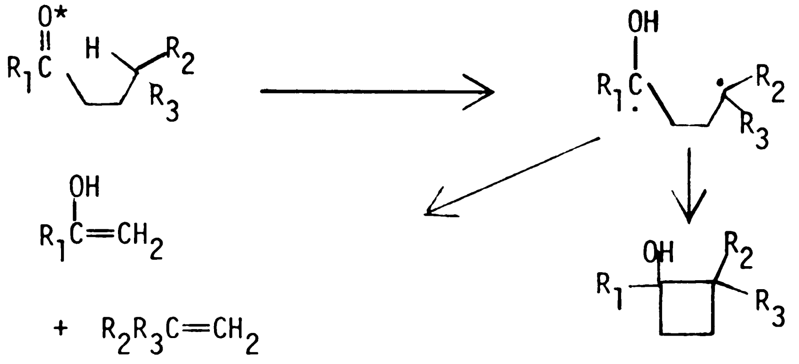

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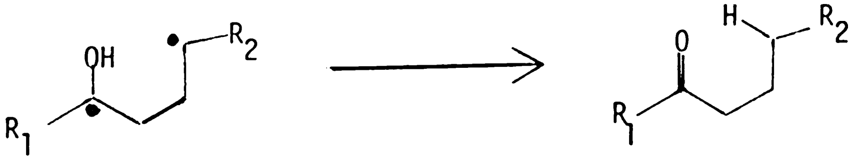
(10)

The quantum yield of the Type II photoelimination is usually less than unity for most ketones. This is somewhat suprising since in most cases the reactivity of the triplets is high enough to compete very efficiently with radiationless decay[54]. Wagner and Hammond have postulated that this inefficiency may be due to the reversal of the hydrogen transfer step[54].



(11)

Work by Yang and Coulson[55] supports this suggestion since they showed that during the photolysis of 2-hexanone-5,5-d_2 the γ hydrogen is directly involved in whatever process returns the majority of the excited ketone molecules back to the ground state. Further proof for the existence of the biradical has come from recent solvent and optical activity studies by Wagner and his group. They found that the quantum yield for valerophenone disappearance rises from 0.45 in hydrocarbon solvents to unity in alcohols and acetonitrile[56]. The explanation for this effect, which has been observed with other aryl ketones[34], is that the polar solvent will hydrogen bond with the hydroxyl group of the biradical and in this manner prevent the disproportionation of the hydroxyl hydrogen back to the γ carbon, which allows all the biradicals to proceed on to product. The disproportionation of the biradical back to ground state ketone is the only logical explanation for the fact that the reactivity of ketones may be increased by certain γ carbon substituents, but yet the overall quantum yield will be lower in these compounds than it is for the unsubstituted ketones[57]. Since ring substituents affect the nature and the reactivity of the triplet state, it is not unreasonable to expect that they also influence the behavior of the biradical intermediate. This was shown to be the case for several substituted butyrophenones[58].

The recent studies of Wagner and Kelso[59] involving the photolysis of optically active γ-methylcaprophenone are the best evidence for a biradical intermediate. Since the rates for the various photoprocesses for this type of ketone are known, they were able to predict the amount of racemization that should occur due to reverse hydrogen transfer at various percent conversion. The results obtained were in agreement with the predicted values. Furthermore, no loss of optical activity occurred when the ketone was photolyzed in the presence of an alcohol.

Early work by several groups indicated that in the case of dialkyl ketones the Type II reaction may proceed from both the singlet and triplet states[60,61] since product formation is not completely quenched by high concentrations of dienes. Elimination from phenyl alkyl ketones, on the other hand, can be quenched completely[54], which is taken as evidence that the reaction proceeds completely from the triplet state.

There are several reasons why the Type II process is the reaction system of choice in the study of the excited states of ketones. The photoreduction of benzophenone or acetophenone is a bimolecular abstraction process based on the donation of a hydrogen atom from either solvent or added donor to the carbonyl of the ketone. Thus the act of varying the hydrogen donor in order to obtain data on the reaction of a ketone with various molecules having different C-H bond strengths at the same time alters the environment of the carbonyl group and introduces additional solvent and viscosity effects. Furthermore, intermolecular photoreduction is not really a "clean reaction" in the sense that the products formed are fairly independent of reaction conditions. Pitts[8] and other workers[62] have found that there are several labile intermediates formed in the photoreduction of benzophenone (and presumable acetophenone also) in isopropyl alcohol which affect both the kinetics and quantum yield of the reaction. Another disadvantage of intermolecular photoreduction is that the products usually formed are high melting, making analysis of product formation by vpc techniques difficult. Instead, starting material disappearance is usually measured by spectroscopic means in the analysis of the reaction.

On the other hand, since in the Type II reaction hydrogen abstraction is a unimolecular process, substituents can be introduced on or near the γ carbon atom which can alter the γ C-H bond in a predictable manner without affecting the physical environment of the whole molecule. This prevents any extraneous solvent and viscosity effects from interferring in the study of the ketone triplet reactivity, since the solvent can be kept the same for a whole series of experiments. The products formed in the Type II process are also fairly well characterized and can be analyzed conveniently on a gas chromatograph, which makes life easier from an experimental standpoint.

With the above considerations in mind, it was decided that a comparison of the effect on the rates of hydrogen abstraction between a series of p-methoxybutyrophenones and their unsubstituted counterparts where successive substitution by electron withdrawing or electron donating groups drastically alters the electronic environment of the hydrogens on the γ carbon, should be a good monitoring procedure capable of indicating what the nature of the excited state is in the photoreduction of these ketones.

There are two mechanistic possibilities for the hydrogen abstraction step by aryl ketone triplets. They are:

a. Only the n-π* type is the reactive species, even when it is not the lowest.

b. The two close lying triplets interact to form mixed states which possess reactivity characteristic of each individual state, such that the lowest triplet can react even when it is mostly π,π* in character.

The reactivity of the electrophillic n-π* triplet of the benzoyl group in the phenyl alkyl ketones should show a different type of selectivity towards C-H bonds having different electronic environments, than the π-π^* triplet of the p-methoxy ketones, if it is the reactive state. Thus inductive effects by electron-withdrawing or donating groups on hydrogen abstraction should give an indication as to what the nature of the reactive state in ketones having lowest π-π^* triplet level is.

The ability to use the Type II reaction as a monitoring tool is predicated upon an understanding of the various processes that occur following the initial absorption of a quantum of light by the ketone. A general mechanism which takes into account equilibration between the two triplet states of p-methoxyphenyl alkyl ketones is given below. Absorption of a quantum of light by the ketone in solution results in the formation of the first excited singlet state, $*K^1$, (rate = I_a) which can intersystem cross to the upper n-π^* triplet, T_n (rate constant = k_{isc}). The triplet T_n can decay to the lower π-π^* triplet, T_π, (rate constant equals k_{21}), react to form a biradical intermediate BR (rate constant equals k_r^n), decay to ground state ketone (rate constant = k_i) or transfer its energy to a quencher Q (rate constant = k_q^n).

Process	Rate	
$K \xrightarrow{h\nu} *K^1$	I_a	(12)
$^1K^* \xrightarrow{k_{isc}} T_n$	$k_{isc}\ (*K^1)$	(13)
$T_n \xrightarrow{k_r} BR$	$k_r^n\ (T_n)$	(14)
$T_n \xrightarrow{k_i} K^0$	$k_i\ (T_n)$	(15)

Process	Rate	
$T_n \xrightarrow{k_{21}} T_\pi$	$k_{21}\ (T_n)$	(16)
$T_n + Q \xrightarrow{k_q^n} K^o + Q^*$	$k_q^n\ (T_n)(Q)$	(17)

The T_π triplet may thermally equilibrate back to the upper triplet, T_n, (rate constant = k_{12}), react to form the biradical intermediate, BR, (rate constant = k_r^π), decay to ground state ketone (rate constant = k_d), or be quenched by a quencher (rate constant = k_q^π).

Process	Rate	
$T_\pi \xrightarrow{k_{12}} T_n$	$k_{12}\ (T_\pi)$	(18)
$T_\pi \xrightarrow{k_r^\pi} BR$	$k_r^\pi\ (T_\pi)$	(19)
$T_\pi \xrightarrow{k_d} K^o$	$k_d\ (T_\pi)$	(20)
$T_\pi + Q \xrightarrow{k_q^\pi} K^o + Q^*$	$k_q^\pi\ (T_\pi)(Q)$	(21)

Finally, the biradical BR may decay to ground state ketone (rate constant = k_d'), cleave to yield an enol and an olefin (rate constant = k_s), or cyclize to yield a cyclobutanol (rate constant = k_c).

Process	Rate	
$BR \xrightarrow{k_d'} K^o$	$k_d'\ (BR)$	(22)
$BR \xrightarrow{k_s}$ Enol and Olefin	$k_s\ (BR)$	(23)

Process	Rate	
$BR \xrightarrow{k_c}$ Cyclobutanol	$k_c\ (BR)$	(24)

These processes can be depicted in terms of an energy level diagram as shown in Figure 3.

The quantum yield for product formation, which is the only quantity that can be measured directly under steady state photolytic conditions, may be defined as:

$$\Phi = \frac{\text{Number of molecules of final product formed}}{\text{Number of quanta of light absorbed by starting material}} \qquad (25)$$

This quantum yield is the product of the probabilities that each step in the overall process will occur. For the Type II reaction,

$$\Phi = \phi_{isc}\phi_{BR}\phi_{P} \qquad (26)$$

where ϕ_{isc} is the probability that the absorption of a quantum of light will produce the requisite triplet excited states, ϕ_{BR} is the probability of biradical formation from the excited states, and ϕ_p is the probability that the biradicals will proceed on to products.

By using steady state kinetics, expressions for the quantum yield in terms of the rate constants for the various processes may be derived[63]. The expression for the three kinetic possibilities for product formation for the p-methoxyphenyl alkyl ketones are as follows:

a. Assuming that only the lowest π-π* triplet reacts, then,

$$\Phi = \phi_{isc}\phi_p k_r^{\pi}\tau = \frac{\phi_{isc}\phi_p \cdot k_r^{\pi}}{k_r^{\pi} + k_d} \qquad (27)$$

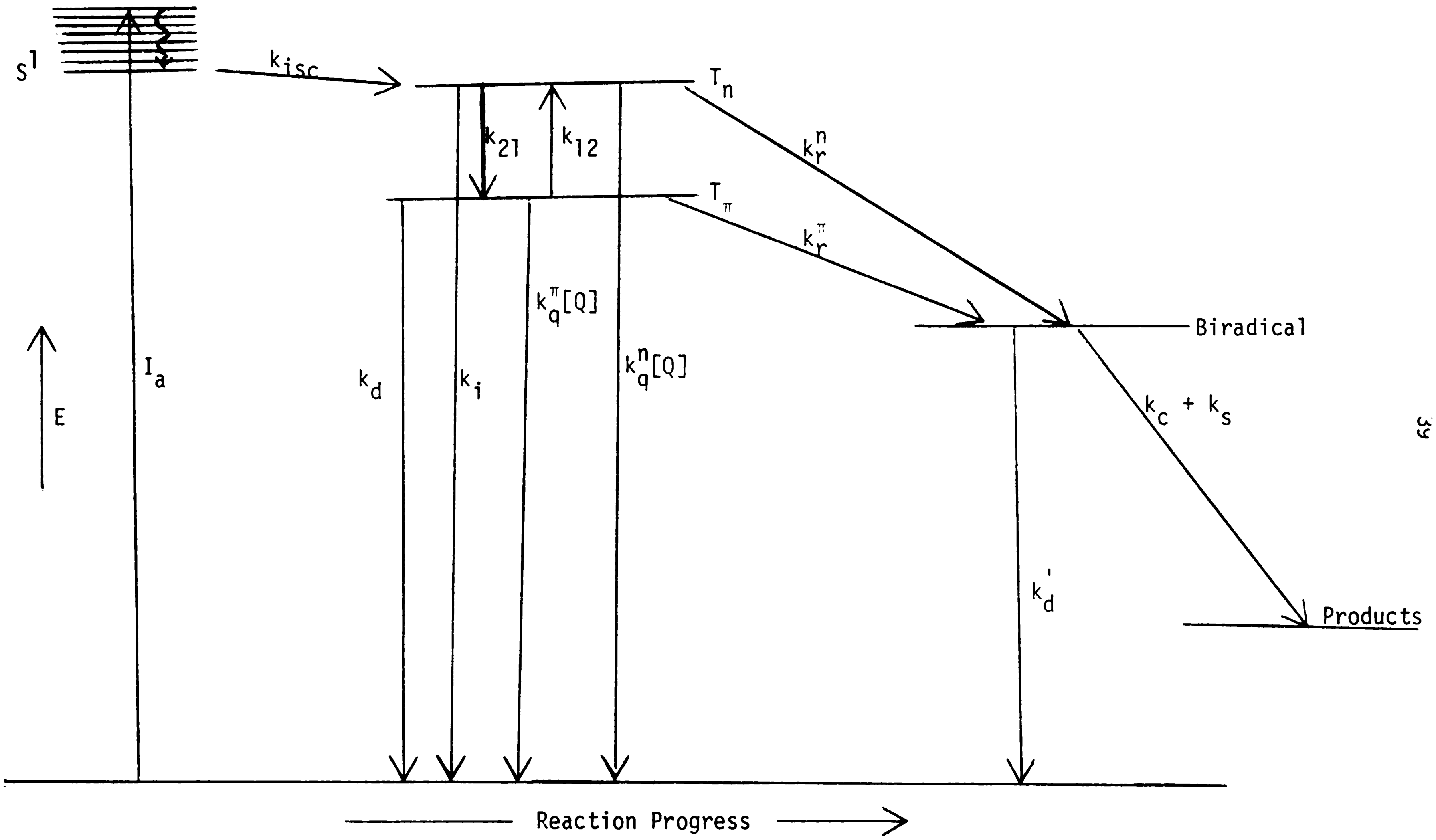


FIGURE 3. Modified Jablonski Diagram for p-Methoxyphenyl Alkyl Ketones

where τ, the lifetime of the triplet, is defined as

$$\tau = \frac{1}{k_r^{\pi} + k_d} \qquad (28)$$

b. If only the upper n-π* triplet reacts, then the expression for the quantum yield becomes:

$$\phi = X_n k_r^n \tau_{eq} \phi_{isc} \phi_p = \phi_{isc} \phi_p \cdot \frac{X_n k_r^n}{X_n (k_r^n + k_i) + X_\pi k_d} \qquad (29)$$

where X_n and X_π are defined as the mole fractions of the n-π* and π-π* triplet, respectively.

$$X_\pi = \frac{k_{21}}{k_{21} + k_{12}} \quad \text{and} \quad X_n = \frac{k_{12}}{k_{12} + k_{21}} \qquad (30)$$

and τ_{eq}, the equilibrium lifetime of the two triplets in this case, is defined as:

$$\tau_{eq} = \frac{1}{X_n \, (k_r^n + k_i) + X_\pi k_d} \qquad (31)$$

c. Finally, if both triplets react, the quantum yield in the absence of quencher is given by equation (32)

$$\phi^0 = (X_n k_r^n + X_\pi k_r^\pi) \, \tau'_{eq} \phi_{isc} \phi_p = \frac{\phi_{isc} \phi_p (X_n k_r^n + X_\pi k_r^\pi)}{X_n (k_r^n + k_i) + X_\pi (k_r^\pi + k_d)} \qquad (32)$$

where τ_{eq}', the equilibrium lifetime of the two states, equals the denominator of the right equation. Since the rate constant for decay from the upper triplet, k_i, is known to be negligibly small compared to k_r^n, it may be ignored[35]. Equation (32) then becomes:

$$\phi^o = (X_n k_r^n + X_\pi k_r^\pi)\, \tau_{eq}' \phi_p \phi_{isc} \qquad (33)$$

where

$$\tau_{eq}' = \frac{1}{X_n k_r^n + X_\pi (k_r^\pi + k_d)} \qquad (34)$$

Assuming that $k_q^n = k_q^\pi = k_q$, since ketone triplets are known to be quenched by dienes at the diffusion controlled rate[64], one can write the expression for the quantum yield in the presence of quencher in the following way:

$$\phi = \phi_{isc}\phi_p \cdot \frac{X_n k_r^n + X_\pi k_r^\pi}{X_n (k_r^n + k_q[Q]) + X_\pi (k_r^\pi + k_d + k_q[Q])} \qquad (35)$$

Division of equation (35) into equation (33) yields the following expression:

$$\frac{\phi^o}{\phi} = \frac{\dfrac{\phi_{isc}\phi_p (X_n k_r^n + X_\pi k_r^\pi)}{X_n (k_r^n) + X_\pi (k_r^\pi + k_d)}}{\dfrac{\phi_{isc}\phi_p (X_n k_r^n + X_\pi k_r^\pi)}{X_n (k_r^n + k_q[Q]) + X_\pi (k_r^\pi + k_d + k_q[Q])}} \qquad (36)$$

which reduces to:

$$\frac{\phi^o}{\phi} = \frac{X_n (k_r^n + k_q[Q]) + X_\pi (k_r^\pi + k_d + k_q[Q])}{X_n k_r^n + X_\pi (k_r^\pi + k_d)} \qquad (37)$$

and on multiplying out, equals:

$$\frac{\Phi^o}{\Phi} = \frac{X_n k_r^n + X_\pi k_r^\pi + X_\pi k_d + (X_n + X_\pi)\, k_q[Q]}{X_n k_r^n + X_\pi k_r^\pi + X_\pi k_d} \qquad (38)$$

which can be rewritten as:

$$\frac{\Phi^o}{\Phi} = 1 + \frac{(X_n + X_\pi)\, k_q\, [Q]}{X_n k_r^n + X_\pi (k_r^\pi + k_d)} \qquad (39)$$

Since $(X_n + X_\pi)$ equals unity, substitution of the value for τ_{eq}' as given in equation (34) into equation (39) yields the familiar Stern-Volmer expression.

$$\frac{\Phi^o}{\Phi} = 1 + k_q[Q]\tau_{eq}' \qquad (40)$$

Equation (40) allows one to determine the observed lifetime of the ketone triplet. By choosing a quencher, such as 2,4-dimethyl-2,5-hexadiene, which is known to quench triplet reactions at close to diffusion controlled rates[64] with $k_q = 5 \times 10^9\ M^{-1}\ sec^{-1}$ in benzene at room temperature[65], plots of Φ^o/Φ versus quencher concentration should give a straight line with an intercept of one and a slope of $k_q\ \tau^{obs}$. Since the value of k_q is known, the value for the observed lifetime can be obtained from expression (41).

$$\tau^{obs} = \frac{1}{k_r^{obs} + X_\pi k_d} = \frac{\text{slope of S-V plot}}{k_q^{diff}} \qquad (41)$$

II. RESULTS

A. Solvent Effects

The effect of polar solvents on the quantum yield for a series of ketones was determined in order to evaluate how ring substituents affect the behavior of the biradical intermediate. Solutions 0.10 M in ketone in benzene or benzene and alcohol as solvent were irradiated at 3130 Å to approximately 20 - 25% conversion. The samples were analyzed by vpc and quantum yields were determined relative to cis-piperylene/acetophenone actinometers[19]. Addition of polar solvents caused the quantum yield to rise until it reached a maximum value at which point it usually leveled off or slowly decreased. Once the quantum yield reached a maximum, it was assumed that enough polar solvent was present to insure that all the biradicals formed proceeded on to products and any remaining inefficiency was due to triplet decay. Solvent effect studies provide a convenient means of determining ϕ_p, the probability of product formation from the biradical intermediate, since ϕ_p equals the ratio of the quantum yield in benzene to the maximum quantum yield in benzene plus alcohol. Table 2 lists the quantum efficiencies for a series of substituted phenyl n-butyl ketones in benzene and benzene plus alcohol, along with the corresponding values of ϕ_p.

TABLE 2. Quantum Yields for Substituted n-Butyl Phenyl Ketones

Substituent	Φ benzene[a]	Φ Alc.[b]	Φ_p
p-MeO	0.18	0.26[c]	0.69
p-Me	0.39	0.80	0.50
None (H)[d]	0.40	1.00	0.40
p-Cl	0.30	0.80	0.37
3-(N)[d]	0.29	1.00	0.29
2-(N)	0.18	1.00	0.18

[a] Total quantum yield for reaction of ketone. [b] Maximum quantum yield values as obtained from plot of Φ versus [t-butanol]. [c] Values for Φ max are 0.26 and 0.25 using methanol and pyridine as added polar solvents, respectively. [d] Values for valerophenone and the aza substituents were determined by Wagner and Capen[34].

B. Quenching Studies

Linear Stern-Volmer plots were obtained in the quenching of the anisyl ketones by low concentrations of 2,5-dimethyl-2,4-hexadiene. As mentioned, this diene is known to quench triplet reactions in benzene at room temperature at close to the diffusion controlled rate[64] with k_q equalling 5 x 10^9 M^{-1} sec^{-1}[65]. Solutions 0.10 M in ketone, with benzene as solvent and octadecane as internal standard, were irradiated at 3130 Å to less than 25% conversion, and quantum yields were determined by either cis-piperylene/acetophenone[19] or valerophenone actinometry.

The quantum yield as given in equation (26) is:

$$\Phi = \phi_{isc}\phi_{BR}\phi_{p} \tag{26}$$

which can be rewritten as:

$$\Phi = k_r^{obs}\,\tau^{obs}\,\phi_{isc}\phi_{p} \tag{42}$$

where $k_r^{obs}\,\tau^{obs}$ has been substituted for ϕ_{BR} since

$$\phi_{BR} = \frac{k_r^{obs}}{k_r^{obs} + X_\pi k_d} \tag{43}$$

Rearrangement of equation (42) yields the following equation for obtaining k_r^{obs}:

$$k_r^{obs} = \frac{\Phi}{\tau^{obs}\phi_p\phi_{isc}} \tag{44}$$

Thus in order to calculate the values for k_r^{obs}, it was necessary to determine the four variables of equation (44). The quantum yield, as mentioned above, was determined directly by actinometry. The observed lifetime, τ^{obs}, was determined from the Stern-Volmer plot using equation (41), and the values for ϕ_p, the probability of the biradical going on to product, were measured in the solvent effect studies. Finally, ϕ_{isc}, the probability of forming the triplet states can be determined by comparing the amount of cis-piperylene isomerized to trans by a ketone such as benzophenone, whose quantum yield of intersystem crossing is known to be unity[19] to that isomerized by the methoxy ketones. In this manner, it was found that the quantum yield of intersystem crossing for o-, p-, and m-methoxyvalerophenone was unity.

Once k_r^{obs} was known, it was also possible to calculate the values for k_d^{obs}, the amount of decay from the π-π^* state in the p-anisyl ketones, by rearranging equation (41) which is:

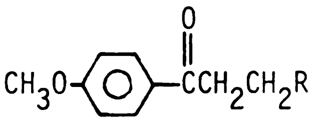
$$\tau^{obs} = \frac{1}{k_r^{obs} + X_\pi k_d} \tag{41}$$

to

$$k_d^{obs} = 1/\tau^{obs} - k_r^{obs} \tag{45}$$

where k_d^{obs} equals $X_\pi k_d$.

A summary of the kinetic parameters obtained for the p-anisyl ketones is given in Table 3, and Table 4 lists the data for the analogous phenyl ketones. Table 5 contains the data for p-methoxyvalerophenone using methanol as a solvent and naphthalene as the diffusion controlled quencher[66].

TABLE 3. Photoelimination of Select p-Anisyl Ketones 

	R	Φ^{a}_{benz}	Φ^{b}_{max}	$k_q\tau$, M^{-1}[c]	τ, 10^{-6} sec	k_r^{obs}, 10^{6} sec^{-1}	k_d, 10^{6} sec^{-1}
A-1	CH_3	0.012	0.04	3300	0.66	0.06	1.5
A-2	CH_2CH_3	0.145	0.26	2300	0.46	0.56	1.6
A-3	$CH(CH_3)_2$	0.22	0.67	1100	0.22	3.00	1.5
A-4	$CH_2CH_2CO_2Et$	0.104	0.14	2500	0.50	0.28	1.7
A-5	CH_2CH_2CN	0.009	0.015	2500	0.50	0.03	1.7
A-6	CH_2CO_2Me[d]	0.008	0.019	830	0.17	0.025	6.0

[a] Quantum yield of Type II product formation in benzene. [b] Maximum yield of product formation in benzene plus t-butyl alcohol. [c] Slope of Stern-Volmer quenching plot. [d] Based on 6% conversion. Values are strongly dependent on per cent conversion (see text).

TABLE 4. Photoelimination of Select Phenyl Ketones $PhCOCH_2CH_2R$[a]

	R	Φ_{π}[b]	$k_q\tau$, M^{-1}[c]	k_r^n, 10^7 sec^{-1}[d]
P1	CH_3	0.36	660	0.8
P2	CH_2CH_3	0.33	40	12.5
P3	$CH(CH_3)_2$	0.25	11	45.0
P4	$CH_2CH_2CO_2CH_3$	0.64	125	4.0
P5	CH_2CH_2CN	0.46	500	1.0
P6	$CH_2CO_2CH_3$	0.46	440	1.1

[a] Data obtained by Wagner and Kemppainen[67]. [b] Quantum yields of acetophenone formation in benzene. [c] Slope of Stern-Volmer quenching plot, averages of duplicate runs. [d] $k_r^n = 1/\tau$.

TABLE 5. Photoelimination of p-Methoxyvalerophenone in Methanol

Ketone	Φ_{II}	$k_q\tau$, M^{-1}[a]	$1/\tau^{obs}$, sec^{-1}	k_r^{obs}, sec^{-1}
PMVP	0.09	13000	1.15×10^6	1.0×10^5

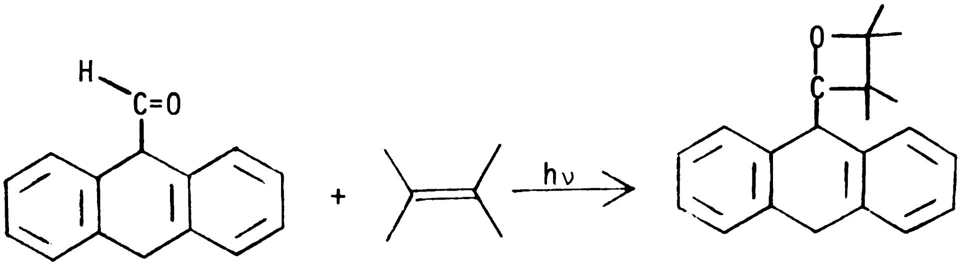
[a] Quencher is naphthalene, k_q equals 1.5×10^{10} sec^{-1} M^{-1}.

III. DISCUSSION

A. Mechanistic Interpretation

Yang[31,32], as a result of his work on the photoreduction of substituted acetophenones, has suggested that the hydrogen abstraction reactions of phenyl alkyl ketones substituted with electron-donating groups occur from a mixed lowest triplet state. This state is mostly π-π^* in character, but has sufficient n-π^* character mixed in due to vibronic coupling to impart it with a slight reactivity. Wagner[35], on the other hand, has suggested that the alternate possibility of thermal equilibration between the lower, unreactive π-π^* triplet and the upper, reactive n-π^* state cannot be ignored.

This suggestion is not unreasonable since participation by upper reactive triplet states has been invoked in other photochemical reactions. Among these are the suggestion by Yang[68] that an upper triplet may be reacting in the photoaddition of 9-anthraldehyde to 2,3-dimethyl-2-butene, and the proposal by Liu and Edman[69] that



(46)

energy transfer from anthracene to bis(perfluoromethyl) bicyclo[2.2.2]-octatriene occurs from an upper triplet level.

Our data strongly support the suggestion that hydrogen abstraction in the p-methoxyphenyl alkyl ketones occurs almost exclusively from the upper reactive n-π* triplet rather than the lower π-π* state. Comparison of the data for the p-methoxy ketones A-1, A-2, and A-3 from Table 3 and the phenyl ketones P-1, P-2, and P-3 from Table 4 indicates that the selectivity of the anisoyl and benzoyl triplets toward primary, secondary, and tertiary C-H bonds is almost identical. The selectivity shown towards abstraction of a primary hydrogen versus a tertiary one is manifested as an approximately fifty-fold increase in the relative k_r values for each ketone series, despite the fact that the triplet of the anisoyl group is only about 1/200th as reactive as the triplet of the benzoyl group. Even more significant are the results obtained by comparing the data for ketones A-2, A-4, and A-5 with the data for ketones P-2, P-4, and P-5. All three ketones in each series possess secondary C-H bonds in the γ position. Ketones A-4 and P-4 have an ester group in the δ position and ketones A-5 and P-5 are substituted with δ-cyano groups. The inductive effect of the two electron-withdrawing groups was expected to strongly deactivate the electrophilic n-π* triplet of the benzoyl group in the abstraction of a hydrogen from the γ carbon. Indeed, the decrease in relative reactivity is greater than an order of magnitude in going from valerophenone to δ-cyanovalerophenone. An identical effect is exerted on the triplet state reactivity of the anisoyl group. The relative reactivity of its triplet drops from 1.00 to 0.06 in going from p-methoxyvalerophenone to δ-cyano-p-methoxyvalerophenone.

The observed inductive effect of the two electron-withdrawing groups on the photoreactivity of the p-methoxy ketones is opposite to the one expected if the lower π-π^* triplet was the reactive state in these compounds. It is extremely unlikely that the nucleophilic π-π^* triplet of the methoxy ketones, which must have a relatively electron-rich oxygen atom (even if some n-π^* character is present due to vibronic coupling), should be subject to identical inductive effects as the electrophilic n-π^* triplet of the benzoyl group. This leads to the conclusion that, rather than having hydrogen abstraction from the lower π-π^* state, almost all reaction takes place from the upper n-π^* triplet.

If hydrogen abstraction is occurring from the upper triplet state, then the only difference between the observed rate constants for abstraction by the anisoyl triplets as compared to the rate constants for the benzoyl triplets, which equal k_r^n, should be due solely to the lower number of reactive n-π^* triplets present in the p-methoxy ketones. In that case,

$$k_r^{obs} = X_n k_r^n \tag{47}$$

Equation (47) can be rearranged to equation (48),

$$X_n = \frac{k_r^{obs}}{k_r^n} \tag{48}$$

which allows calculation of the mole fraction of reactive n-π^* triplets present in the p-methoxy ketones. Substitution of appropriate values for k_r^{obs} from Table 3 and values for k_r^n from Table 4 into equation (48) yields 0.005 as the average value of

X_n, the mole fraction of reactive n-π* triplets present in these ketones.

Knowledge of the numerical value of X_n permits calculation of the approximate energy difference, Δ E, that separates the two triplet states in these ketones at room temperature in benzene. Equation (49) is the general expression for determining the value of K, the thermodynamic equilibrium constant based on concentrations.

$$K = e^{-\Delta E/RT} \tag{49}$$

where R = the gas constant and T is the temperature in degrees Kelvin. The equilibrium constant, K, in this case, represents the ratio of X_n to X_π. That is,

$$K = \frac{X_n}{X_\pi} = \frac{k_{12}}{k_{21}} \tag{50}$$

If 0.005 is used as the value for X_n, then $X_\pi = 1.00 - 0.005 \simeq 1.00$ and K will also equal 0.005. Rewriting equation (49) into equation (51) and substituting the values for K, R, and T into

$$\Delta E = -RT \ln K \tag{51}$$

it yields a value of about 3 kilocalories per mole as the energy separation between the two triplet levels.

Thus, rather than hydrogen abstraction occurring from the lowest π-π* state, all reaction takes place from a level that is about three kilocalories above the lowest vibrational level of the triplet π-π^* state. This upper level should be mostly n-π^* in character regardless whether or not it is discrete or mixed with the upper vibrational levels of the π-π^* triplet[70]. Even if vibronic mixing of the states occurs, it apparently is too weak to be the primary factor that determines the behavior of the anisoyl triplets towards different types of hydrogens[71]. Although the exact rate at which the lower π-π^* triplet returns to the reactive upper n-π^* triplet is not known, it should be at least 10^9 sec^{-1} if only vibrational excitation is required, since decay from a higher vibrational level to a lower one proceeds at a rate greater than 10^{12} sec^{-1}[22]. Saltiel has shown that the reasonably short lived triplet of benzophenone apparently has enough time to equilibrate thermally with the excited singlet state, which is believed to lie five kilocalories above the triplet[72].

The data in Table 3 and Table 4 deserve one or two additional comments. It should be pointed out that ketone A-6 and P-6 have their electron-withdrawing substituent attached directly to the γ carbon atom. The low quantum yield and high τ value for the anisyl ketone indicate that its behavior is similar to that of ketones A-4 and A-5. However, determination of the kinetic rate constants for ketones A-6 and P-6 are complicated by the fact that the olefin formed in the Type II reaction, methyl acrylate, is also a quencher. In ketones where a product is a quencher, the quantum yield will be inversely proportional to the per cent conversion that the reaction is carried out to. The data given in Table 3 and Table 4 for ketones A-6 and P-6 are those obtained under conditions where quenching by product occurred. The value for k_r^{obs} for ketone A-6 may be correct, but the larger k_d value, and consequently the shorter lifetime, are attributable to quenching by product. Thus compounds of this type belong to a separate class and deserve to be investigated further.

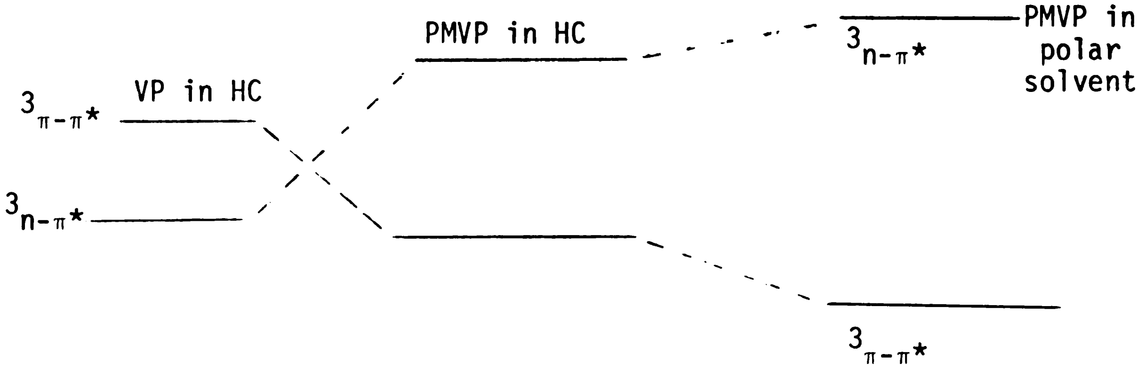
The other additional point of interest concerns the rate of decay of the π-π* triplets. The values obtained for the ketones A-1 through A-5 are fairly uniform, but the puzzling feature is the fact that the rate of decay is extremely rapid. The rate of decay for many π-π* triplets at room temperature in benzene of comparable purity to that used here is 10^3 sec^{-1}[73], which is some three orders of magnitude slower than that for the p-methoxy ketones. This rapid rate of decay most likely is an inherent property of the π-π* triplets of the p-methoxyphenyl alkyl ketones.

B. Solvent Effects

Our result indicating that the energy separation between the upper n-π* triplet and the lower π-π* state is only 3 kilocalories per mole in benzene is somewhat in disagreement with the value of 5 to 6 kilocalories obtained both by Kearns and Case[23] and by Yang[31] using phosphorescence excitation methods. However, their results are for ketones irradiated in polar glasses at 77°K. Analysis of the data in Table 5 for the photolysis of p-methoxyvalerophenone in methanol, as given below, indicates that the energy difference between the two triplet levels increases in going from a non-polar (benzene) to a highly polar (methanol) medium and approaches the value reported by Yang and Kearns.

The Stern-Volmer slope for the quenching of p-methoxyvalerophenone triplets in methanol by naphthalene is 13,000 M^{-1}, which is almost six times as large as the corresponding slope in benzene. This dramatic increase in the slope must be due to either an increase in the rate constant for quenching the triplet state, k_q, or an increase in the observed lifetime of the triplet state, τ^{obs}, or both, since the slope equals the product of these two terms. Using a high value of 1.5 x 10^{10} sec^{-1} M^{-1} as the quenching rate constant, Equation (41) gives a value of 8.7 x 10^{-7} seconds for τ^{obs}, and $1/\tau^{obs}$ equals 1.15 x 10^6 sec^{-1}. Equation (44) gives a value of 1 x 10^5 for k_r^{obs}, which in turn gives a value of about 0.0008 for X_n, the number of reactive n-π* triplets present in methanol. The energy separation corresponding to this value of X_n is about 4.3 kilocalories per mole, which approaches the reported value. The k_d value of 1.05 x 10^6 sec^{-1} is, as expected, close to that found in benzene.

The effect of polar solvents on the two triplet levels of valerophenone (VP) and p-methoxyvalerophenone (PMVP) is shown in the diagram below, (where HC is hydrocarbon).



It is readily conceivable that polar solvents may increase the magnitude of the energy separation between the $^3n\text{-}\pi^*$ state and the $^3\pi\text{-}\pi^*$ state until a point is reached where any increase in quantum yield due to solvation of the biradical is outweighed by the decrease in the probability of biradical formation due to the lowering of the equilibrium concentration of reactive n-π* triplets. If the energy gap between the two states becomes sufficiently large, the concentration of reactive states will be so small as to render the ketone unreactive from the n-π* triplet, and the only reactivity remaining under these circumstances would be that which is imparted to the π-π* state from vibronic interaction with the n-π* state.

Several other facts can be obtained from the information in Table 2. The trend of substituent effects on ϕ_p, the probability of biradical going on to product, indicates quite clearly that disproportionation of the biradical is favored by electron-withdrawing groups on the ring, suggesting strongly that the disproportionation reaction is sensitive to the acidity of the hydroxyl group of the biradical. It is also interesting to note that the chloro-, methyl-, and methoxy substituted valerophenones, all of which possess lowest π-π* triplets[23], undergo some direct radiationless decay which competes with the chemical reactions of the triplet state. This is not the case with valerophenone itself or the pyridyl ketones, all of which possess lowest n-π* triplets[34], since their maximum quantum yield in alcohol rises to unity.

C. Summary

Our results indicate that hydrogen abstraction in the Type II reaction of p-methoxyphenyl alkyl ketones occurs from a small number of upper reactive n-π* triplets rather than from the lower π-π* triplets. The inductive effects exerted by electron-withdrawing groups in the vicinity of the γ carbon on benzoyl triplets of phenyl alkyl ketones during hydrogen abstraction are identical to those experienced by the anisoyl triplets in the p-methoxyphenyl alkyl ketones. Since it is unlikely that the nucleophilic π-π* triplet state of the methoxy ketones would be subject to the identical inductive effect as the n-π* triplet state of the phenyl ketones, it can be concluded that all reaction in the p-methoxy ketones takes place from an equilibrium concentration of upper n-π* triplets. The energy separation between the two states is approximately three kilocalories in benzene, but increases in going from a non-polar to a polar solvent.

D. Further Experiments

Presumably equilibration between a lower π-π* triplet and an upper n-π* triplet can occur in all ketones where the two states are sufficiently close together for this equilibration to occur. Further experiments or work that can be performed on systems like the one studied in this thesis include the following:

a. The number of ketones studied with electron withdrawing substituents near the γ carbon should be increased so that the total range of electron-withdrawing substituents, from weak ones like chlorine, to strong ones like trifluoromethyl, is covered.

b. The effect of varying the position of ring substituents on the behavior of the two triplet states should be investigated. For example, Wagner and Kemppainen[35] have found that the rate of radiationless decay for meta substituted ketones is an order of magnitude greater than that for the para substituted ones, although the apparent rate of hydrogen abstraction is approximately the same for both.

c. Temperature effect studies need to be performed on the Type II reaction. Since the equilibrium concentration of each state is temperature dependent, it should be possible to increase or decrease the mole fraction of reactive n-π^* triplets by correspondingly increasing or decreasing the temperature.

d. The effect of solvents on the relative position of the two triplets should be investigated further in order to disentangle the various factors that influence the quantum yields of ketones in polar solvents.

Finally, these studies need not be confined to the Type II reaction alone, but should be extended to include other triplet state reactions such as oxetane formation or photorearrangements to see whether these reactions also take place from equilibrium concentrations of upper reactive triplet states.

IV. EXPERIMENTAL

A. Chemicals

1. Solvents

a. Benzene. Analytical grade benzene was stirred with concentrated sulfuric acid until the acid no longer turned yellow. It was then washed with dilute sodium hydroxide solution, water, and sodium chloride solution, respectively, and dried over anhydrous magnesium sulfate. After drying, the benzene was distilled from phosphorous pentoxide, and only the middle fraction retained.

b. Methanol. Reagent grade methanol was distilled from magnesium turnings and only the middle fraction was retained.

c. Pyridine. Reagent grade pyridine was distilled from barium oxide and only the middle fraction was retained.

d. t-Butanol. Reagent grade t-butanol was distilled from sodium shavings and only the middle fraction was retained.

2. Ketones

The ketones used in the photolysis were either purchased or prepared via common organic reactions. All melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected.

a. p-Methoxyacetophenone (PMACP). p-Methoxyacetophenone (Aldrich Chemical Company, Milwaukee, Wisconsin) was recrystallized twice from petroleum ether (bp 60-90°C.). Vpc analysis revealed no significant impurities (M.P. 39°C).

b. p-Methoxyvalerophenone (PMVP). Method A: PMVP was prepared from the addition of n-butylcadmium to p-anisoyl chloride according to the general method of Cason[74]. After hydrolysis and ether extraction, the ketone was vacuum distilled (bp 135-40°C. at 3-5 torr.) and recrystallized several times from a pentane-methanol mixture.

Method B: Valeryl chloride was used in the Friedel-Crafts acylation of anisole. The catalyst employed was aluminum chloride and benzene was used as a solvent. The ketone was vacuum distilled (bp as above) and recrystallized several times from methanol-pentane solution (total per cent yield equals ∿50%).

c. γ-Methyl-p-methoxyvalerophenone (GMPMVP). To the Grignard reagent prepared from 1-bromo-3-methylbutane (Eastman Organic Chemicals, Rochester, N.Y.) in ether was added an ether solution of p-anisonitrile according to the general method of Hauser[75]. After hydrolysis of the imine salt, the ketone was vacuum distilled (bp 137-38°C. at 3 torr.) and recrystallized several times from a pentane-methanol solution. Vpc analysis showed no appreciable impurities. (Total per cent yield equals ∿25% after purification.)

d. p-Methoxybutyrophenone (PMBP). Butyryl chloride was used in the Friedel-Crafts acylation of anisole with aluminum chloride as catalyst and carbon disulfide as solvent. The crude ketone was vacuum distilled (bp 113-115°C at 3 torr.) and recrystallized several times from a pentane-ethanol mixture. The recrystallized product was vacuum sublimed using a dry ice-acetone cooled sublimer. Vpc analysis showed no appreciable impurities. (Total per cent yield equals ∿60%).

e. p-Chlorovalerophenone (PCVP). Pfaltz and Bauer p-chlorovalerophenone was recrystallized several times from hexane. Vpc analysis showed no appreciable impurities (mp 31-32°).

f. p-Methylvalerophenone (PMeVP). Pfaltz and Bauer (Flushing, N.Y.) p-methylvalerophenone was recrystallized several times from hexane. Vpc analysis showed no appreciable impurities (mp 19-20°C.).

g. m-Trifluoromethylvalerophenone (MTFVP). m-Trifluoromethylvalerophenone was prepared by Professor Peter J. Wagner and purified by vacuum distillation (bp 116-117°C at 11 torr).

h. Acetophenone (ACP). Matheson, Coleman and Bell (Norwood, Ohio) acetophenone was distilled under reduced pressure (bp 55°C at 3 torr). Vpc analysis showed no appreciable impurities.

i. δ-Carboethoxy-p-methoxyvalerophenone (DCEPMVP). The general procedure of Diaper was used[76]. To the Grignard reagent prepared from 0.5 moles of p-bromoanisole in ether was added an ether solution of cyclohexanone. After hydrolysis of the Grignard salt by dilute hydrochloric acid, the anisyl cyclohexanol was obtained by ether extraction. The anisyl cyclohexanol was dehydrated to the corresponding anisyl cyclohexene by refluxing it in benzene with a catalytic amount of p-toluenesulfonic acid and collecting the water in a Dean-Stark trap. After the dehydration was complete, the solution was washed with dilute sodium bicarbonate and water to remove any acid and then dried over magnesium sulfate. Vacuum distillation of the mixture yields relatively pure olefin, (bp 147-148°C at 6 torr, literature[77]: bp 155°C at 14 torr, mp 35°C.) in 63% of theoretical yield. The anisyl cyclohexene was dissolved in excess ethyl acetate, and ozonized at dry ice-acetone temperatures by passing a stream of 1% ozone in oxygen through the solution from a Welsbach ozone generator. After ozone absorption ceased (measured by a potassium iodide indicator solution), the ozonide was decomposed by adding the ethyl acetate solution dropwise to 3 grams of zinc in 300 ml water and a little acetic acid. After stirring for several hours the mixture was filtered to remove the zinc, and the crude ketoaldehyde, which was not isolated, was oxidized to the ketoacid directly by addition of excess 30% hydrogen peroxide and formic acid to the filtrate. The mixture was allowed to stir for at least 12 hours and then extracted with ether. The combined ether extracts were washed several times with aqueous ferrous sulfate to destroy any peroxides present and then extracted with sodium carbonate solution until the sodium carbonate solution remained basic to litmus. The combined sodium carbonate extracts were acidified cautiously and the precipitated acid was collected by suction filtration. The crude acid was converted to the ethyl ester by refluxing it with excess ethanol and a trace of concentrated sulfuric acid in benzene and removing the water with a Dean-Stark trap. The dark mixture was washed with sodium bicarbonate solution to remove any acid, dried with magnesium sulfate, and the solvent removed by a rotary evaporator. The dark oil was dissolved in hot ethanol and treated with decolorizing carbon several times, The fairly white solid obtained was recrystallized from pentane-benzene solution at least twelve times until vpc analysis showed that no appreciable impurities were present (mp 54°, overall percent yield equals $\sim$20%).

j. δ-Cyano-p-methoxyvalerophenone (DCPMVP). The general procedure of Cason[74] was used. To the Grignard reagent prepared from 0.25 moles of p-bromoanisole in ether was added an ether solution of 4-chlorobutyronitrile. After the addition was completed, the mixture was allowed to stir for 30 minutes while being heated on a steambath and then poured into a cold dilute hydrochloric acid solution. The organic layer that formed was separated, and the aqueous layer was heated for several hours on the steam bath to hydrolyze the imine salt. On cooling of the mixture, a dark oil separated out, which on standing solidified. The collected solid was dissolved in the ether extract of the aqueous filtrate, and the ether solution was treated with decolorizing carbon and magnesium sulfate to dry it. On dilution with pentane or hexane and cooling, crystals formed which were collected and recrystallized several times from hexane-ether mixtures. The crude chloroketone obtained in this manner was dissolved in dry dimethylsulfoxide and excess sodium cyanide was added. The mixture was heated to 90° for two hours and then poured into water. The solid that formed was collected and recrystallized several times from ether-hexane solution after treatment with decolorizing carbon. The white solid obtained (mp 61°C.) showed no appreciable impurities on vpc analysis (overall percent yield equals ∿ 30%).

k. Valerophenone (VP). Eastman Chemical Company (Rochester, N.Y.) valerophenone purified by A. E. Kemppainen was used.

1. γ-Carbomethoxy-p-methoxybutyrophenone. The procedure of Johnson[78] was used in the preparation of this ketone. The compound was purified by repeated crystallization from methanol (mp 54-55°, overall percent yield equals 50%).

3. Internal Standards

a. Tetradecane. Columbia Chemical Company (Columbia, S.C.) tetradecane was treated in the same manner as benzene and vacuum distilled (bp 92.5° at 4 torr).

b. Pentadecane. Pentadecane (Columbia Chemical Company, Columbia, S.C.) was treated in the same manner as benzene and vacuum distilled (bp 132° at 10 torr).

c. Hexadecane. Aldrich hexadecane was treated in the same manner as benzene and vacuum distilled (bp 146° at 10 torr).

d. Octadecane. Octadecane (Chemical Samples Company, Columbus, Ohio) was treated in the same manner as benzene and then recrystallized from ethanol (mp 30°).

4. Quenchers

a. Lanthanide Chlorides. The lanthanide chlorides were purchased from Alfa Inorganics (Beverly, Mass.) and used as obtained. All were of greater than 99% purity, and all, except the europium chloride, were the hexahydrates.

b. Naphthalene. Aldrich Chemical Company (Milwaukee, Wisconsin) naphthalene was recrystallized twice from ethanol.

c. 2,4-Dimethyl-2,5-hexadiene. Aldrich Chemical Company (Milwaukee, Wisconsin) 2,4-dimethyl-2,5-hexadiene was recrystallized from itself and allowed to sublime on standing in the refrigerator.

d. cis-Piperylene. Chemical Samples Company (Columbus, Ohio) cis-piperylene (greater than 99% pure) was used as purchased.

B. General Procedures

1. Stern-Volmer Quenching Studies

Two stock solutions were prepared for each run. One solution contained the ketone and the appropriate internal standard, and the other containing the triplet quencher. Both stock solutions were prepared by weighing the appropriate amount of compound into a volumetric flask followed by dilution with benzene up to the volume line. The concentration and volume of ketone and quencher stock solutions depended upon the number of samples to be prepared for that individual run. Equal aliquots of the ketone-standard solution were pipetted into 10 ml volumetric flasks. To these were added varying aliquots of the quencher solution, followed by benzene addition to dilute the sample up to the volumetric mark. The concentrations of ketone and standard generally, were about 0.10 M and 0.004 M, respectively, unless specified differently for a specific run. The concentration of the quencher stock solution and the amount of final quencher in the samples that were to be photolyzed depended on the lifetime of the ketone triplet which was to be quenched. In general quencher concentrations greater than 10^{-2} M were not used in the samples, if the quencher was an organic compound. Usually each run contained two samples without quencher which were photolyzed, and one sample without quencher which was unphotolyzed and retained as a blank.

In the runs where the lanthanide chlorides were used as quenchers, the ketone stock solution was prepared as above, except that methanol was used as solvent. Due to solubility limitations, stock solutions of the lanthanide chlorides could not be prepared. Instead, varying amounts of the lanthanide chloride were weighed into 10 ml volumetric flasks to which equal aliquots of the stock ketone solutions were added, followed by dilution with methanol to the volumetric mark.

2. Polar Solvent Effect Studies

Two stock solutions were again prepared for each run. One solution contained the ketone and the internal standard, just as in the quenching studies, dissolved in benzene. The other was a 10 molar solution of the polar solvent in benzene. From this 10 molar stock solution, a substock solution 1.0 molar in polar solvent was prepared, which was to be used in the preparation of samples containing less than 1.0 molar polar solvent. Both stock solutions were prepared by weighing the appropriate amount of compound into a volumetric flask followed by dilution with benzene up to the volume mark. Equal aliquots of the ketone-standard solution were pipetted into 10 ml volumetric flasks. To these were added varying aliquots of the polar solvent master solution, and the volume was then brought up to the volumetric mark by addition of benzene. The concentration of polar solvent in the samples generally ranged from 0.10 M to 8.0 M. Usually each run contained two samples without any polar solvent which were photolyzed, and one sample without any polar solvent that was kept as a blank.

3. Photolysis

After the solutions containing proper concentrations of ketone, internal standard, and quencher or added polar solvent were prepared, 2.8 ml aliquots of each were placed in 13 x 10 mm Pyrex tubes using a 5 ml syringe with a six inch needle. The tubes had previously been constricted about 2 cm from the top, so that they could be easily sealed after being degassed by four freeze-thaw cycles ($P < 0.005$ torr), using liquid nitrogen. The samples were irradiated in parallel using a water bath immersed merry-go-round apparatus[79] to insure that all the samples received the same amount of incident light and that the temperature remained constant. A 450 watt Hanovia medium pressure mercury lamp was used as light source, and the 3130 Å region was isolated by a 1 cm path of a 0.002 M potassium chromate - 1% potassium carbonate aqueous filter solution. The 3660 Å line, used in quenching studies with naphthalene, was isolated by a set of Corning No. 7083 filters.

4. Vapor Phase Chromatography

Analysis for acetophenones, cyclobutanols, and alkane internal standards were conducted on either an Aerograph Hy-Fi, Model 600-D, or a Varian Aerograph Hy-Fi III, Series 1200, chromatograph. The instruments used a flame ionization detector and were equipped with a 6' x 1/8" column containing 4% QF-1 and 1% Carbowax 20 M on Chromosorb G (Column A). A column temperature of 150-160° effectively separated p-methoxyacetophenone and octadecane. Lower temperatures used for analysis of other acetophenones and alkanes will be specified for that individual run. *Cis*-piperylene/acetophenone actinometers were analyzed on a Aerograph Hy-Fi Model 600-D equipped with a 20' x 1/8" aluminum column packed with 25% 1,2,3-tris(2-cyanoethoxy)propane on 60/80 Chromosorb P (Column B). A column temperature of 50 degrees allowed good separation of the *trans* isomer from the *cis*. The recorders used with these chromatographs were equipped with Disc integrators, from which the relative peak areas are given in integrator counts.

5. Valerophenone Actinometry

Samples containing 0.10 M valerophenone and 0.004 M tetradecane as internal standard were irradiated concurrently, for less than 2.0 hour periods, with ketone samples whose quantum yield was to be determined. Analysis for acetophenone and tetradecane were performed using column A at a temperature of 106-110°. The Type II quantum yield for valerophenone was taken to equal 0.33[35]. Since the vpc detector will respond differently to each compound, it is necessary to include a standardization factor, (S.F.), in the analysis of the amount of product formed. This S.F. equals the ratio of area/mole of standard to area/mole of product. For acetophenone, the standardization factor equals 2.0 (Note: all S.F. used in this thesis were determined by A. E. Kemppainen[80]) and the concentration of acetophenone formed will equal:

$$[\text{acetophenone}] = [\text{tetradecane}] \times \text{S.F.} \times \frac{\text{Counts of ACP}}{\text{Counts of } C_{14}} \qquad (52)$$

The number of incident light quanta on the samples during the period of irradiation of the actinometer tube will then equal

$$\frac{\text{quanta absorbed}}{\ell.} = \frac{[\text{Acetophenone}]}{0.33} \tag{53}$$

6. Cis-piperylene/Acetophenone Actinometry

Samples containing 0.10 M acetophenone and 0.20 M *cis*-piperylene were irradiated concurrently with ketone samples whose quantum yield was to be determined. All the incident light is absorbed by the acetophenone, which intersystem crosses to the triplet state quantitatively[19]. The triplet acetophenone is completely quenched by *cis*-piperylene, whose triplet state then decays to a mixture of the *cis* and *trans* isomers of the diene. Irradiation of actinometer tubes were usually carried out to less than 15 percent *trans* formation, and column B was used in the vpc analysis to determine the percent *trans*-piperylene formed. The following relationship gives the number of incident quanta of light on the actinometer sample during the photolysis time[19].

$$[\textit{cis}\text{-piperylene}]_0 \times \ln \frac{.555}{.555 - \%\ \textit{trans}} \tag{54}$$

$$= [\text{excited triplet piperylene}]$$

where the concentration of excited piperylene equals the intensity of incident light on the sample.

III. LITERATURE CITED

LITERATURE CITED

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IV. APPENDIX

APPENDIX

TABLE 6. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by Naphthalene in Methanol.

Sample	[Naphthalene][a]	$\frac{\text{Counts PMACP}^b}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ^d
0[c]	None	1.15	1.00
1	2.0×10^{-5} M	1.00	1.15
2	4.0×10^{-5} M	0.715	1.61
3	6.0×10^{-5} M	0.620	1.85
4	8.0×10^{-5} M	0.580	1.98

[a] All concentrations in moles per liter. [b] 0.004 M $C_{18}H_{38}$ used as internal standard. [c] Average of two samples, samples irradiated for one week at 3660 Å. [d] $k_q\tau$ equals 13,100 M^{-1}.

TABLE 7. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by Naphthalene in Methanol[a].

Sample	[Naphthalene][b]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ^d
0[e]	None	0.80	1.00
1	2×10^{-5} M	0.70	1.15
2	4×10^{-5} M	0.53	1.52
3	6×10^{-5} M	0.44	1.82
4	8×10^{-5} M	0.38	2.09

[a] Plotted in Figure 4. [b] All concentrations in moles per liter. [c] 0.004 M $C_{18}H_{38}$ used as internal standard. [d] $k_q\tau$ equals 13,000 M^{-1}. [e] Average of two samples, samples irradiated for one week at 3660 Å.

FIGURE 4. Stern-Volmer Plot for the Quenching of p-Methoxyvalerophenone by Naphthalene in Methanol

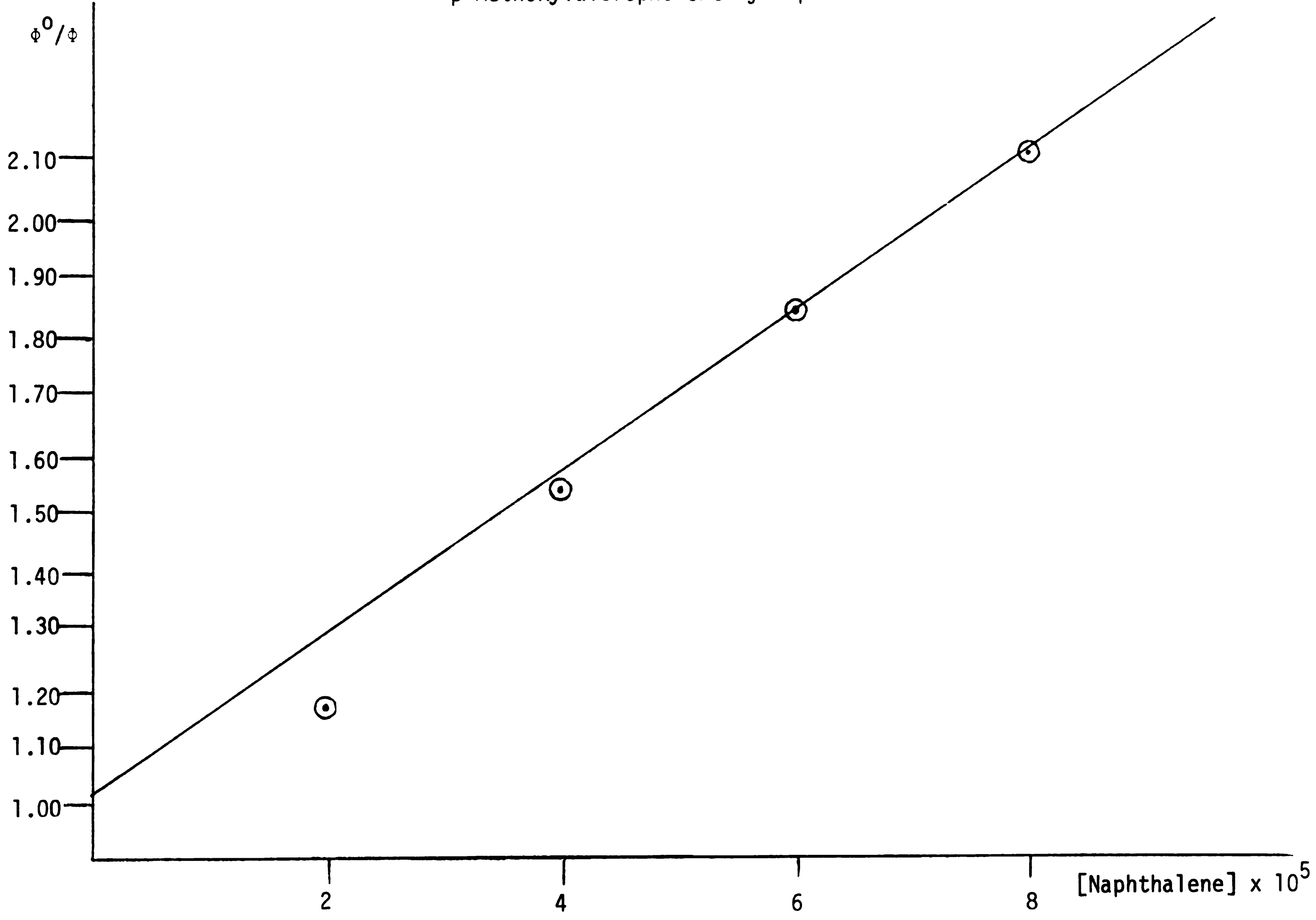

TABLE 8. Stern-Volmer Quenching Study of 0.1 M p-Methoxyvalerophenone by $EuCl_3$ in Methanol[a].

Sample[b]	$[Eu^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	1.85	1.00
1	0.001 M	1.42	1.30
2	0.002 M	----	----
3	0.003 M	0.79	2.34
4	0.004 M	0.74	2.50

[a] k_q τ equals 400 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples irridiated for 14 hours at 3130 Å. Tubes had turned yellow.

TABLE 9. Stern-Volmer Quenching Study of 0.1 M p-Methoxyvalerophenone by $EuCl_3$ in Methanol[a].

Sample[b]	$[Eu^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	1.87	1.00
1	0.001 M	1.50	1.25
2	0.002 M	1.26	1.47
3	0.003 M	1.00	1.87
4	0.004 M	0.935	1.98

[a] k_q τ equals 250 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples irradiated for 15 hours at 3130 Å.

TABLE 10. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by $SmCl_3 \cdot 6H_2O$ in Methanol[a].

Sample[b]	$[Sm^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	1.98	1.00
1	0.010 M	1.18	1.68
2	0.013 M	1.25	1.58
3	0.016 M	1.09	1.81
4	0.020 M	1.02	1.94

[a] $k_q \tau$ equals 48 M^{-1}. [b] Solutions contain 0.004 M C_{18} as internal standard. [c] Samples irradiated for 14 hours at 3130 Å.

TABLE 11. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by $TbCl_3 \cdot 6H_2O$ in Methanol[a].

Sample[b]	$[Tb^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	1.95	1.00
1	0.01	1.00	1.95
2	0.02	0.84	2.32
3	0.03	0.68	2.87
4	0.04	0.65	3.00

[a] $k_q \tau$ equals 62.5 M^{-1}. [b] Solutions contain 0.004 M C_{18} as internal standard. [c] Samples irradiated for 11 hours at 3130 Å.

TABLE 12. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by $TbCl_3 \cdot 6H_2O$ in Methanol[a].

Sample[b]	$[Tb^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	1.68	1.00
1	0.010	1.05	1.60
2	0.013	0.98	1.71
3	0.016	0.96	1.75
4	0.020	0.84	2.00

[a] $k_q\ \tau$ equals 50 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples irradiated for 12 hours at 3130 Å.

TABLE 13. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by $DyCl_3 \cdot 6H_2O$ in Methanol[a].

Sample[b]	$[Dy^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	3.11	1.00
1	0.01	1.63	1.90
2	0.02	1.63	1.90
3	0.03	1.27	2.44

[a] $k_q\ \tau$ equals 50 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples irradiated for 12 hours at 3130 Å.

TABLE 14. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by $DyCl_3 \cdot 6H_2O$ in Methanol[a].

Sample[b]	$[Dy^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	2.08	1.00
1	0.01	0.99	2.10
2	0.02	0.86	2.42
3	0.03	0.83	2.50
4	0.04	0.69	3.02

[a] $k_q \tau$ equals 57 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples irradiated for 12 hours at 3130 Å.

TABLE 15. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by $ErCl_3 \cdot 6H_2O$ in Methanol[a].

Sample[b]	$[Er^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	0.97	1.00
1	0.01	0.52	1.87
2	0.02	0.34	2.75
3[d]	0.03	0.39	2.49
4	0.04	0.17	5.70

[a] $k_q \tau$ equals 111 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples irradiated for 21 hours at 3130 Å. [d] Windows formed in samples with higher quencher concentration.

TABLE 16. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by $ErCl_3 \cdot 6H_2O$ in Methanol[a].

Sample[b]	$[Er^{+3}]$	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ
0	None	2.26	1.00
1	0.010	1.38	1.64
2	0.013	1.33	1.70
3[d]	0.016	1.12	2.02
4	0.020	0.95	2.39

[a] $k_q\tau$ equals 70 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standards. [c] Samples irradiated at 3130 Å for 21 hours. [d] Windows formed in samples with higher quencher concentrations.

TABLE 17. Type II Quantum Yield Determinations for p-Methoxyphenyl Alkyl Ketones[a]

Ketone	Counts PMACP / Counts $C_{18}H_{38}$	[PMACP]	$[C_{18}H_{38}]$	I/I.	Φ_{II}
PMBP[b]	0.71	0.006 M	0.004 M	0.540	0.012
PMVP[c]	2.82	0.026 M	0.004 M	0.178	0.145
GMPMVP[d]	2.50	0.023 M	0.004 M	0.104	0.22
PMVP[e,f]	1.97	0.018 M	0.004 M	0.200	0.09

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[a] Values determined by acetophenone/<u>cis</u>-piperylene actinometry. [b] Samples photolyzed for 20 hours at 3130 Å. [c] Samples photolyzed for 10 hours at 3130 Å. [d] Samples photolyzed for 6 hours at 3130 Å. [e] Samples photolyzed for 8 hours at 3130 Å in methanol. [f] Valerophenone actinometry used.

TABLE 18. Acetophenone/<u>cis</u>-Piperylene Actinometry for p-Methoxyvalerophenone and γ-Methyl-p-methoxyvalerophenone

Sample	Photolysis Time	% trans	Light Quanta Absorbed / 2.5 hour 1.	Cumulative light quanta
A1	2.5 hours	10.5	0.0414	0.0414
A2	2.5 hours	11.0	0.0446	0.860
A3	2.5 hours	11.2	0.0454	0.1314
A4	2.5 hours	11.6	0.0470	0.1784

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[a] 0.10 M Acetophenone and 0.20 M <u>cis</u>-piperylene in benzene.

TABLE 19. Acetophenone/cis-Piperylene Actinometry[a] for p-Methoxybutyrophenone

Sample	Photolysis Time	% trans	Light Quanta Absorbed hour 1,
A1	1.28 hours	9.5	0.030
A2	2.00 hours	14.1	0.029
A3	1.60 hours	9.2	0.025

[a] 0.10 M Acetophenone and 0.20 M cis-piperylene in benzene.

TABLE 20. Type II Quantum Yield Determinations for Ring Substituted Valerophenones[a]

Substituent	Product Counts / Standard Counts	SF	$[C_nH_{2n+2}]$	Φ_{II}
p-Cl[b]	0.925	2.3	6.0×10^{-3}M	0.253
m-CF_3[c]	0.79	1.8	"	0.175
p-CH_3[d]	1.18	2.2	"	0.31

[a] Based on actinometer (0.10 M acetophenone and 0.205 M cis-piperylene) isomerization to 12.30% trans. Photolysis time is 1.5 hours. [b] VPC column #A, Column Temperature = 150°C. [c] VPC column #A, Column Temperature = 115°C. [d] VPC column #A, Column Temperature = 125°C.

TABLE 21. Type II Quantum Yield Determination for δ-Substituted p-Methoxyvalerophenones

Substituents	$\frac{\text{Counts PMACP}}{\text{Counts } C_{18}H_{38}}$	[PMACP]	$[C_{18}H_{38}]$	Φ_{II}
δ -CO_2Et[a]	2.10	0.0193 M	4 x 10^{-3} M	0.104
δ -CN[b]	0.45	0.0041 M	4 x 10^{-3} M	0.009

[a] 0.05 M ketone, S.F. = 2.3, photolyzed for 12 hours at 3130 Å.

[b] 0.05 M ketone, S.F. = 2.3, photolyzed for 27 hours at 3130 Å.

TABLE 22. Valerophenone Actinometry for δ-Carboethoxy-p-methoxyvalerophenone and γ-Carbomethoxy-p-methoxybutyrophenone

Sample[a]	$\frac{\text{Counts ACP}}{\text{Counts } C_{14}H_{30}}$	[ACP]	$\frac{\text{Light Quanta Absorbed}^{b}}{\text{hour l.}}$
A1	0.65	5.2 x 10^{-3}M	0.0155
A2	0.63	5.0 x 10^{-3}M	0.0151
A3	0.66	5.3 x 10^{-3}M	0.0158
A4	0.64	5.1 x 10^{-3}M	0.0153
A5	0.65	5.2 x 10^{-3}M	0.0155
A6	0.64	5.1 x 10^{-3}M	0.0153

[a] 0.10 M ketone, 0.004 M $C_{14}H_{30}$ as internal standard, S.F. = 2.0.

[b] Average lamp output = 0.0155 quanta (of incident light) per hour per liter.

TABLE 23. Valerophenone Actinometry for
δ-Cyano-p-methoxyvalerophenone

Sample[a]	Counts ACP / Counts $C_{14}H_{30}$	[ACP]	Light Quanta Absorbed / hour l.
A1	0.69	5.5×10^{-3}M	0.0165
A2	0.70	5.6×10^{-3}M	0.0168
A3	0.73	5.8×10^{-3}M	0.0170
A4	0.68	5.4×10^{-3}M	0.0160
A5	0.68	5.4×10^{-3}M	0.0160

[a] 0.10 M valerophenone, 0.004 M $C_{14}H_{38}$ as internal standard, S.F. = 2.0. [b] Average lamp output = 0.0165 quanta (of incident light) per hour per liter.

TABLE 24. Valerophenone Actinometry for
p-Methoxyvalerophenone in Methanol

Sample[a]	Counts ACP / Counts $C_{14}H_{30}$	[ACP]	Light Quanta Absorbed / hour l.
A1	2.35	0.019	0.026
A2	2.02	0.016	0.025
A3	1.07	0.0085	0.026

[a] Solutions contain 0.10 M valerophenone and 0.004 M $C_{14}H_{30}$ as internal standard. [b] Average lamp output equals 0.0255 quanta per hour per liter.

TABLE 25. Determination of ϕ_{isc} for ortho, meta, and para-Methoxyvalerophenone in Benzene by Isomerization of cis-Piperylene[a]

Ketone[b]	Sample 1 % trans	Sample 2 % trans	Average[c] % trans
Benzophenone	16.4	16.6	16.5
OMVP	15.9	15.8	15.8
MMVP	16.4	16.0	16.2
PMVP	16.5	16.1	16.3

[a] Solutions contained 0.10 M ketone and 0.20 M cis-piperylene. [b] Samples irradiated for 2.5 hours at 3130 Å. [c] VPC analysis performed using column B.

TABLE 26. The Photolysis of 0.10 M p-Methoxyvalerophenone in Benzene and added Methanol

Sample[a]	[Methanol]	$\frac{\text{Counts PMACP}^b}{\text{Counts } C_{18}H_{38}}$	Φ_A/Φ_B	Φ_{II}
0	None	1.51	1.00	0.145
1	0.10M	1.78	1.18	0.171
2	0.20M	1.99	1.32	0.191
3	0.40M	1.94	1.28	0.186
4	0.60M	1.63	1.08	0.157
5	0.80M	1.88	1.24	0.180
6	1.00M	1.91	1.26	0.183
7	2.00M	1.32	0.87	0.126
8	3.00M	1.12	0.74	0.108
9	4.00M	0.39	0.26	0.038
10	5.00M	0.37	0.25	0.036

[a] Solutions contain 0.0056M $C_{18}H_{38}$ as internal standard. [b] Samples photolyzed for 10 hours at 3130 Å.

TABLE 27. The Photolysis of 0.10 M p-Methoxyvalerophenone in Benzene and added t-Butanol

Sample[a]	[t-butanol]	$\frac{\text{Counts PMACP}^b}{\text{Counts } C_{18}H_{38}}$	Φ_A/Φ_B	Φ_{II}
0	None	1.86	1.00	0.145
1	0.10M	2.25	1.21	0.175
2	0.20M	2.32	1.25	0.181
3	0.40M	2.72	1.46	0.212
4	0.60M	2.72	1.46	0.212
5	0.80M	2.79	1.50	0.218
6	1.00M	2.80	1.51	0.218
7	1.60M	2.95	1.59	0.230
8	2.40M	2.87	1.54	0.224
9	3.20M	2.75	1.48	0.216
10	4.00M	2.35	1.26	0.183

[a] Solutions contain 0.0050 M $C_{18}H_{38}$ as internal standard. [b] Samples photolyzed for 9 hours at 3130 Å.

TABLE 28. The Photolysis of 0.10 M p-Methoxyvalerophenone in Benzene and added Pyridine.

Sample[a]	[Pyridine]	$\frac{\text{Counts PMACP}^b}{\text{Counts } C_{18}H_{38}}$	Φ_P/Φ_P	Φ_{II}
0	None	1.56	1.00	0.145
1	0.10M	1.70	1.09	0.158
2	0.20M	1.93	1.24	0.180
3	0.40M	2.06	1.32	0.192
4	0.60M	2.13	1.37	0.199
5	0.80M	2.13	1.37	0.199
6	1.00M	2.14	1.37	0.199
7	2.00M	2.10	1.35	0.196
8	3.00M	1.98	1.27	0.184
9	4.00M	1.89	1.21	0.176
10	5.00M	1.72	1.10	0.160

[a] Solutions contain 0.005 M $C_{18}H_{38}$ as internal standard. [b] Samples photolyzed for 9.5 hours at 3130 Å.

TABLE 29. The Photolysis of 0.10 M γ-Methyl-p-methoxyvalerophenone in Benzene and Added t-Butanol

Sample[a]	[t-butanol]	$\frac{\text{Counts PMACP}^b}{\text{Counts } C_{18}H_{38}}$	Φ_A/Φ_B	Φ_{II}
0	None	2.48	1.00	0.22
1	0.50M	5.73	2.32	0.29
2	1.00M	6.83	2.76	0.39
3	2.00M	6.89	2.80	0.40
4	4.00M	6.25	2.53	0.33
5	6.00M	2.48	1.00	0.22
6	8.00M	1.82	0.74	0.16

[a] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [b] Samples were photolyzed for 10 hours 3130 Å.

TABLE 30. Photolysis of 0.10 M p-Methoxybutyrophenone in Benzene and Added t-Butanol

Sample[a]	[t-Butanol]	$\frac{\text{Counts PMACP}^b}{\text{Counts } C_{18}H_{38}}$	Φ_A/Φ_B	Φ_{II}
0	None	0.415	1.00	0.0121
1	0.10M	0.430	1.04	0.0125
2	0.20M	0.42	1.03	0.0124
3	0.50M	0.80	1.93	0.0232
4	1.00M	1.08	2.60	0.0312
5	2.00M	1.24	2.98	0.0358
6	4.00M	1.24	2.98	0.0358

[a] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard.

[b] Samples photolyzed for 24 hours at 3130 Å.

TABLE 31. Photolysis of 0.06 M m-Trifluoromethylvalerophenone in Benzene and t-Butanol

Sample[a]	[t-Butanol]	$\frac{\text{Counts MTFACP}}{\text{Counts } C_{14}H_{30}}$[b]	Φ_A/Φ_B	Φ_{II}
0	None	1.23	1.00	0.175
1	2.0M	2.53	2.02	0.35
2	4.0M	2.72	2.17	0.39
3	6.0M	2.80	2.28	0.40
4	8.0M	3.15	2.56	0.45

[a] Solution contains 0.004 M $C_{14}H_{30}$ as internal standard.
[b] Samples photolyzed for 1.5 hours at 3130 Å.

TABLE 32. Photolysis of 0.06 M p-Methylvalerophenone in Benzene and t-Butanol

Sample[a]	[t-Butanol]	$\frac{\text{Counts PMeACP}}{\text{Counts } C_{15}H_{32}}$[b]	Φ_A/Φ_B	Φ_{II}
0	None	2.12	1.00	0.31
1	2.0M	4.51	2.13	0.66
2	4.0M	4.62	2.18	0.68
3	6.0M	4.64	2.19	0.68
4	8.0M	2.25	1.06	0.32

[a] Solutions contain 0.004 M $C_{15}H_{32}$ as internal standard.
[b] Samples photolyzed at 3130 Å for 1.5 hours.

TABLE 33. Photolysis of 0.06 M p-Chlorovalerophenone in Benzene and Added t-Butanol

Sample[a]	[t-Butanol]	$\frac{\text{Counts PCACP}^b}{\text{Counts } C_{16}H_{34}}$	Φ_A/Φ_B	Φ_{II}
0	None	1.59	1.00	0.25
1	2.0M	4.08	2.57	0.64
2	4.0M	4.44	2.78	0.70
3	6.0M	4.59	2.88	0.72
4	8.0M	4.35	2.74	0.68

[a] Solutions contain 0.004 M $C_{16}H_{34}$ as internal standard.
[b] Samples photolyzed for 1.5 hours at 3130 Å.

TABLE 34. Photolysis of 0.05 M δ-Carboethoxy-p-methoxyvalerophenone in Benzene and Added t-Butanol

Sample[a]	[t-Butanol]	$\frac{\text{Counts PMACP}^b}{\text{Counts } C_{18}H_{38}}$	Φ_A/Φ_B	Φ_{II}
0	None	1.79	1.00	0.104
1[c]	None	1.78	1.00	0.104
2	0.3M	1.96	1.10	0.114
3	0.5M	1.89	1.06	0.111
4	1.0M	2.34	1.32	0.137
5	2.0M	1.97	1.12	0.116
6	4.0M	1.85	1.05	0.108
7	6.0M	1.00	0.56	0.058
8	8.0M	0.78	0.44	0.046

[a] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [b] Samples photolyzed for 9 hours at 3130 Å. [c] Sample contains 0.10 M ketone.

TABLE 35. Photolysis of δ-Cyano-p-methoxyvalerophenone in Benzene and Added t-Butanol

Sample[a]	[t-Butanol]	$\frac{\text{Counts PMACP}^{b}}{\text{Counts } C_{18}H_{38}}$	Φ_A/Φ_B	Φ_{II}
0	None	0.45	1.00	0.009
1	0.1M	0.31	0.69	0.006
2	0.3M	0.35	0.78	0.007
3	0.5M	0.41	0.92	0.008
4	1.0M	0.59	1.51	0.014
5	2.0M	0.62	1.37	0.012
6	4.0M	0.59	1.31	0.012
7	6.0M	0.48	1.06	0.010

[a] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard.

[b] Samples photolyzed for 26 hours at 3130 Å.

TABLE 36. Values of Maximum Quantum Yields of Selected Phenyl n-Butyl Ketones

Ketone	[t-Butanol]	$\frac{\text{Counts Cyclobutanol}}{\text{Counts Standard}}$	Φ cycl.[a,b]	Φ_{II}	Φ_{total}
p-Meo	None	0.50	0.03	0.15	0.18
p-Meo	1.6M	0.64	0.04	0.23	0.27
p-Me	None	0.78	0.07	0.31	0.38
p-Me	6.0M	1.05	0.10	0.68	0.78
p-Cl	None	0.40	0.05	0.25	0.30
p-Cl	6.0M	0.49	0.08	0.72	0.80

[a] Quantum yield values in alcohol are maximum quantum yields reached on addition of polar solvents. [b] Values are ± 10%.

TABLE 37. Stern-Volmer Quenching Study of 0.10 M p-Methoxyvalerophenone by 2,4-Dimethyl-2,5-hexadiene in Benzene[a]

Sample[b]	[Diene]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o_{II}/Φ_{II}
0	None	2.87	1.00
1	0.5×10^{-4} M	1.45	1.98
2	1.0 x " "	0.91	3.18
3	1.5 x " "	0.66	4.35
4	2.0 x " "	0.51	5.66

[a] $k_q \tau$ equals 2300 M^{-1}. [b] Solution contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples photolyzed for 9.5 hours at 3130 Å.

TABLE 38. Stern-Volmer Quenching Study of 0.10 M γ-Methyl-p-methoxyvalerophenone by 2,4-Dimethyl-2,5-hexadiene in Benzene[a]

Sample[b]	[Diene]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o_{II}/Φ_{II}
0	None	2.50	1.00
1	1.0×10^{-3} M	1.32	1.90
2	2.0 x " "	0.77	3.24
3	3.0 x " "	0.57	4.38
4	4.0 x " "	0.47	5.32

[a] $k_q \tau$ equals 1100 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples photolyzed for 6 hours at 3130 Å.

TABLE 39. Stern-Volmer Quenching Study of 0.10 M p-Methoxybutyrophenone by 2,4-Dimethyl-2,5-hexadiene in Benzene[a]

Sample[b]	[Diene]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o_{II}/Φ_{II}
0	None	0.415	1.00
1	4.0×10^{-4}M	0.166	2.44
2	6.0 x " "	0.158	2.58
3	8.0 x " "	0.113	3.78

[a] $k_q\tau$ equals 3300 M^{-1}. [b] Solutions contain 0.044 M $C_{18}H_{38}$ as internal standard. [c] Samples photolyzed for 24 hours at 3130 Å.

TABLE 40. Stern-Volmer Quenching Study of p-Methoxybutyrophenone by 2,4-Dimethyl-2,5-hexadiene in Benzene[a]

Sample[b]	[Diene]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o_{II}/Φ_{II}
0	None	0.90	1.00
1	1.0×10^{-4}M	0.66	1.36
2	2.0 x " "	0.57	1.58
3	3.0 x " "	0.45	2.02
4	4.0 x " "	0.39	2.31

[a] $k_q\tau$ equals 3300 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Tubes photolyzed at 3130° for 24 hours.

TABLE 41. Stern-Volmer Quenching Study of 0.05 M γ-Carbomethoxy-p-methoxybutyrophenone by 2,4-Dimethyl-2,5-hexadiene in Benzene[a]

Sample[b]	[Diene]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o_{II}/Φ_{II}
0	None	0.32	1.00
1	0.001 M	0.215	1.49
2	0.002 M	0.112	2.87
3	0.003 M	0.101	3.18
4	0.004 M	0.074	4.34

[a] k_q τ equals 830 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples photolyzed for 29 hours at 3130 Å. [d] Based on 6% conversion; values are strongly dependent on per cent conversion.

TABLE 42. Stern-Volmer Quenching Study of 0.05 M δ-Carboethoxy-p-methoxyvalerophenone by 2,4-Dimethyl-2,5-hexadiene in Benzene[a]

Sample[b]	[Diene]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o/Φ_{II}
0	None	2.10	1.00
1	2.0 x 10^{-3}M	0.45	4.67
2	4.0 x " "	0.21	10.00
3	6.0 x " "	0.14	11.20
4	8.0 x " "	0.10	20.80

[a] k_q τ equals 2500 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples photolyzed for 12 hours at 3130 Å.

TABLE 43. Stern-Volmer Quenching Study of 0.05 M δ-Cyano-p-methoxyvalerophenone by 2,4-Dimethyl-2,5-hexadiene in Benzene[a]

Sample[b]	[Diene]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o_{II}/Φ_{II}
0	None	0.45	1.00
1	1.0×10^{-4}M	0.38	1.17
2	2.0 x " "	0.35	1.26
3	3.0 x " "	0.25	1.80
4	4.0 x " "	0.22	2.04

[a] $k_q \tau$ equals 2500 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Samples photolyzed for 27 hours at 3130 Å.

TABLE 44. Stern-Volmer Quenching Study of 0.05 M δ-Cyano-p-methoxyvalerophenone by 2,4-Dimethyl-2,5-hexadiene in Benzene[a]

Sample[b]	[Diene]	$\frac{\text{Counts PMACP}^c}{\text{Counts } C_{18}H_{38}}$	Φ^o_{II}/Φ_{II}
0	None	0.55	1.00
1	2.0×10^{-4}M	0.39	1.40
2	4.0 x " "	0.26	2.12
3	6.0 x " "	0.22	2.56
4	8.0 x " "	0.18	3.04

[a] $k_q \tau$ equals 2500 M^{-1}. [b] Solutions contain 0.004 M $C_{18}H_{38}$ as internal standard. [c] Tubes photolyzed for 25 hours at 3130 Å.