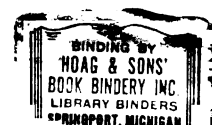
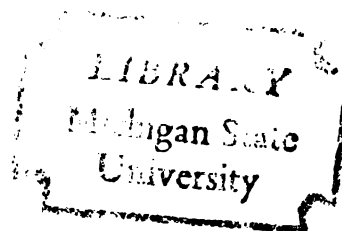


A STUDY OF CHARGE TRANSFER
CHARACTER IN THE PHOTOREDUCTION OF
VARIOUS α -TRIFLUOROACETOPHENONES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
HENRY MAN HUNG LAM

1975

THESIS



69073

ABSTRACT

A STUDY OF CHARGE TRANSFER CHARACTER IN THE PHOTOREDUCTION OF VARIOUS α -TRIFLUOROACETOPHENONES

By

Henry Man Hung Lam

The photoreduction of α -trifluoroacetophenone by toluene in acetonitrile has been examined. Since the ability of alkylbenzenes to quench triplet α -trifluoroacetophenone is linearly dependent on their ionization potentials, the presence of charge transfer process in the triplet quenching is affirmed. The slope from a plot of log quenching rate constant versus ionization potential indicates only $\sim 21\%$ electron transfer in the triplet charge transfer complex.

The photoreduction of several substituted α -trifluoroacetophenones having either $n\pi^*$ and $\pi\pi^*$ lowest triplet has been studied. The $\pi\pi^*$ lowest triplet ketones have lower reactivity than the $n\pi^*$ low-lying triplet ketones. The plot of log quenching rate constant versus the sum of triplet energy and reduction potential does not show a good linear relationship and thus obscures the interpretation of the data. Perhaps the different nature of the two lowest excited states may explain the difference in reactivities. However, the $\pi\pi^*$ lowest triplet ketones may be quenched by

Henry Man Hung Lam

an hydrogen abstraction process rather than a charge transfer process as observed in the quenching of $n\pi^*$ lowest triplet ketones.

A STUDY OF CHARGE TRANSFER CHARACTER IN THE
PHOTOREDUCTION OF VARIOUS α -TRIFLUOROACETOPHENONES

By

Henry Man Hung Lam

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1975

ACKNOWLEDGMENT

I wish to thank Professor Peter J. Wagner, who has provided me with the opportunity to complete this work. His guidance, and inspiration are sincerely appreciated.

I am particularly thankful to my fellow graduate students for their helpful assistance.

I would also like to acknowledge financial assistance from the Department of Chemistry throughout the course of my study.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
General Mechanistic Process	3
The Nature of the Excited States	4
The Correlations between the Reactivities of Hydrogen Abstraction and the Nature of the Excited State	6
Charge Transfer Mechanism	7
Previous Study of the Photoreduction of Trifluoroacetophenone	10
Objectives	11
Kinetics Expressions	12
RESULTS	15
Quantum Yield Determinations	15
Triplet Quenching Studies	15
Intersystem Crossing	16
Absorbance and Emission Spectra	17
DISCUSSION	29
EXPERIMENTAL	39
PART I: PROCEDURE	39
A. Preparation and Purification	39
1. Ketones	39
2. Solvent	41
3. Hydrogen Donors	41
4. Quenchers	42
5. Internal Standard	42

TABLE OF CONTENTS -- Continued.

	Page
B. Photolysis , . .	43
1. Irradiation Procedure	43
2. Analysis of Sample	43
C. Absorption and Emission Spectra . . .	46
D. Reduction Potential	46
PART II: KINETIC DATA	47
A. Quantum Yield of Bibenzyl Formation .	47
B. Quenching Studies	49
C. Determination of Intersystem Crossing Quantum Yield	56
LIST OF REFERENCES	57

LIST OF TABLES

Table	Page
1. Least squares slope and intercept values from ϕ_{BB}^{-1} versus $[BH]^{-1}$ plot for the photoreduction of indicated ketones with toluene	17
2. Triplet quenching parameters for the reaction of indicated ketone with 1M toluene by using the quencher, naphthalene in acetonitrile . .	18
3. Triplet quenching parameters for trifluoroacetophenone	18
4. Kinetics data for photoreduction of 0.05M indicated ketones with toluene in acetonitrile	19
5. Ultra violet absorption bands of indicated ketones	19
6. Phosphorescence data of indicated ketones . .	20
7. Substituent effects on triplet ketones . . .	37
8. Quantum yield of bibenzyl formation for 0.05M ketone in acetonitrile with toluene, indicated C_n and conditions	47
Part A: α -Trifluoroacetophenone	47
Part B: p -Methoxy- α -trifluoroacetophenone .	47
Part C: p -Methyl- α -trifluoroacetophenone . .	48
Part D: m -Chloro- α -trifluoroacetophenone . .	48
Part E: m -Trifluoromethyl- α -trifluoroacetophenone	48
Part F: p -Trifluoromethyl- α -trifluoroacetophenone	48
9. System with 0.05M α -trifluoroacetophenone and 0.1M toluene in acetonitrile quenching with specific quencher in indicated C_n and conditions	49
Part A: Anisole	49
Part B: Benzene	49
Part C: Benzotrifluoride	50
Part D: Benzonitrile	50
Part E: Chlorobenzene	50

LIST OF TABLES -- Continued.

Table	Page
Part F: Fluorobenzene	51
Part G: <u>p</u> -Dimethoxybenzene	51
Part H: <u>p</u> -Dichlorobenzene	51
10. System with 0.05M α -trifluoroacetophenone, 0.001M C ₂₀ and indicated amount of toluene in acetonitrile quenching with naphthalene . . .	52
Part A: 1M Toluene	52
Part B: 0.4M Toluene	52
11. System with 0.05M <u>p</u> -methoxy- α -trifluoroaceto- phenone, 0.001M C ₂₀ and indicated amount of toluene in acetonitrile, quenching with naphthalene	53
Part A: 1M Toluene	53
Part B: 2M Toluene	53
12. 0.05M <u>m</u> -Trifluoromethyl- α -trifluoroaceto- phenone-0.1M toluene system in acetonitrile quenching with indicated concentration of naphthalene	54
13. 0.05M <u>m</u> -Chloro- α -trifluoroacetophenone-1M toluene system in acetonitrile quenching with indicated concentration of naphthalene . . .	54
14. 0.05M <u>p</u> -Methyl- α -trifluoroacetophenone-1M toluene system in acetonitrile quenching with indicated concentration of naphthalene . . .	55
15. 0.05M <u>p</u> -Trifluoromethyl- α -trifluoroaceto- phenone-0.1M toluene system in acetonitrile quenching with indicated concentration of naphthalene	55
15. Triplet sensitized <u>cis-trans</u> isomerization of piperylene	56

LIST OF FIGURES

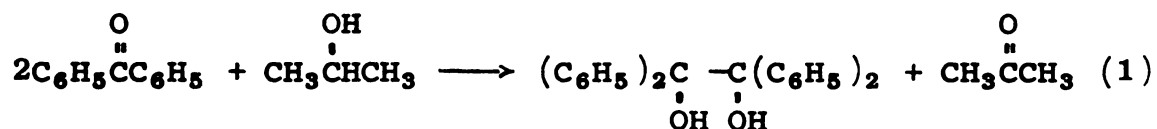
Figure	Page
1. Jablon'ski's diagram	4
2. Reciprocal quantum yield plot for indicated ketones with toluene	21
3. Reciprocal quantum yield plot for indicated ketones with toluene	22
4. Stern-Volmer plots for naphthalene quenching of photoreduction of indicated ketones by 1M toluene	22
5. Stern-Volmer plots for naphthalene quenching of photoreduction of indicated ketones by indicated concentration of toluene	23
6. Stern-Volmer plots for naphthalene quenching of photoreduction of indicated ketones by 0.1M toluene	23
7. Stern-Volmer plots for the quenching of photoreduction of α -trifluoroacetophenone with 0.1M toluene by indicated quenchers	24
8. Stern-Volmer plots for the quenching of photoreduction of α -trifluoroacetophenone with 0.1M toluene by indicated quenchers	25
9. Stern-Volmer plots for the quenching of photoreduction of α -trifluoroacetophenone with 0.1M toluene by anisole	25
10. Phosphorescence of <u>p</u> -trifluoromethyl- α -trifluoroacetophenone at 77°K	26
11. Phosphorescence of <u>m</u> -trifluoromethyl- α -trifluoroacetophenone at 77°K	26
12. Phosphorescence of <u>m</u> -chloro- α -trifluoroacetophenone at 77°K	27

LIST OF FIGURES--Continued.

Figure	Page
13. Phosphorescence of α -trifluoroacetophenone at 77°K	27
14. Phosphorescence of p-methyl- α -trifluoroacetophenone at 77°K	28
15. Phosphorescence of p-methoxy- α -trifluoroacetophenone at 77°K	28
16. Correlation of rate constant for quenching of triplet α -trifluoroacetophenone by aromatics with their ionization potentials in acetonitrile	30
17. Log k_r for quenching of acceptor triplets by toluene <u>vs</u> triplet energy minus reduction potential	33
18. Fluorescence quenching rate constants k_q as a function of the free enthalpy ΔG	35

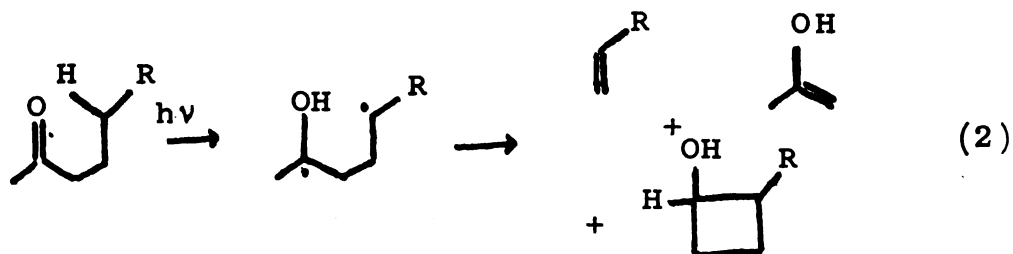
INTRODUCTION

Photoreduction of ketones has become a common topic for investigation since the original discovery by Ciamician and Silber¹ that the action of sunlight on benzophenone in 2-propanol yields benzopinacol and acetone. Studies of the mechanism of photochemical pinacolization were intensely

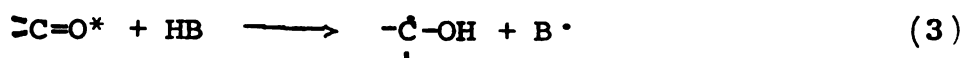


conducted since 1900. Most of the work done in the 1950's emphasized synthetic application because the chemical yields in some of these photochemical reactions were good and the products were more readily prepared than by non-photochemical methods. The advancement of technology during the past few years enabled more thorough investigation on the mechanism of photoreduction.

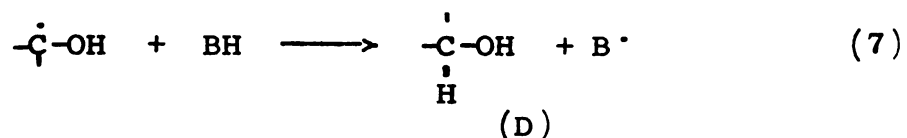
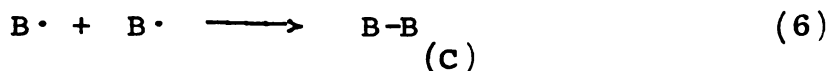
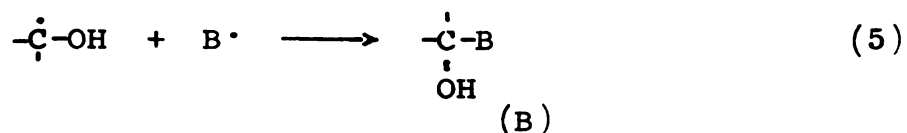
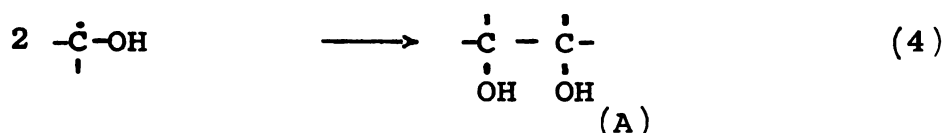
The photoreduction of ketones, either intra- or intermolecular, involving hydrogen abstraction could be divided into radical-like and charge-transfer processes. Radical-like intramolecular photoreduction, usually referred to as the Norrish type II reactions, involves the transfer of γ hydrogen to the carbonyl oxygen in the excited state and the subsequent reaction of the 1,4-biradical.²



Intermolecular photoreduction represents the abstraction of hydrogen from a substrate, which can be an alcohol,³ hydrogen bromide,⁴ toluene,⁵ alkanes,⁶ and amines,⁷ by the electronically excited carbonyl compound.

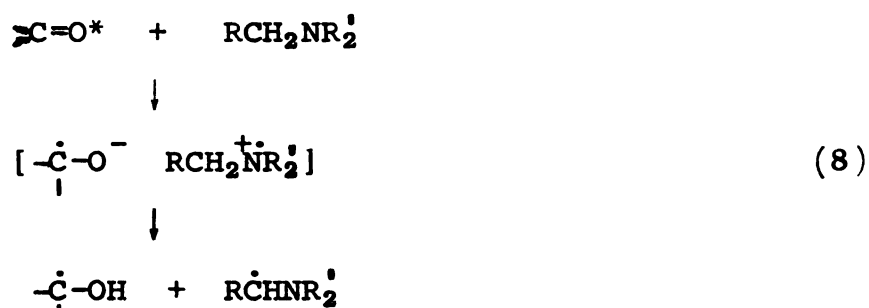


The resulting radicals may proceed to form different products depending on the reaction conditions.⁸



The reaction of benzophenone with toluene^{5,9} gives products A, B, and C which are shown in equations 4, 5, and 6, but the photoreduction of acetone by tributyl stannane¹⁰ gives only product D. Although aliphatic ketones usually undergo

radical-like photoreduction with alcohols, many aromatic ketones as fluorenone, aminobenzophenone, α and β -naphthyl carbonyl compounds are not efficiently photoreduced by alcohols. Recent studies reveal that these aromatic ketones could be photoreduced efficiently in a charge-transfer mechanism by amines which contain α -hydrogens.¹¹



General Mechanistic Process

Before any further discussion on photoreduction of ketones, a brief description of the fate of the electronic excitation is necessary to achieve a better understanding of the mechanism.

Figure 1 is a modern elaboration of Jablonski's diagram, representing the energies of the various low-lying states of a typical molecule with respect to the ground state S_0 . In solution, when an organic molecule absorbs light, it is elicited to an excited singlet state, and then decays rapidly to the lowest singlet state ($\sim 10^{-10}$ sec). The lowest singlet state either deactivates to ground state by fluorescence and radiationless decay or populates triplet states by intersystem crossing. Since the rate of intersystem crossing

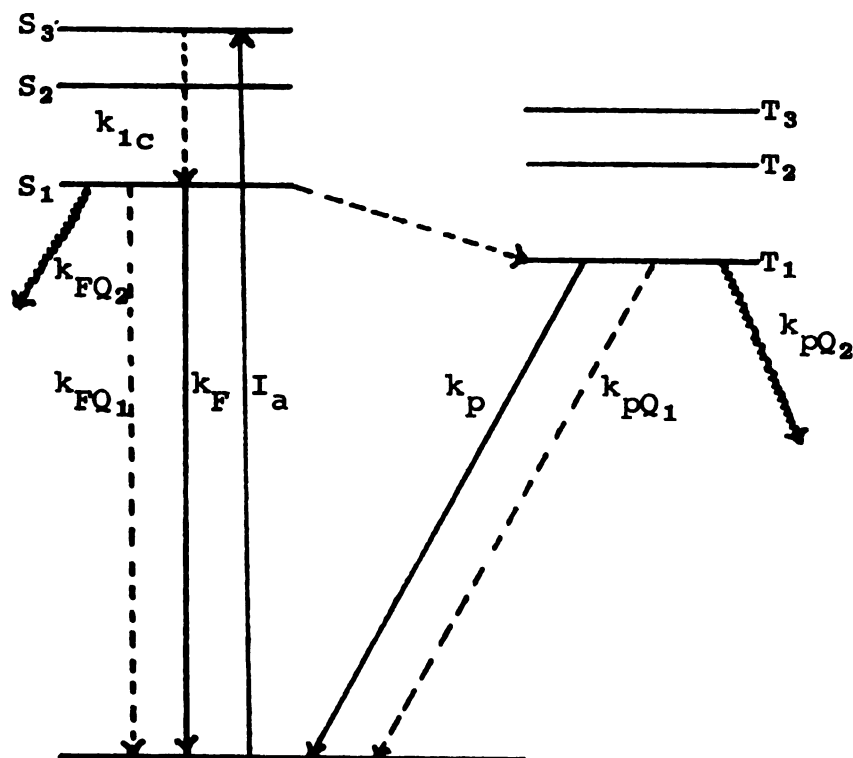


Figure 1. Jablon'ski's diagram. Solid arrows represent radiative processes, corresponding to absorption or emission of light. Dashed and wiggly lines denote non-radiative unimolecular and bimolecular processes respectively.

for phenyl ketones is much faster than the rate of fluorescence and radiationless decay, the triplet state is usually populated with unit efficiency.¹² Subsequent emission from the lowest triplet state to ground state is known as phosphorescence.

The Nature of the Excited States

The molecular electronic state, as mentioned in the last section, can be described by the appropriate electronic configuration and electron distribution, which are expressed in terms of one-electron wave functions by molecular-orbital

methods. Recent studies have concentrated on the chemical properties of the two lowest electronic states $n\pi^*$ and $\pi\pi^*$.

$n\pi^*$ transition is the promotion of an electron from the non-bonding orbital on oxygen to an antibonding π orbital. As a result, the excited state is electrophilic and radical-like in the proximity of the oxygen atom and nucleophilic (and possibly radical-like) above and below the carbonyl faces.¹³⁻¹⁵ Alkoxy radicals have been found to be good analogues of $n\pi^*$ carbonyl triplets in relation to their behaviors in radical-like hydrogen abstraction reactions^{6,16-18}

The formation of a $\pi\pi^*$ triplet involves the promotion of a π electron of the conjugated carbonyl group to an antibonding π^* orbital. Although the nature of the 'pure' $\pi\pi^*$ triplet of the benzoyl group is not altogether clear, it can be alternatively viewed as having its excitation localized on the aromatic ring with carbonyl providing a strong energetic perturbation,¹⁹ or as a charge-transfer state with electron migration from the benzene ring to the carbonyl.²⁰ It might be a mixture of both and therefore the carbonyl oxygen in a $\pi\pi^*$ triplet should always be electron rich as compared with $n\pi^*$ triplet.²¹

It is also known that the electronic transitions of benzene are strongly affected by substituents.²² Experimental results^{23,24} show that the addition of an electron-donating group to the benzene ring stabilizes the $\pi\pi^*$ triplet with respect to the $n\pi^*$ triplet. Electron-withdrawing substituents, on the other hand, tend to lower the $n\pi^*$

triplet. Solvent effect on the electronic states has also been studied. Polar solvents usually stabilize $\pi\pi^*$ relative to $n\pi^*$ state.

The Correlations between the Reactivities of Hydrogen Abstraction and the Nature of the Excited State

Recent studies showed that those ketones which are mostly $\pi\pi^*$ in character display highly reduced reactivity in hydrogen abstraction reactions relative to those ketones with $n\pi^*$ low-lying triplet.²⁵ But in aromatic carbonyl compounds, since the excited state associated with the aromatic ring is frequently mixed into the lowest $\pi\pi^*$ states of the carbonyl, the subsequent lowering of the $\pi\pi^*$ states which in some cases leads to the energetic proximity of $n\pi^*$ and $\pi\pi^*$ triplet, has caused the interpretation in ketone reactivities to become more challenging. In studying the correlation of the photochemical reactivity and the nature of excited states of acetophenone and substituted acetophenones, Yang^{23,26} observed a significant decrease in triplet reactivity when the $\pi\pi^*$ triplet is lower than the $n\pi^*$ triplet. Since the vibronic coupling between two states will increase as the energy gap decreases, the enhanced photochemical reactivity of the low-lying $\pi\pi^*$ state of p-methyl and 3,4-dimethyl acetophenone with respect to those ketones possessing a much lower lying $\pi\pi^*$ triplet state could be explained by the vibronic coupling of the $\pi\pi^*$ triplet with the nearby $n\pi^*$ triplet in methylated acetophenones.

Wagner,^{27,28} on the other hand, suggested that a thermal equilibrium between two states would allow the reactive upper $n\pi^*$ triplet to be responsible for the observed reactivity. In studying the reactivity of various *p*-methoxy phenyl ketones which have $\pi\pi^*$ lowest triplets, it was reported that the observed rates of triplet state γ -hydrogen abstraction of *p*-methoxy phenyl ketones and the rate of simple phenyl ketones which have $n\pi^*$ lowest triplet vary identically with C-H bond strength and with the inductive effect of substituents. It was then concluded that the hydrogen abstraction comes from the low equilibrium populations of the upper $n\pi^*$ triplet.²⁹ Recently, the observation that interchromophore energy transfer in 1-benzoyl-4-anisoyl-butane is fast enough to allow almost complete equilibration between the $n\pi^*$ triplet of the benzoyl group and the $\pi\pi^*$ triplet of the anisoyl group supports the proposed theory of intrachromophore energy transfer between $n\pi^*$ triplet and $\pi\pi^*$ triplet.³⁰

This interesting correlation of the nature of the excited states with the reactivities of direct hydrogen abstraction leads us to question whether the same correlation would appear in charge transfer reactions.

Charge Transfer Mechanism

Quenching of fluorescence from aromatic compounds has been observed¹⁹ even when the lowest excited singlet of the quenchers have higher excitation energies than those of the

qu

ch

dc

at

wt

in

t:

ac

le

w.

r

at

f

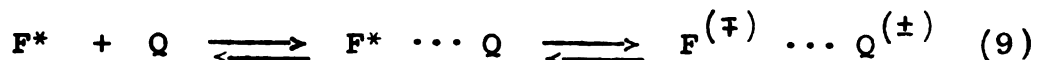
s

p

w

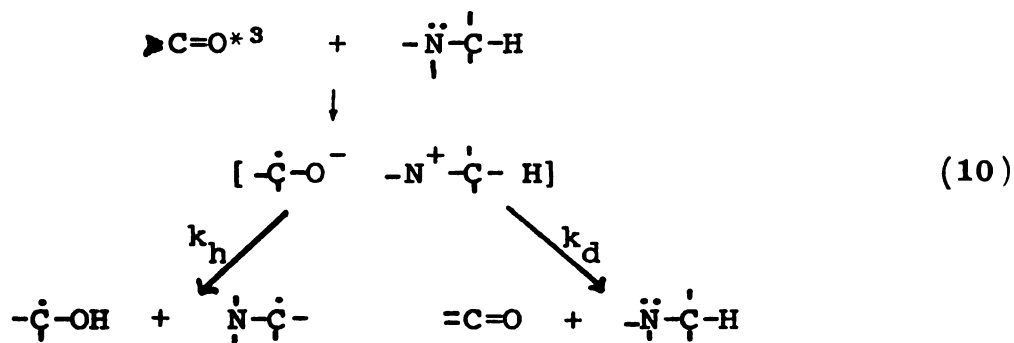
l

quenched molecules. In order to explain this observation, charge transfer mechanism has been proposed to be the pre-dominant quenching mechanism for the singlet states of aromatic compounds with amines,³¹ and quadricyclene,³²



where F^* is the excited molecules and Q is the quenchers.

Charge transfer interactions have also been suggested in the quenching of triplet ketones and aldehydes. Reductions of ketones by amines appear to occur by rapid interaction at the non-bonding electrons of the heteroatom leading to a charge transfer complex.^{11,33} The complex will either go through a transfer of α -hydrogen to form radicals or a charge destruction to regenerate ketone and amine. Although the rate of charge transfer is usually faster than expected for direct hydrogen abstraction, the



subsequent self-quenching of the charge transfer complex prevents the attainment of a maximum quantum yield of 2, which has been observed in benzophenone-isopropanol reaction.³⁴ In order to support the proposal of the charge transfer

mechanism, Davidson and Wilson³⁵ confirmed the production of 9-hydroxy fluorenyl radical in the photoreduction of fluorenone with tertiary amines by e.s.r. study.

To obtain a quantitative relationship between kinetics of charge transfer and thermodynamic properties of the reactants, Cohen and Guttenplan³⁶ modified the published equation for singlet quenching by electron transfer³¹ to equations 11 and 12,

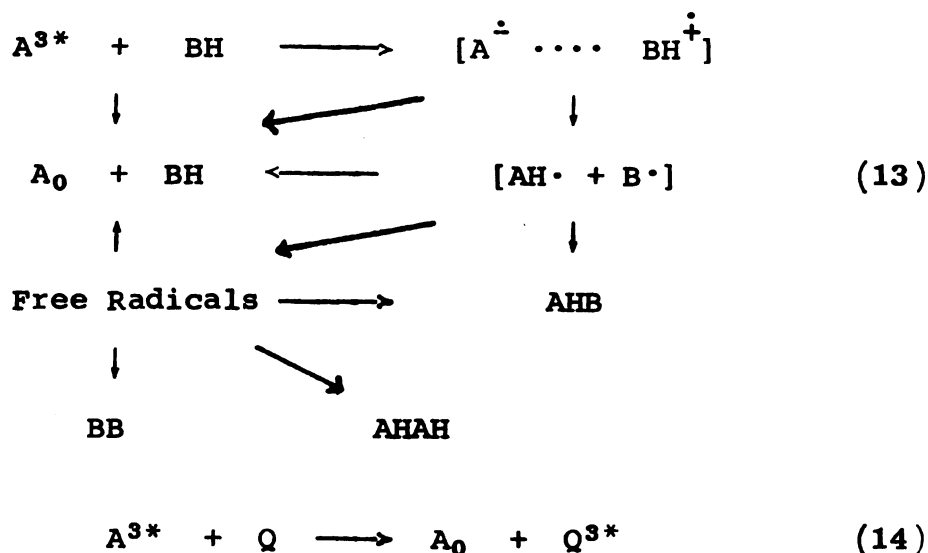
$$\Delta G_c \approx -^3\Delta E_{0,0} + IP_D - E(A^-/A) + C \quad (11)$$

$$\log k_r \approx K \cdot \Delta G_c \quad (12)$$

where k_r is the rate constant of a quenching interaction between an electron donor D and an acceptor A, ΔG_c is the free energy change for charge transfer formation in triplet excited state, $^3\Delta E_{0,0}$ is the triplet energy of the excited species at the 0,0 band, IP_D is the ionization potential of the donor, $E(A^-/A)$ is the reduction potential of the acceptor, and C is a constant. For the reaction of an acceptor with a series of donors, $\log k_r \sim IP_D + C'$ and a reasonably linear relationship was observed for interaction of $n\pi^*$ triplet benzophenone with 17 donors,³⁶ and $\pi\pi^*$ triplet fluorenone with a limited series of compounds.³⁷ For a series of acceptors with a constant donor, the equation $\log k_r \sim [-^3\Delta E_{0,0} - E(A^-/A)] + C$ is applicable and a linear relationship was reported for the interaction of triethylamine with a series of carbonyl acceptors with varying reduction potential, triplet energy, and triplet configuration.³⁷

Previous Study of the Photoreduction of Trifluoroacetophenone

The involvement of charge transfer in the photoreduction of trifluoroacetophenone by alkylbenzenes has been suggested^{38,39}. The general mechanistic scheme can be written for the photoreduction of ketone A, by substrate BH, in the presence of quencher, Q.



Charge transfer interaction was suggested to be involved in the photoreduction of trifluoroacetophenone by toluene, because the photoreactivities do not depend on the C-H bond strength of the donor, but depend on their ionization potential. A small solvent effect and a small slope in the $\log k_r$ vs IP plot indicates only partial charge transfer in the transitional state. Deuterium isotope effects suggest that the reaction of trifluoroacetophenone with cumene involves both charge transfer and direct hydrogen abstraction. Since the rate of hydrogen abstraction in the reaction of cyclohexane with trifluoroacetophenone is

faster than with acetophenone, the addition of the trifluoromethyl group to the carbonyl not only increases the rate of charge transfer complexing, but also increases the rate of direct hydrogen abstraction. Although the $\pi\pi^*$ triplet in trifluoroacetophenone is lower in energy than the $n\pi^*$ triplet, they are so close that it is difficult to determine the extent to which each state is taking part in the charge transfer photoreduction.

Objectives

In order to confirm the involvement of partial charge transfer in the transitional state of the photoreduction of trifluoroacetophenone, experiments were set up similar to what Cohen and Guttenplan³⁶ did on the triplet quenching of benzophenone by different amines in benzene. The kinetics of the photoreduction for trifluoroacetophenone with several substituted benzenes were examined in acetonitrile solvent and a quantitative relationship between rate constants for charge transfer and thermodynamic properties of the reactants was drawn.

As mentioned above, correlations have been shown between relative disposition of $n\pi^*$ and $\pi\pi^*$ triplets with reactivity of triplets in direct hydrogen abstraction. Analysis of the reactivity of various *p*-methoxy phenyl ketones suggests that hydrogen abstraction occurs by equilibrium concentrations of upper $n\pi^*$ triplet,²⁹ but so far no data are available leading to the same conclusion on

charge transfer photoreduction. As proposed by Cohen,³⁷ a linear relationship could be obtained by plotting $\log k_r$ with $-^3\Delta E_{0,0} - E(A^-/A)$ in the system of a series of acceptors reacting with a constant donor. But in studying a series of substituted trifluoroacetophenones with $n\pi^*$ or $\pi\pi^*$ lowest triplet, if the ketones with $n\pi^*$ and $\pi\pi^*$ lowest triplet have different reactivities in charge transfer reactions, a linear relationship could not be found on the plot of $\log k_r$ vs $-^3\Delta E_{0,0} - E(A^-/A)$ because the different reactivities of $n\pi^*$ and $\pi\pi^*$ triplets are not taken into account in that quantitative relationship.

Kinetics Expressions

Quantum yield is the only kinetic parameter associated with a photoreaction which is directly measurable under steady state conditions and is generally defined by the relationship between the number of molecules which react or are formed and the number of photons absorbed.⁴⁰

$$\phi = \frac{\text{no. of molecules or ions of X formed/cm}^3, \text{sec}}{\text{No. of quanta absorbed by reactant/cm}^3, \text{sec}} \quad (15)$$

The quantum yield of a particular photoreaction can also be defined.⁴¹

$$\phi_i = \phi_{ES} \phi_R P_i \quad (16)$$

Where ϕ_{ES} represents the probability that absorption of light will produce the requisite excited state, ϕ_R is the

probability that the excited state will undergo the primary photoreaction necessary for process i , and P_i is the probability that any metastable ground state intermediate will proceed to stable product. Since the probability, ϕ_R , that the excited state will react in the manner responsible for process i depends on the rates of all the competing processes of the reactive excited state, a bimolecular reaction with BH would give the following expression,

$$\phi_R = k_r[BH]\tau \quad (17)$$

where k_r is the rate constant for interaction of the excited state with BH and the lifetime, τ , is the reciprocal of the sum of the rate of all reactions undergone by the excited state.

Applying equations 14 and 15 to the mechanistic scheme of the photoreduction of trifluoroacetophenone with toluene, an useful expression can be obtained

$$\phi_{BB} = Y_{BB} P_{BB} (k_r[BH]\tau) \quad (18)$$

where Y_{BB} , the actual chemical yield of the product, is defined as $\frac{[BB]}{2[BB]+[AHB]}$ because the measured quantum yield is based on only one of the products containing $B^\bullet$ radical. Since

$$\tau = \frac{1}{k_d + k_r[BH]} \quad (19)$$

the reciprocal of equation 17 would give

$$\phi_{BB}^{-1} = Y_{BB}^{-1} P_{BB}^{-1} \left(1 + \frac{k_d}{k_r [BH]} \right) \quad (20)$$

A plot of reciprocal quantum yield ϕ_{BB}^{-1} versus reciprocal substrate concentration $[BH]^{-1}$ is linear and a slope/intercept value gives k_d/k_r .

When a triplet quencher is used, equation 17 becomes

$$\phi_{BB} = Y_{BB} P_{BB} \left(\frac{k_r [BH]}{k_r [BH] + k_d + k_q [Q]} \right) \quad (21)$$

Dividing equation 18 by 21 gives the Stern-Volmer equation

$$\phi^0/\phi = 1 + k_q [Q] \tau \quad (22)$$

where ϕ^0 and ϕ represent the quantum yield of BB formation in the absence and presence of quencher respectively. A plot of ϕ^0/ϕ versus the concentration of the quencher gives a linear plot with a slope equal to $k_q \tau$. Using a quencher with known k_q , we can calculate τ , which equals $[k_r (BH) + k_d]^{-1}$. Since the ratio of k_d/k_r is known, the rate constant of the excited state reaction can be obtained.

RESULTS

Quantum Yield Determinations

Absolute quantum yields of bibenzyl formation were determined for trifluoroacetophenone and substituted trifluoroacetophenone as a function of toluene concentration. Degassed acetonitrile solutions containing 0.05M ketone, 0.001M C₁₇ and various concentrations of toluene were irradiated at 313 nm and analyzed for bibenzyl concentration by VPC. Valerophenone actinometry, described in the experimental section, was used to calculate the light absorption. Reciprocal quantum yield vs reciprocal toluene concentration plots were shown in Figures 2 and 3. Slope and intercept values, obtained from Figures 2 and 3 were used to calculate k_d/k_r and ϕ_{BB}^{max} which were shown in Table 4.

Triplet Quenching Studies

The lifetimes of trifluoroacetophenone and substituted trifluoroacetophenones in acetonitrile were obtained by using the Stern-Volmer relationship and an assumed constant, the k_q value for naphthalene. Degassed acetonitrile solution containing 0.05M ketone, 0.001M C₁₇ and various concentrations of naphthalene were irradiated at 366 nm. Bibenzyl and C₁₇ peak areas were analyzed and linear Stern-Volmer

plots were obtained as shown in Figures 4 - 6. With the lifetime as indicated in Table 2 and the k_d/k_r ratio obtained from the absolute quantum yield determination, k_d and k_r were calculated and shown in Table 4.

On the other hand, the rate constants of different quenchers in quenching the reaction of trifluoroacetophenone with toluene were revealed. Degassed solutions containing 0.05M ketones, 0.001M C_{17} , 0.1M or 1M toluene and different concentrations of quenchers were irradiated in parallel at 313 nm to less than 5 percent ketone conversion. Bibenzyl and C_{20} peak areas which were analyzed by VPC permitted the calculation of ϕ_{BB}^O/ϕ_{BB} . The $k_q\tau$ values obtained from the Stern-Volmer plots in Figures 7 - 9 were shown in Table 3.

Intersystem Crossing

A comparison of the amount of cis-piperylene isomerized to trans-piperylene by p-methoxy- α -trifluoroacetophenone and m-trifluoromethyl- α -trifluoroacetophenone with acetophenone would give the ϕ_{isc} of the substituted trifluoroacetophenones, since the ϕ_{isc} of acetophenone is unity.¹² Degassed acetonitrile solutions containing 0.1M ketone and 0.2 M cis-piperylene were irradiated in parallel at 313 nm. The ϕ_{isc} of p-methoxy- α -trifluoroacetophenone is considered to be unity within experimental error, but the ϕ_{isc} of m-trifluoromethyl- α -trifluoroacetophenone in 0.94.

Absorbance and Emission Spectra

Table 5 showed the ${}^1B_{2u} \leftarrow {}^1A_{1g}({}^1L_b \leftarrow {}^1A)$ and ${}^1B_{1u} \leftarrow {}^1a_{1g}({}^1L_a \leftarrow {}^1A)$ bands of different ketones. The 0-0 band and the lifetime of the phosphorescence of trifluoroacetophenone and substituted trifluoroacetophenone were given in Table 6. Figures 10 - 15 show the phosphorescence spectra of the six ketones.

Table 1. Least squares slope and intercept values from ϕ_{BB}^{-1} versus $[BH]^{-1}$ plot for the photoreduction of indicated ketones with toluene

Ketone	Slope ^b	Intercept
TFA ^a	6.23	26.63
p-MeO-TFA	106.18	15.9
p-Me-TFA	13.66	13.5
m-Cl-TFA	1.92	15.11
p-CF ₃ -TFA	0.47	9.58
m-CF ₃ -TFA	0.61	20.06

^aTrifluoroacetophenone.

^bSingle run.

Table 2. Triplet quenching parameters for the reaction of indicated ketone with 1M toluene by using the quencher, naphthalene, in acetonitrile.

Ketone	$k_q \tau, M^{-1}$ ^{a,b}	τ , sec.	$1/\tau$, sec ⁻¹
TFA	790	7.89×10^{-8}	1.3×10^7
p-MeO-TFA	24300	2.43×10^{-6}	4.1×10^5
p-Me-TFA	5400	5.40×10^{-7}	1.8×10^6
m-Cl-TFA	180	1.80×10^{-8}	5.6×10^7
p-CF ₃ -TFA	93	9.30×10^{-9}	1.1×10^8
m-CF ₃ -TFA	76	7.64×10^{-9}	1.3×10^8

^a $k_q = 1.0 \times 10^{10} M^{-1} \text{ sec}^{-1}$. ^bSingle run.

Table 3. Triplet quenching parameters for trifluoroacetophenone with toluene.

Quencher	$k_q \tau, M^{-1}$ ^{a,b}	$k_q, M^{-1} \text{ sec}^{-1}$	$1P_D^c$, e.v.
Anisole	60	1.9×10^8	8.2
Benzene	0.14	4.5×10^5	9.25
Chlorobenzene	0.32	1.0×10^6	9.07
Benzonitrile	0.025	9.9×10^4	9.7
Benzotrifluoride	0.04	1.3×10^5	9.68
p-Dichlorobenzene	0.42	1.3×10^6	8.94
Fluorobenzene	0.1	3.2×10^5	9.19
p-Dimethoxybenzene	3780	1.2×10^{10}	--
Toluene	--	1.1×10^7	8.80

^a $\tau = 3.1 \times 10^{-5} \text{ sec}$. ^bSingle run. ^cReference 42.

Table 4. Kinetic data for photoreduction of 0.05M indicated ketones with toluene in acetonitrile.

Ketone	$\phi_{BB}^{max^a}$	k_d/k_r^b	$k_r, M^{-1}sec^{-1}^c$	k_d, sec^{-1}^c	$E(A^-/A)^d$ e.v.
TFA	0.0375	0.2342	$1.07 \times 10^7^e$	1.75×10^6	-1.37
p-MeO-TFA	0.0627	6.665	$5.13 \times 10^4^f$	3.42×10^5	-1.72
p-Me-TFA	0.0740	1.0118	$9.2 \times 10^5^f$	9.3×10^5	-1.71
m-Cl-TFA	0.0660	0.1276	$4.9 \times 10^7^f$	6.28×10^6	-1.20
p-CF ₃ -TFA	0.1043	0.0499	$7.17 \times 10^8^f$	3.57×10^7	-1.11
m-CF ₃ -TFA	0.0498	0.0304	1.00×10^9	3.04×10^7	-1.17

^aExtrapolated quantum yield of bibenzyl at infinite toluene concentration.

^bSlope/intercept value from Table 1.

^cCalculated from τ values in Table 2 and k_d/k_r values in this table.

^dReduction potential.

^eThe standard deviation of k_r for TFA and p-MeO-TFA is 0.05 and 0.16 respectively. They are measured by triplet quenching of the two particular ketones with different concentrations of toluene by naphthalene.

Table 5. Ultra violet absorption bands of indicated ketones.

Ketone	$^1B_{2u} \leftarrow ^1A_{1g}, \text{\AA}$	$^1B_{1u} \leftarrow ^1A_{1g}, \text{\AA}$
TFA	2940	2520
p-MeO-TFA	--	2870
p-Me-TFA	--	2640
m-Cl-TFA	3010	2580
m-CF ₃ -TFA	2930	2510
p-CF ₃ -TFA	2980	2445

Table 6. Phosphorescence data of indicated ketones at 77°K.^a

Ketone	Lifetime, sec	O-O Bands	
		nm	Kcal/mole
TFA	57	406±1	70.41
p-MeO-TFA	~600	430	66.48
p-Me-TFA	208.5	414	69.05
m-Cl-TFA	85.6	409	69.90
p-CF ₃ -TFA	18.2	406	70.41
m-CF ₃ -TFA	24	405	70.59

^aSolvent is 4:1 mixture of methyl cyclohexane and isopentane.

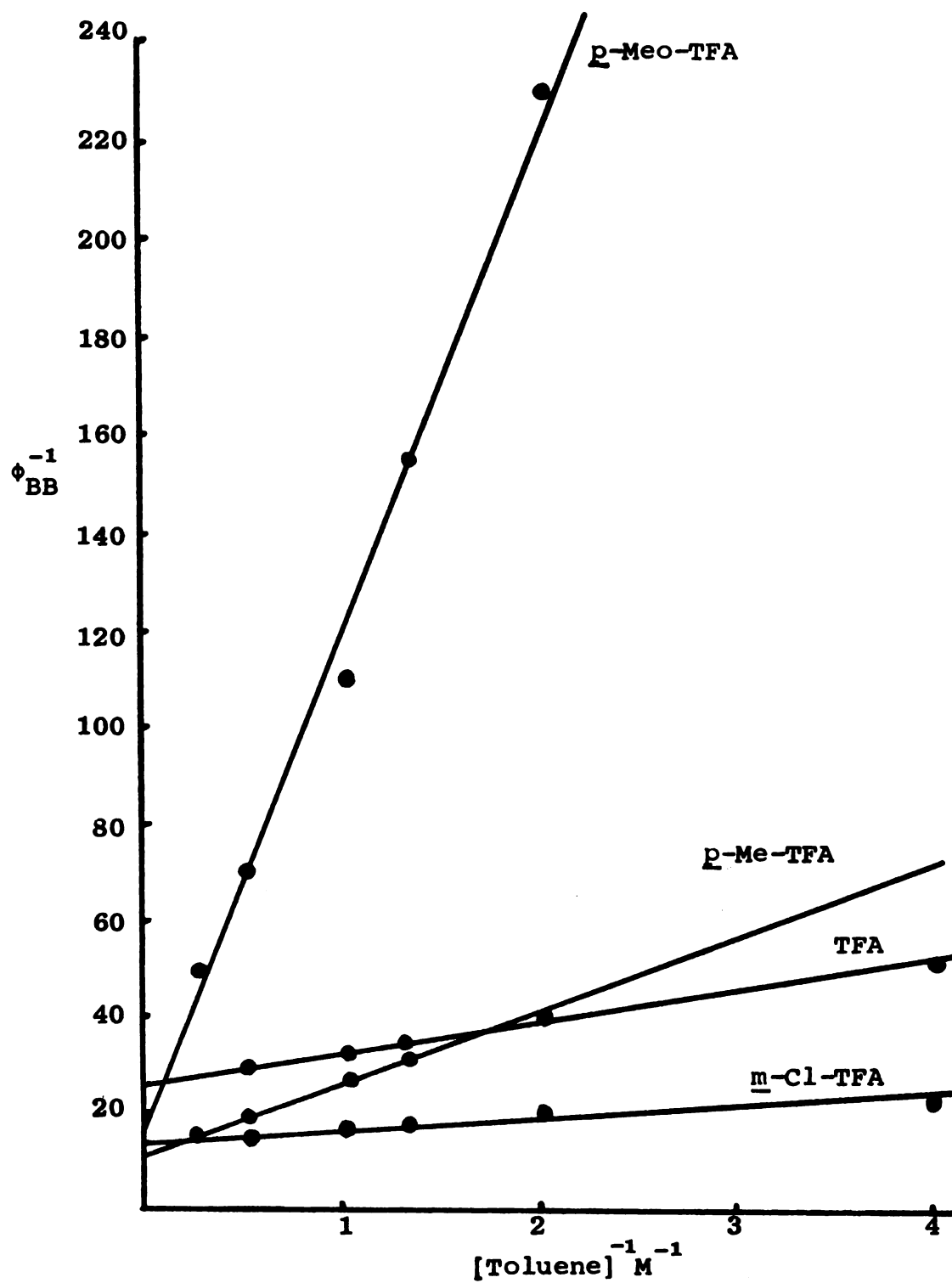


Figure 2. Reciprocal quantum yield plot for indicated ketones with toluene

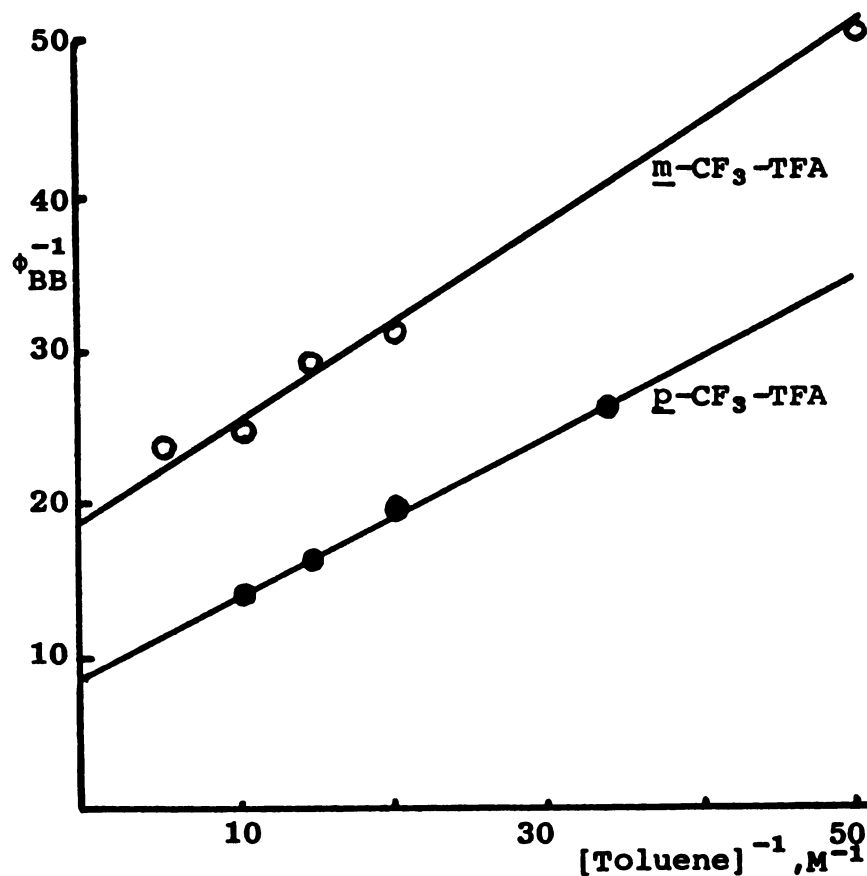


Figure 3. Reciprocal quantum yield plot for indicated ketones with toluene.

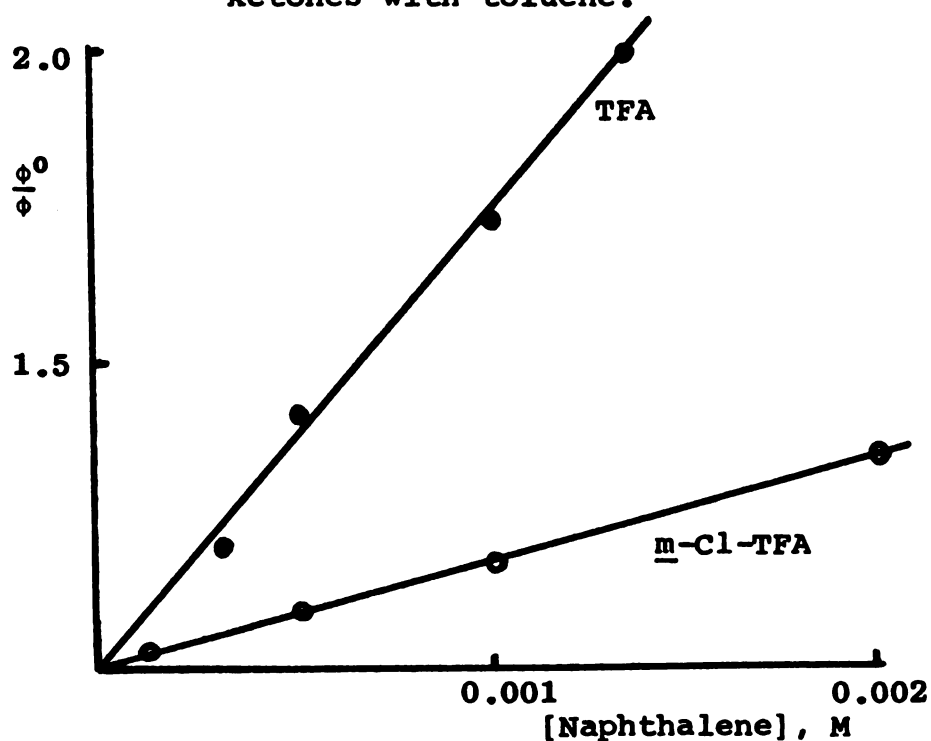


Figure 4. Stern-Volmer plots for naphthalene quenching of photoreduction of indicated ketones by 1M toluene.

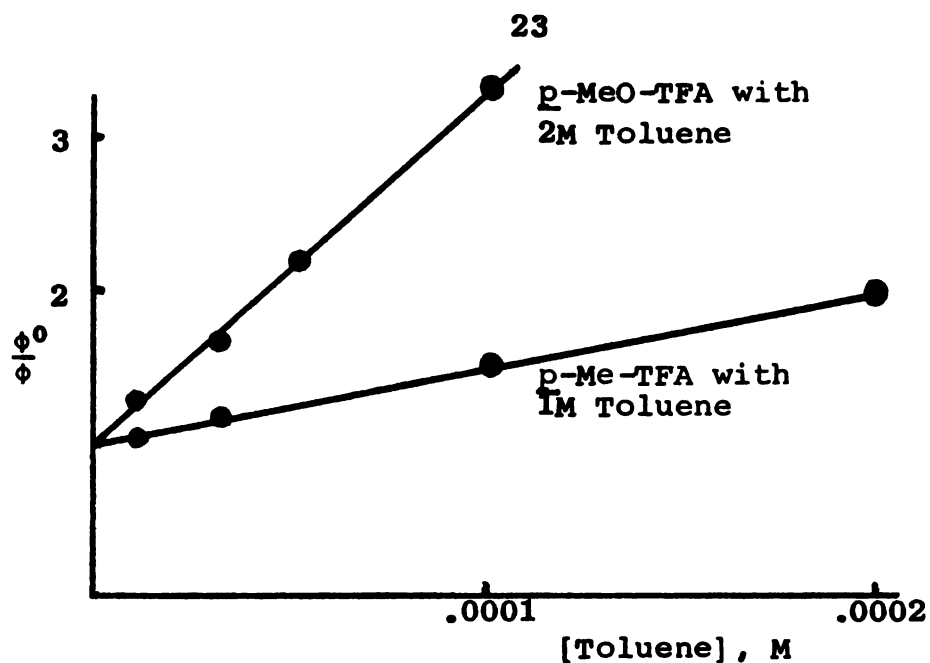


Figure 5. Stern-Volmer plots for naphthalene quenching of photoreduction of indicated ketone by indicated concentration of toluene.

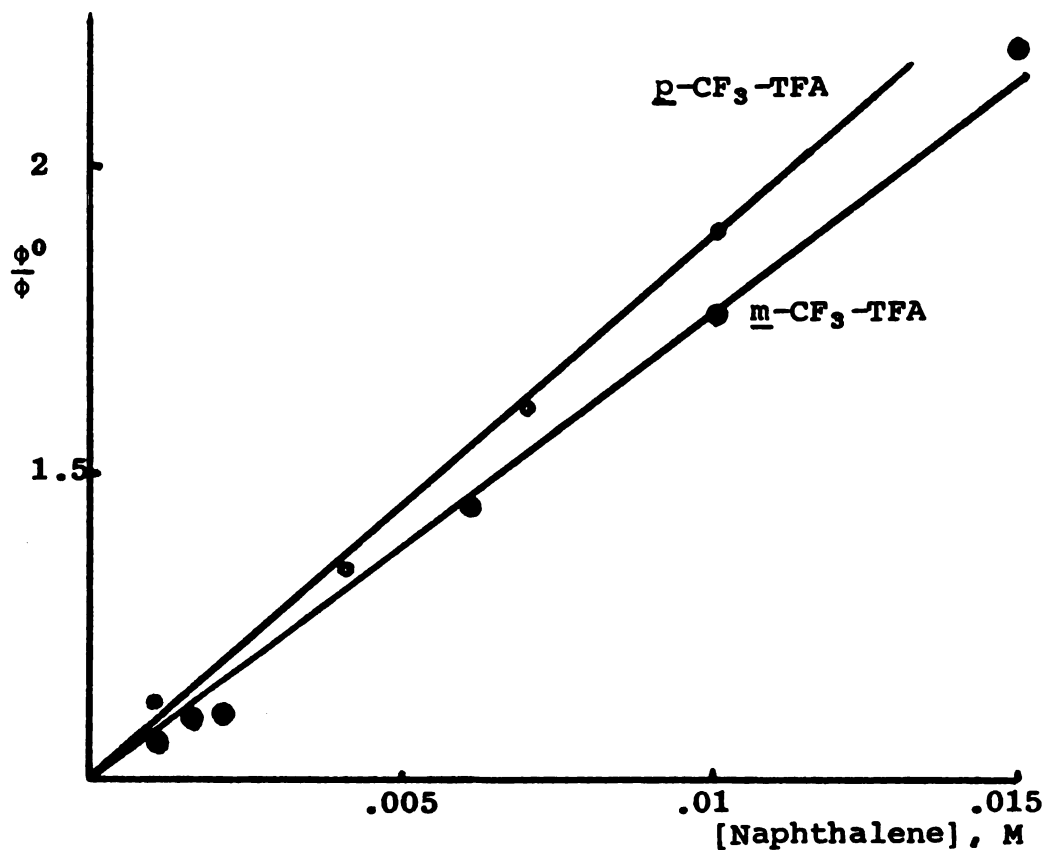


Figure 6. Stern-Volmer plots for naphthalene quenching of photoreduction of indicated ketones by 0.1M toluene.

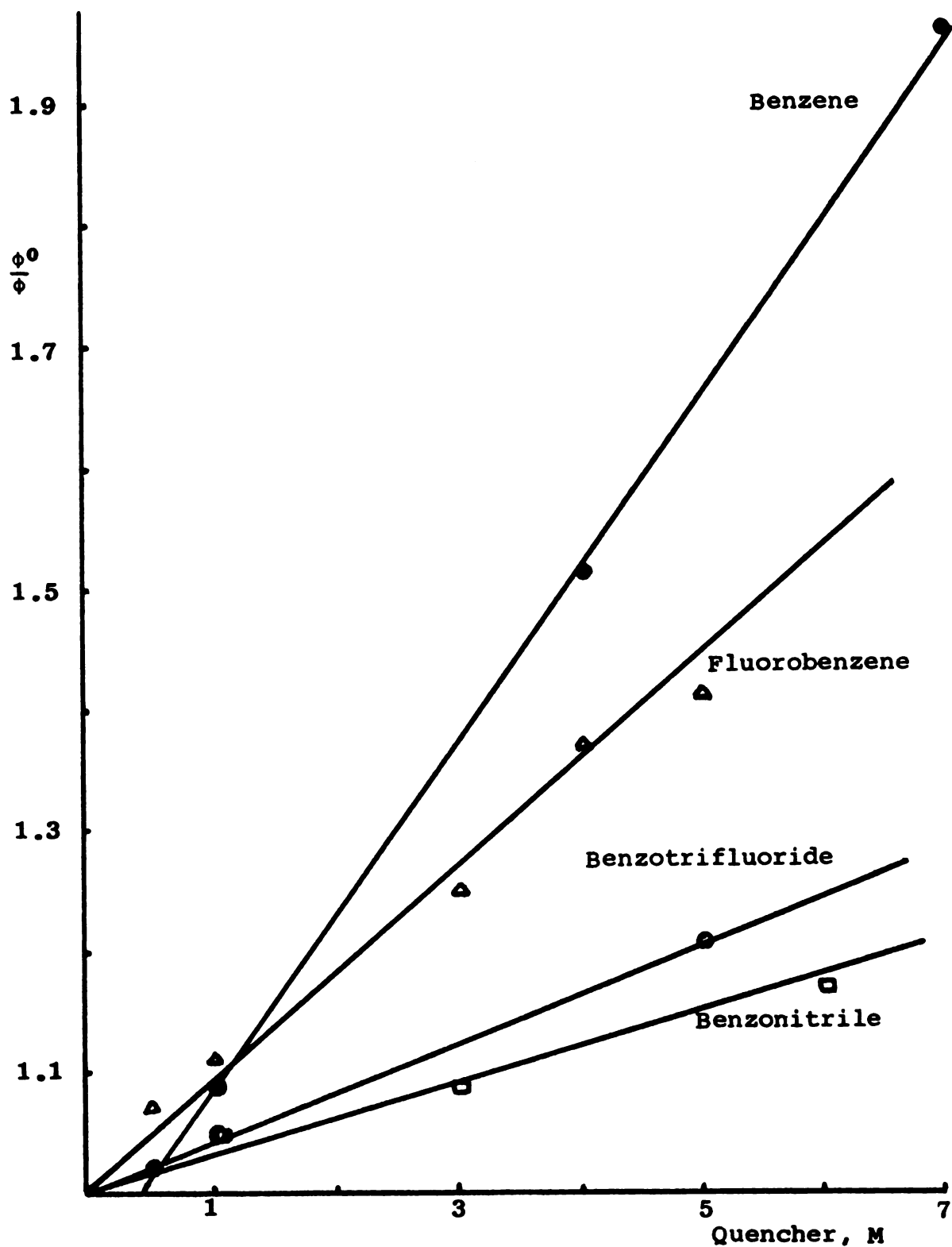


Figure 7. Stern-Volmer plots for the quenching of photoreduction of α -trifluoroacetophenone with 0.1M toluene by indicated quenchers.

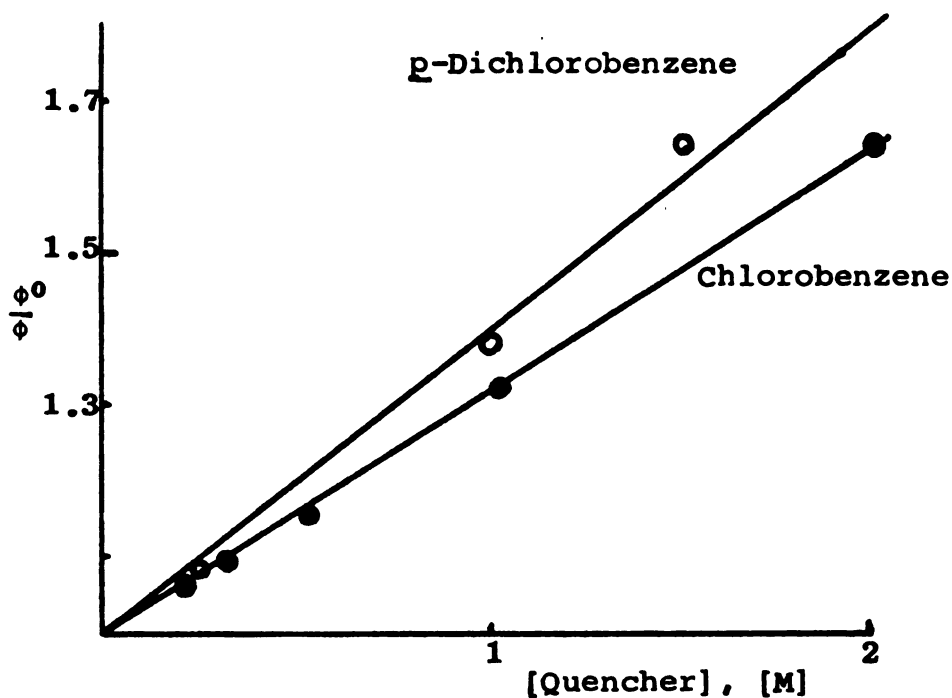


Figure 8. Stern-Volmer plots for the quenching of photoreduction of α -trifluoroacetophenone with 0.1M toluene by indicated quenchers.

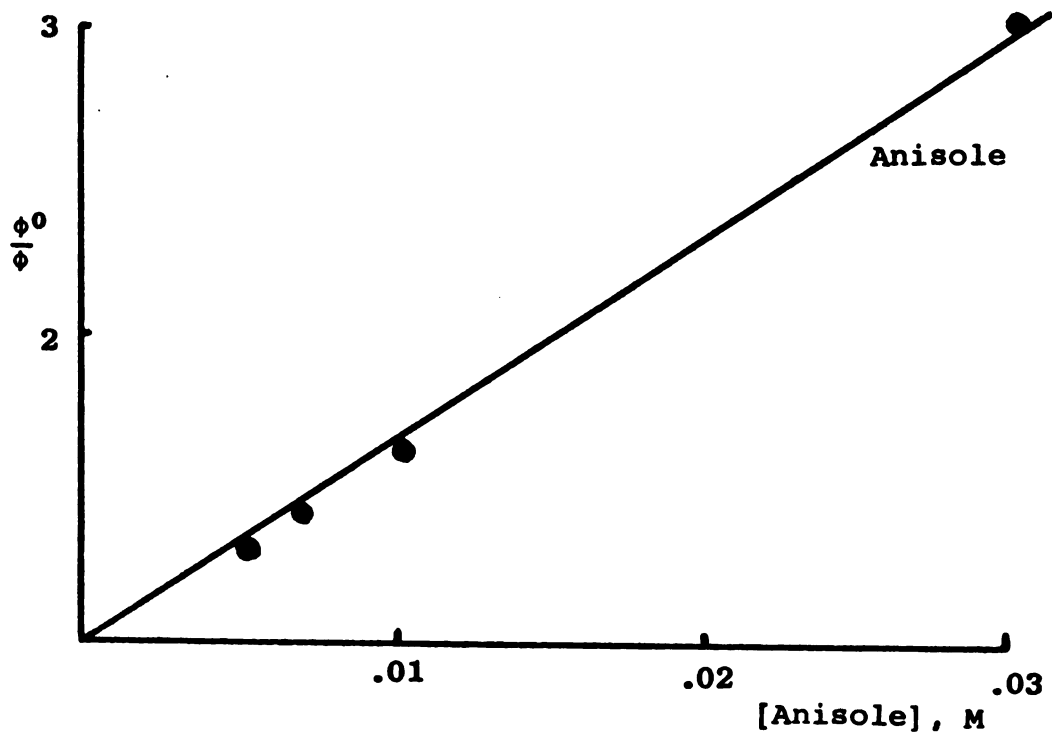


Figure 9. Stern-Volmer plots for the quenching of photoreduction of α -trifluoroacetophenone with 0.1M toluene by anisole.

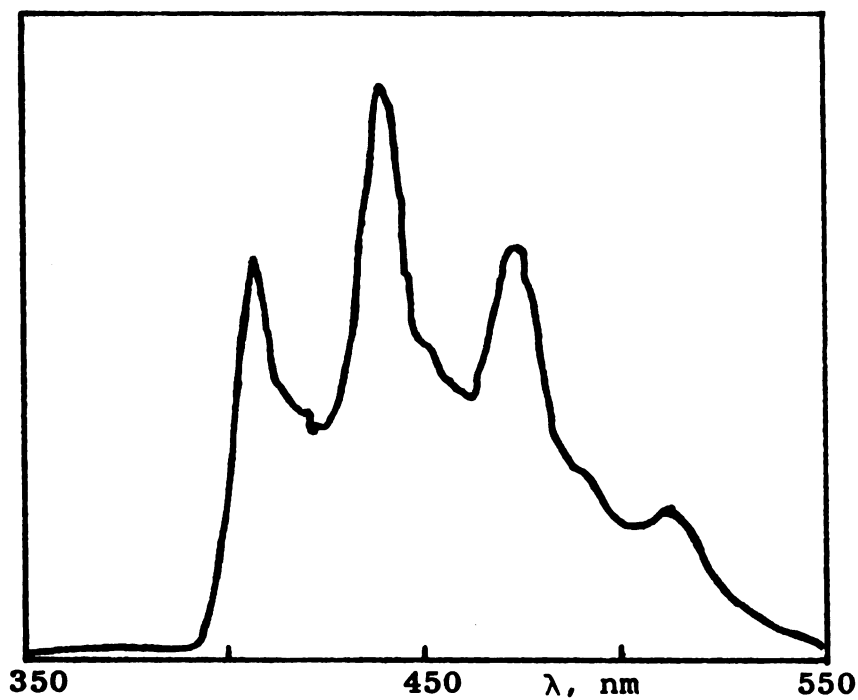


Figure 10. Phosphorescence of p-trifluoromethyl- α -trifluoroacetophenone at 77°K.^a

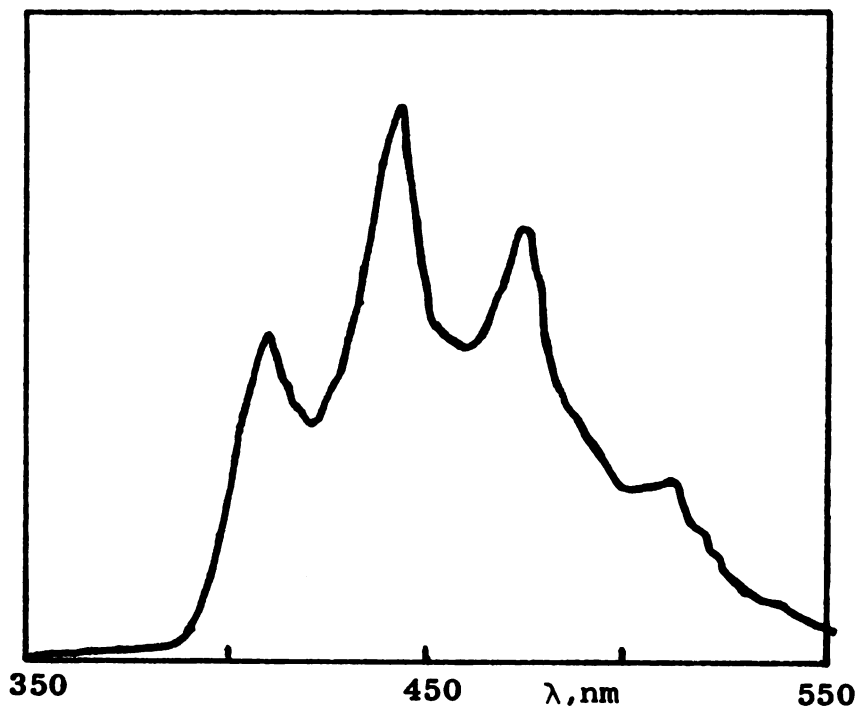


Figure 11. Phosphorescence of m-trifluoromethyl- α -trifluoroacetophenone at 77°K.^a

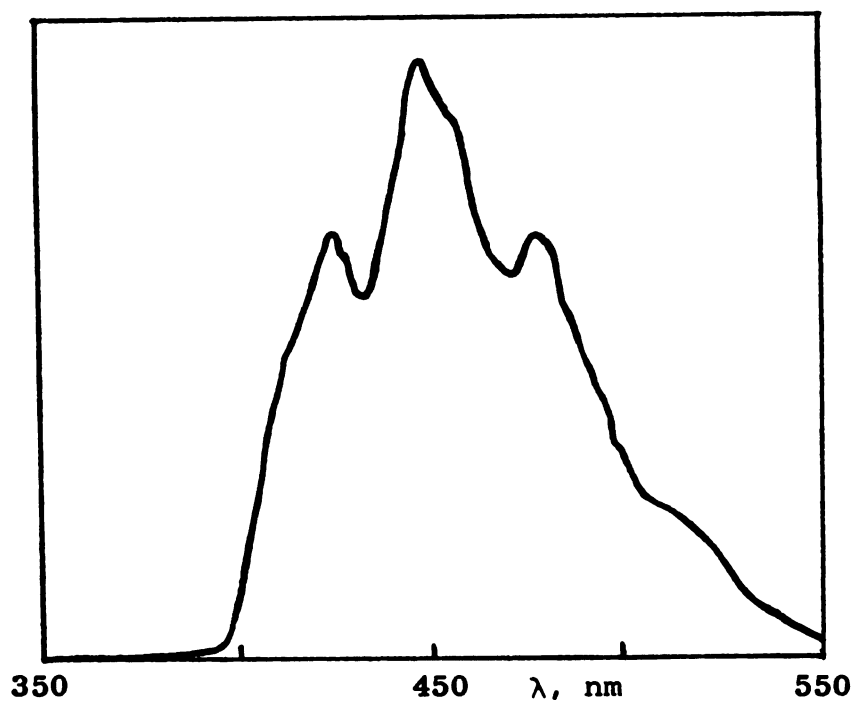


Figure 12. Phosphorescence of *m*-chloro- α -trifluoroacetophenone at 77°K.^a

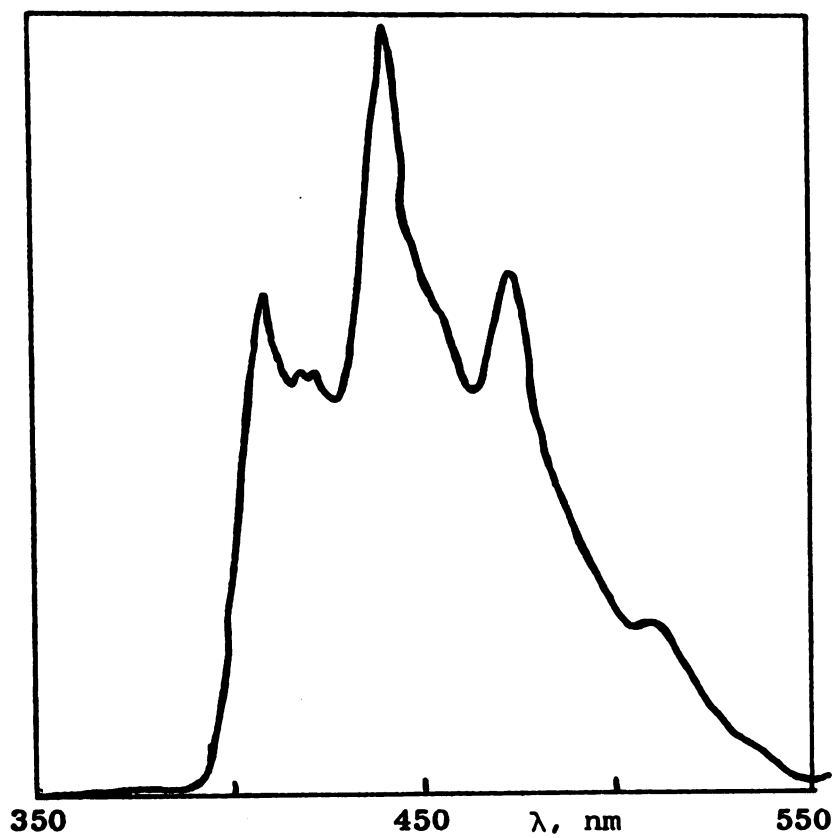


Figure 13. Phosphorescence of α -trifluoroacetophenone at 77°K.^a

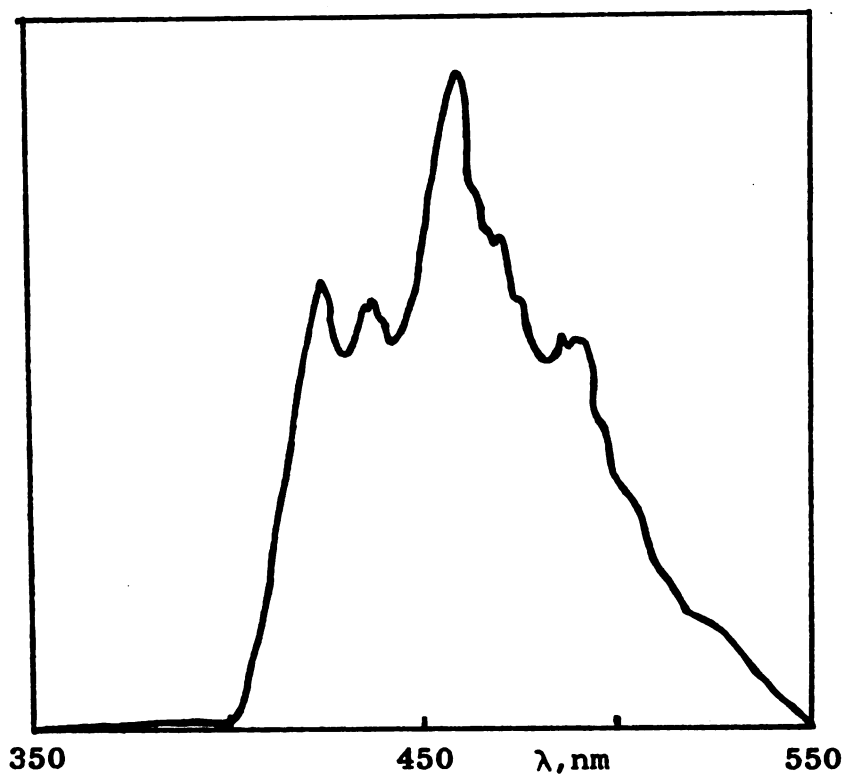


Figure 14. Phosphorescence of *p*-methyl- α -trifluoroacetophenone at 77°K.^a

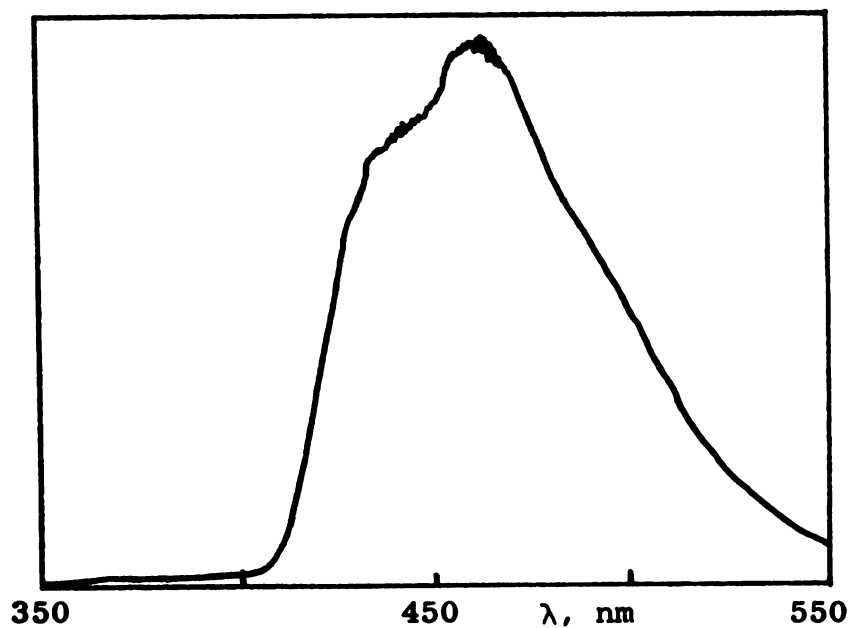


Figure 15. Phosphorescence of *p*-methoxy- α -trifluoroacetophenone at 77°K.^a

^aThe phosphorescence intensities of all the six ketones are not exactly measured.

DISCUSSION

PART I

A quantitative relationship³⁶ between kinetics of charge transfer and thermodynamic properties of the reactants has been established. The details of equation 23 have

$$\log k_r \approx -^3\Delta E_{0,0} + IP_D - E(A^-/A) + C \quad (23)$$

already been thoroughly reviewed during the discussion of charge transfer reactions in the introduction. Since it has been shown that the photoreduction of α -trifluoroacetophenone by toluene in benzene involves charge transfer complexing with only a modest degree of electron transfer,³⁸ the linear relationship between the logarithm of the rate constant, k_r , for quenching α -trifluoroacetophenone in benzene and the ionization potential of aromatic electron donors, IP_D , supports the same conclusion.³⁹ To confirm the involvement of partial charge transfer reaction, the relation of $\log k_r$ to IP_D in quenching triplet α -trifluoroacetophenone by substituted aromatics in acetonitrile has been studied. The plot of these data, Figure 16, has a slope of -2.22 / e.v. which is parallel to the slope of the same reaction in benzene. However, the value of the slope is much lower than the -17.06 / e.v. observed in systems in which

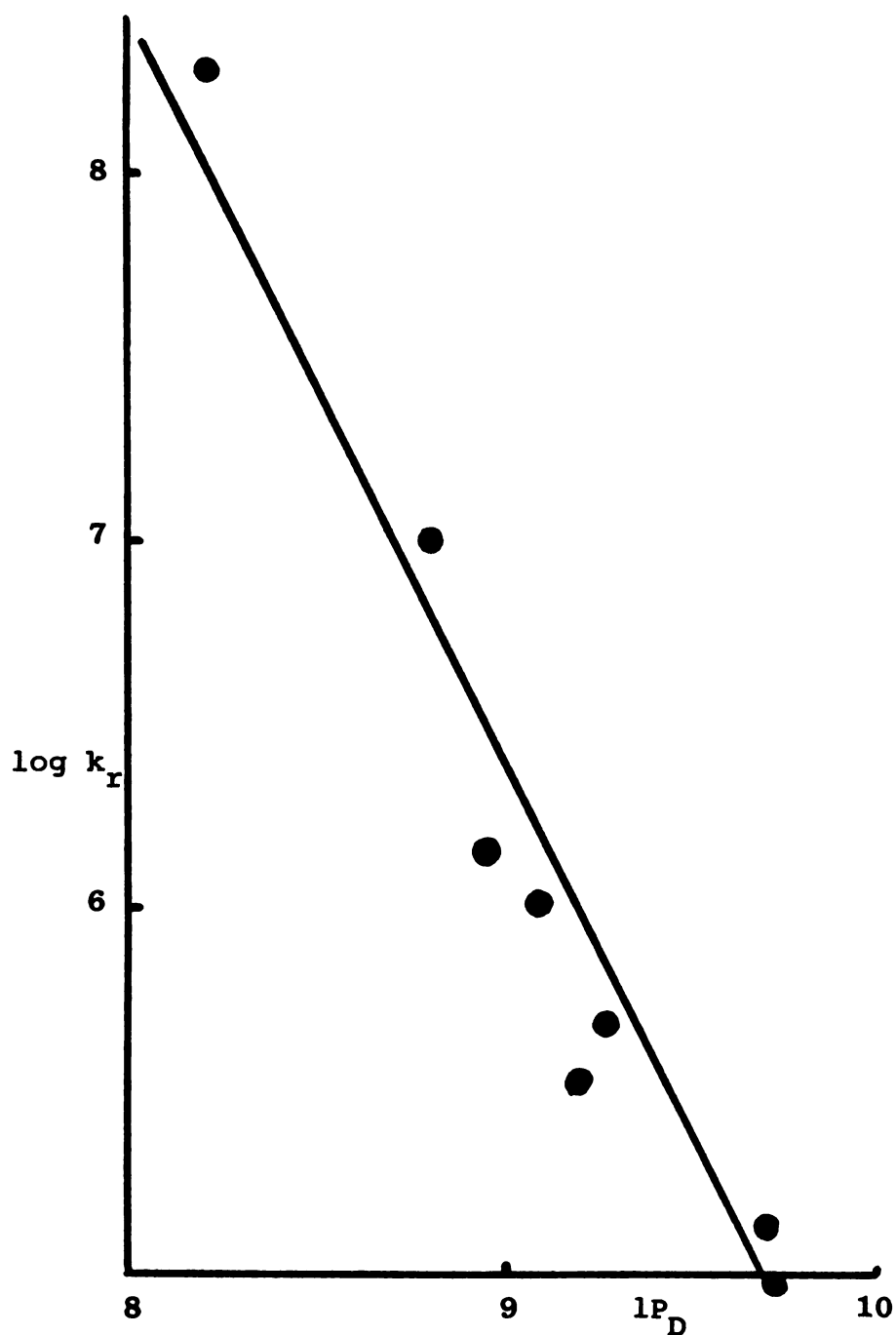


Figure 16. Correlation of rate constant for quenching of triplet α -trifluoroacetophenone by aromatics with their ionization potentials in acetonitrile.

quenching of fluorescence occurs by complete electron transfer.⁴³ The value 17.06/e.v. is obtained from the plot of quenching rate versus half-wave potential of the quenchers, whereas in quenching α -trifluoroacetophenone, the quenching rate is plotted against ionization potential instead of the half-wave potential of the monosubstituted aromatic quenchers because the unstable cations of the quenchers eliminate the possibility of achieving accurate half-wave potential. The correlation between ionization and half-wave potential has been established from the data of aromatic compounds with known ionization and reduction potentials. Although this relationship⁴⁴ is deduced from stable cations generated from

$$E_{1/2} = 0.66 \text{ IP} - 3.86 \quad (24)$$

aromatic molecules, the linear relationship could be extrapolated to those monosubstituted benzene cations. Conversion of the plot $\log k_T$ vs IP to $\log k_T$ vs half-wave potential for triplet quenching of α -trifluoroacetophenone by monosubstituted benzene in acetonitrile increases the value of the slope only by a factor of 1.5. The readjusted slope indicates that only 21% of the reaction is by electron transfer.

A small solvent effect is observed. The rate constant for the α -trifluoroacetophenone-toluene system in acetonitrile is only twice as large as in benzene, but the rate of fluorescence quenching of aniline, N,N-dimethyl- and N,N-diethyl-aniline involving full electron transfer in

acetonitrile is 13 times larger than in benzene.⁴⁵ The available data seem to support our proposed theory that photoreduction of α -trifluoroacetophenone with toluene in acetonitrile is by charge transfer.

PART II

In investigating the correlation of the nature of excited states and the reactivities of a charge transfer reaction, six ketones with $\pi\pi^*$ or $n\pi^*$ low lying triplet state have been studied. The plot of $\log k_r$ versus $-^3\Delta E_{0,0} - E(A^-/A)$ should give a straight line according to Weller's equation³¹ if the photoreduction of the six ketones involves charge transfer. However, problems arise in relating the six points in the plot as shown in Figure 17. Two straight lines or a curve linking all the six points could be drawn, but a straight line through all six points could also be proposed. Statistically speaking, the standard deviation and correlation coefficient of the straight line that is drawn through the six points and the four point line are 0.49; 0.96; and 0.51; 0.94, respectively. The values are so close to each other that it is difficult to distinguish which is the better line to interpret the data. The six-point line suggests that the nature of the lowest excited state does not have any effect on the charge transfer reaction. The low lying $\pi\pi^*$ triplet α -trifluoroacetophenones are at least as reactive as the low lying $n\pi^*$ triplet ketones. The terms in equation 23, as Weller

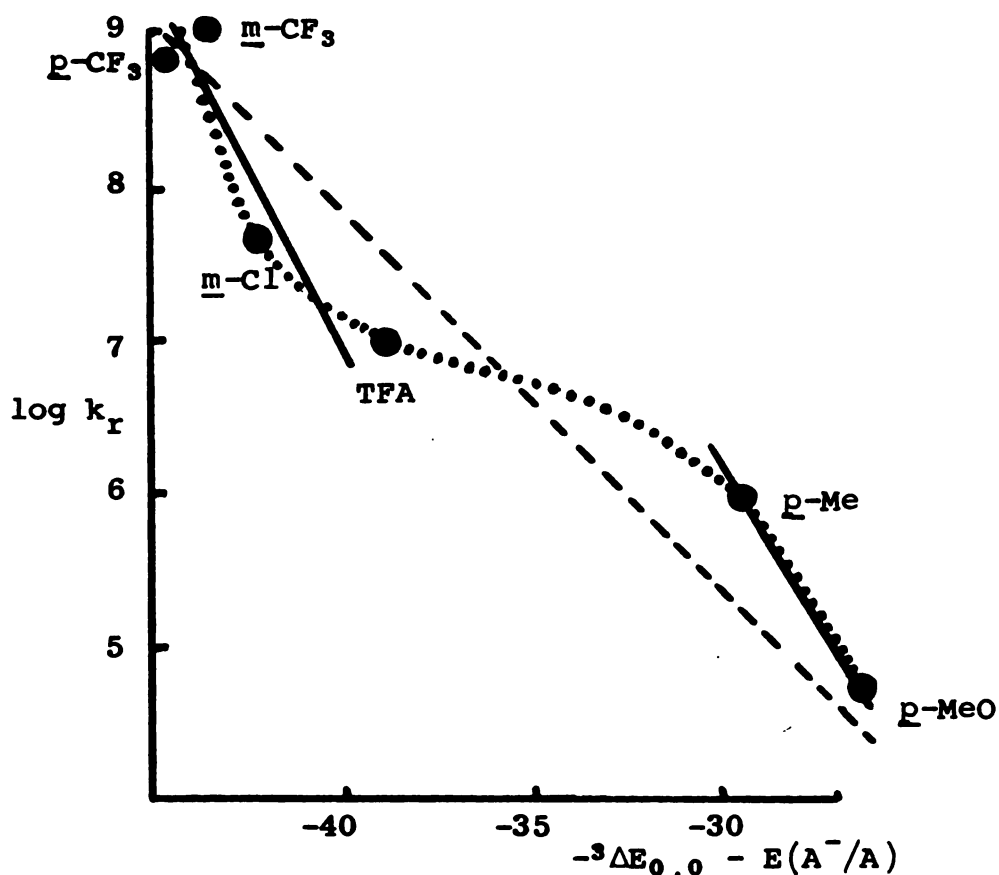


Figure 17. $\log k_r$ for quenching of acceptor triplets by toluene vs triplet energy minus reduction potential.

originally proposed, have already accounted for all the factors affecting the charge-transfer reaction. But the standard deviation of the straight line is 49%, whereas the greatest experimental error in individual determinations is only 16%. The absence of large experimental error suggests that the straight line is improbable to interpret the correlation of the six ketones.

An S-shaped curve can be proposed as the correlation among those points. The slope of the curve on the portion of $n\pi^*$ low lying triplet ketones is sharp as compared with

the zero slope when the $n\pi^*$ state of the ketone is close to the $\pi\pi^*$ state. When the curve reaches the *p*-methyl- α -trifluoroacetophenone, the slope increases again, but to a smaller extent than the limiting slope of the lowest $n\pi^*$ ketone. The large slope between α -trifluoroacetophenone and the $n\pi^*$ low lying triplet *p*-trifluoromethyl- α -trifluoroacetophenone, reveals that a difference of 6 kcal/mole in reduction potential causes a 70 fold difference in reactivity when the triplet energies of the ketones are about the same although their low lying triplet state is different. By comparing *p*-methyl and unsubstituted α -trifluoroacetophenone, both with low lying $\pi\pi^*$ triplets, a difference of 7.8 kcal/mole in reduction potential induces only a factor of 10 difference in reactivity and their difference in triplet energy is only 0.5 kcal. This phenomenon explains the discontinuity of the two slopes for $n\pi^*$ and $\pi\pi^*$ low lying triplet ketone. However, the higher sensitivity of $\log k_r$ to the reduction potential of $n\pi^*$ low lying triplet ketones indicates a higher degree of electron transfer. The lower sensitivity observed in *p*-methyl- and *p*-methoxy- α -trifluoroacetophenone implies that a lower degree of electron transfer might be due to the difference in the nature of energy state.

In an electron transfer process, the electron would first occupy the lowest n orbital if it transfers from the donor to the $n\pi^*$ low lying triplet ketones, but it would occupy the lowest empty π orbital if the low lying triplet is $\pi\pi^*$. For a charge transfer reaction, the formation of

an exciplex by interaction of the molecular orbital of the donor with the lowest empty orbital of the excited ketone is rate determining for the photoreduction of α -trifluoroacetophenone. It is assumed that the rate determining step for substituted and unsubstituted α -trifluoroacetophenone would be the same in the following discussion. For the $\pi\pi^*$ low lying triplet ketones, the π electron donor may interact with the aromatic ring or the localized aromatic ring with carbonyl, but for the $n\pi^*$ low lying triplet ketones, during exciplex formation it interacts with the oxygen of the carbonyl group. The difference in activation energy for the two processes could explain the reactivity differences between the $n\pi^*$ and $\pi\pi^*$ triplet ketones.

Weller, in studying the kinetics of fluorescence quenching, plotted $\log k_q$ versus ΔG as shown in Figure 18.⁴⁶

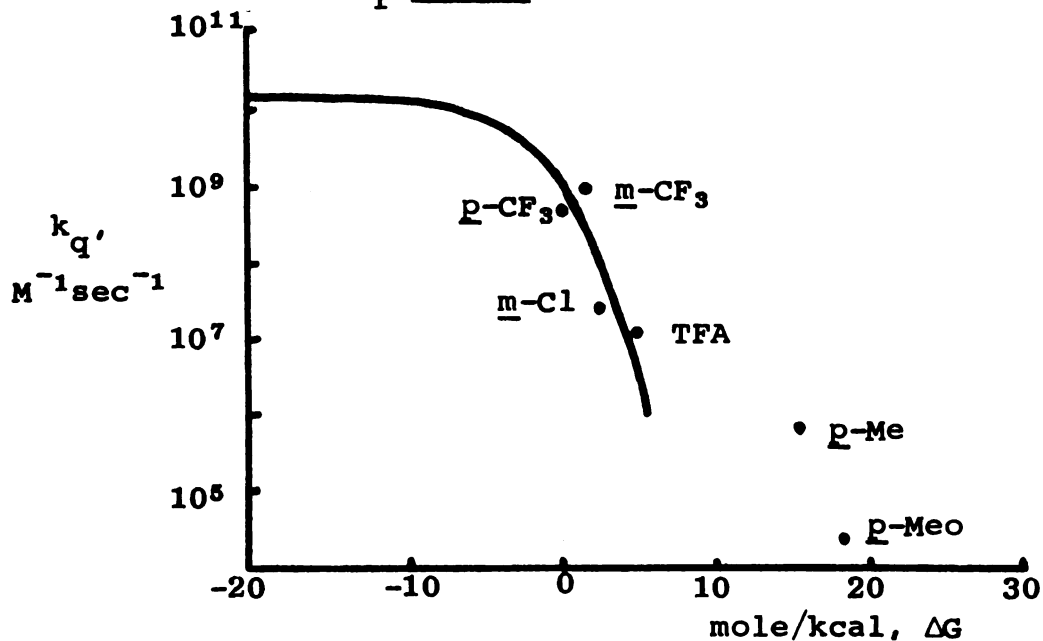


Figure 18. Fluorescence quenching rate constants k_q as a function of the free enthalpy ΔG .
 — experimental data of electron transfer process done by Weller.

However, the difference of ΔS between the photoreduction of substituted and unsubstituted α -trifluoroacetophenone with the reaction system that Weller studied would only shift the curve along the x-axis rather than change the shape of the curve. Para- and meta- α -trifluoromethyl, para-chloro and the unsubstituted α -trifluoroacetophenone fall within Weller's curve, but the other two $\pi\pi^*$ low lying triplet ketones have a much higher reactivity than expected for an electron transfer reaction according to the extrapolation of Weller's curve. Although the differences in the nature of states might explain the higher reactivity of the $\pi\pi^*$ low lying triplet ketone, without any experimental evidence, it cannot rule out the possibility that a different mechanism is involved. A comparison of reactivity among α -trifluoroacetophenone, acetophenone and valerophenone as shown in Table 7 suggests that the photoreduction of p-methyl and p-methoxy- α -trifluoroacetophenone might possibly occur via hydrogen abstraction, because 10-fold difference in reactivity between α -trifluoroacetophenone and p-methyl- α -trifluoroacetophenone can be observed as in the case of acetophenone and p-methyl-acetophenone. A 200-fold difference in reactivity between p-methyl and unsubstituted valerophenone is very close to the difference between p-methoxy and unsubstituted α -trifluoroacetophenone. On comparing the difference in reactivity, it seems evident that the photoreduction of the $\pi\pi^*$ low lying α -trifluoroacetophenone with toluene is a charge transfer reaction, but the photoreduction

Table 7. Substituent effects on triplet ketones.

Ketone	$k_r, M^{-1}sec^{-1}$	$\Delta^3E_{0,0}$ kcal/mole
TFA	1.1×10^7	70.41
<i>p</i> -Me-TFA	9.1×10^5	69.05
<i>p</i> -MeO-TFA	5.1×10^4	66.48
Acetophenone ^a	8.6×10^5	
<i>p</i> -Me-ACP	7.8×10^4	
Valerophenone ^b	$1.2 \times 10^8 \text{ sec}^{-1}$	72
<i>p</i> -Me-VAL	$1.8 \times 10^7 \text{ sec}^{-1}$	73
<i>p</i> -MeO-VAL	$5 \times 10^5 \text{ sec}^{-1}$	71

^aReference 26.^bReference 29.

of the $n\pi^*$ low lying acetophenone and valerophenone is via hydrogen abstraction. However, the coincidence of the reactivity difference among various substituted and unsubstituted ketones suggests the possibility of the involvement of hydrogen abstraction which could explain the reactivities of the two $\pi\pi^*$ lowest triplet ketones.

A definite conclusion cannot be drawn to explain the available data. Further experiments must be conducted before the reactions could be fully interpreted and explained.

The six points on the plot, in fact, are not sufficient to show the exact shape of the curve. Since the

p-methyl- α -trifluoroacetophenone is the inflection point of the curve, any experimental error on that point could cause large deviation on the shape of the curve. It would be desirable to obtain more points between the trifluoromethyl- α -trifluoroacetophenone and p-methoxy- α -trifluoroacetophenone in order to confirm the shape of the curve.

If the nature of the energy state affects the reactivity of ketones in a charge transfer reaction, the site of charge transfer on the ketone would be the determining factor on the reactivities. In order to judge whether an electron donor would interact with the aromatic ring or with the carbonyl of the $\pi\pi^*$ triplet ketones, substituting bulky groups on the benzene ring might decrease the reactivity of the $\pi\pi^*$ low lying triplet ketones to a greater extent than that of the $n\pi^*$ ketones. On the other hand, the relation of $\log k_r$ vs LP for the triplet quenching of p-t-butyl- α -trifluoroacetophenone by a series of substituted t-butyl benzenes would suggest the possibility of any interaction of localized π electrons with the donor.

The above discussed shows that apart from charge transfer, hydrogen abstraction might possibly be another mechanism for the photoreduction of p-methyl- and p-methoxy- α -trifluoroacetophenone. For an hydrogen abstraction reaction, there would be a significant deuterium isotope effect on k_r . More work on deuterium isotope effects is required in order to confirm the possible involvement of hydrogen abstraction on the low lying $\pi\pi^*$ triplet ketones.

EXPERIMENTAL

PART I. PROCEDURE

A. Preparation and Purification

1. Ketones

a) α -Trifluoroacetophenone (Columbia Organic Chemicals). Purification by spinning band distillation with 20 mm vacuum at 50° gave a center cut of >99.9% pure trifluoroacetophenone.

b) *p*-Methoxy- α -trifluoroacetophenone was prepared by the method of Dishan and Levine.⁴⁷ In a dry 1-liter 3-necked round bottom flask fitted with a mechanical stirrer, an addition funnel and an efficient reflux condenser, 0.6 g-atom of magnesium turnings were placed. The reaction required 0.6 mole of *p*-bromoanisole, 10 ml of *p*-bromoanisole with 50 ml of ether and a small crystal of iodine were added to the magnesium turnings. Nitrogen was passed through during the reaction. When the color of the solution changed to yellow after mild heating with no stirring, the remaining *p*-bromoanisole/ether mixture was added dropwise. The reaction mixture was stirred vigorously for two hours at room temperature. The reaction mixture was

refluxed for fifteen minutes, then 0.2 mole of trifluoroacetic acid in ether was added to the Grignard solution slowly within two hours, and the solution was refluxed for another hour. The reaction mixture was cooled and poured into a 10% hydrochloric acid. After the extraction, the ether layer was washed with sodium bicarbonate solution and dried. The product was purified by spinning band distillation with 0.9 mm vacuum at 75°. The purity of the product was $\geq 99.9\%$.

c) p-Methyl- α -trifluoroacetophenone was prepared by the Grignard procedure essentially as described for p-methoxy- α -trifluoroacetophenone, starting with p-bromotoluene.

d) m-Chloro- α -trifluoroacetophenone was prepared by the Grignard procedure essentially as described for p-methoxy- α -trifluoroacetophenone, starting with m-bromochlorobenzene.

e) m-Trifluoromethyl- α -trifluoroacetophenone was prepared by the Grignard procedure essentially as described for p-methoxy- α -trifluoroacetophenone, starting with m-bromotrifluoromethyl benzene.

f) p-Trifluoromethyl- α -trifluoroacetophenone was prepared by the Grignard procedure essentially as described for p-methoxy- α -trifluoroacetophenone, starting with p-bromotrifluoromethyl benzene.

g) Valerophenone (Aldrich Chemical Company) was distilled under reduced pressure, passed through alumina, and redistilled.

2. Solvent

a) Acetonitrile (Fisher Scientific Company) was distilled from KMnO_4 and Na_2CO_3 according to the procedure of O'Donnell, Ayres and Mann.⁴⁸ The final cut of the final fractional distillation was retained.

b) Benzene (Mallinckrodt Chemical Works) was purified by stirring over concentrated H_2SO_4 several times until the acid layer no longer turned yellow. The benzene was washed with NaOH solution, distilled water and NaCl solution, followed by drying over anhydrous MgSO_4 and fractional distillation from P_2O_5 . The middle 80% was collected.

3. Hydrogen Donors

a) Toluene (Fisher Scientific Company) was purified analogous to benzene.

b) Anisole (Matheson, Coleman and Bell) was purified by successively washing with 1M NaOH, distilled water and saturated NaCl solution. After it was dried over anhydrous MgSO_4 , pure anisole was obtained by the center cut from fractional distillation.

c) Chlorobenzene (Matheson, Coleman and Bell) was purified analogous to benzene.

d) Benzonitrile (Eastman Organic Chemicals) was purified analogous to anisole.

e) Benzotrifluoride was purified analogous to anisole.

f) *p*-Dichlorobenzene (Matheson, Coleman and Bell) was fractionally distilled and subsequently sublimed at reduced pressure.

g) Fluorobenzene (Aldrich Chemical Co.) was purified analogous to benzene.

h) *p*-Dimethoxybenzene was purified by Dr. Michael Thomas.

4. Quenchers

a) cis-Piperylene (Aldrich Chemical Co.) was passed through alumina followed by distillation.

b) Naphthalene (Matheson, Coleman and Bell) was purified by three crystallizations from ethanol.

5. Internal Standard

a) Hexadecane (Aldrich Chemical Co.) was purified analogous to benzene.

b) Heptadecane (Chemical Sample Co.) was purified analogous to benzene.

c) Eicosane (Matheson, Coleman and Bell) was used without further purification.

B. Photolysis

1. Irradiation Procedure

After solutions of proper concentration were prepared, two to three 2.8 ml portions from each solution were withdrawn and injected into 13 x 100 mm culture tubes. The solutions were degassed four times at 3×10^{-4} torr vacuum in freeze-thaw cycles and sealed off with a torch. The sample tubes were irradiated in parallel on a rotating "merry-go-around" apparatus⁴⁹ immersed in a water bath to make sure that each sample absorbed the same amount of light. A 450 watt Hanovia medium pressure mercury lamp was used for photolysis. The quantum yield determinations and most of the quenching studies were done in 300-320 nm region which was isolated with a filter solution of 0.002M potassium chromate in a 1% aqueous solution of potassium carbonate. For naphthalene quenching experiments, the 366 nm region was isolated with a set of Corning No. 7083 filter combinations.

2. Analysis of Sample

a) Instruments: Analysis for all photoproducts and standards were made on the following two vpc's which used flame ionization detectors.

VPC-1: Aerograph Hy-Fi model 600D gas chromatograph with 550 oven and 328 programmer connected to Leeds and Northrup Speedomax H recorder. This vpc was equipped with a 25' x 1/8" aluminum column containing 25% 1,2,3-tris-(2-cyanoethoxy)propane on 60/80 chromosorb P.

VPC-2: Varian Aerograph 1200 gas chromatograph connected to Leeds and Northrup Speedomax W recorder. This vpc was equipped with a 8' x 1/8" aluminum column containing 4% QF-1, 1% carbowax 20M on 60/80 chromosorb G.

Both instruments were connected to an Infrotronics Automatic Digital Integrator model CRS-208.

b) Standardization: Known amounts of internal standard had to be used to determine the concentration of a photoproduct. The internal standard was selected not to overlap with any peaks in the vpc traces, and the concentration of the internal standard had to be adjusted so that the peak area of internal standard would be close to the area of the larger product peak. The standardization factor SF, which is different for different combinations of internal standards and photoproducts, could be determined by the following expression:

$$SF = \frac{[\text{Product}]}{[\text{IS}]} \times \frac{\text{Area of IS Peak}}{\text{Area of Product Peak}} \quad (25)$$

where [IS] is the concentration of the internal standard.

With the known SF, the concentration of the product could be determined:

$$[\text{Product}] = \text{SF} \times [\text{IS}] \times \frac{\text{Area of Product Peak}}{\text{Area of IS Peak}} \quad (26)$$

c) Actinometry and Quantum Yield Determination:

The amount of light absorbed by the parent ketone had to be determined in order to calculate the quantum yield of the reaction. Parallel irradiation of the actinometer tubes containing 0.1M valerophenone and 0.01M C₁₆ internal standard in benzene provided a measurable amount of acetophenone produced via the type II elimination of valerophenone. Since the quantum yield of acetophenone formation under these conditions was 0.33,²⁵ the amount of light absorbed by the reaction could be measured

$$I_a = \frac{[\text{ACP}]}{0.33} \quad (27)$$

The quantum yield of the parent ketone reaction would then be measured from equation

$$\phi = \frac{[\text{Product}]}{I_a} \quad (28)$$

The intersystem quantum yield for m-CF₃ and p-methoxy- α -trifluoroacetophenone were measured by using cis-piperylene-acetophenone actinometry. Tubes containing 0.2M cis-piperylene and 0.1M ketones in acetonitrile were irradiated in parallel at 313 nm. Since the amount

$$[\text{cis-pip}]_0 \ln \frac{.555}{.555 - \% \text{ trans}} = [\text{pip}^*3] \quad (29)$$

of excited triplets produced could be calculated for

acetophenone (ACP), m-trifluoromethyl- α -trifluoroacetophenone (m-CF₃-TFA) and p-methoxy- α -trifluoroacetophenone (p-MeO-TFA). The intersystem quantum yield could be derived from the following expression by knowing that the intersystem quantum yield of acetophenone is 1.

$$(\phi_{isc})_{\text{p-MeO-TFA}} = (\phi_{isc})_{\text{ACP}} \frac{[\text{Pip}^{*3}]_{\text{p-MeO-TFA}}}{[\text{Pip}^{*3}]_{\text{ACP}}} \quad (30)$$

C. Absorption and Emission Spectra

Ultra violet spectra were taken on a Varian Cary 17 recording spectrophotometer. Phosphorescence spectra were taken on Aminco Bowman Spectrophotofluorometer equipped with a Houston Instrument 2000 Recorder. Lifetime of the ketones were measured on the apparatus of Professor Alfred Haug²⁸ in the MSU-AEC Plant Research Laboratory.

D. Reduction Potential

Reduction potential of the ketones were measured at a dropping mercury electrode with a Sargent Model XV polarograph. A saturated potassium chloride bridge connected sample solutions (10⁻³M ketone and 0.1M TEAP as supporting electrolyte in acetonitrile) to a freshly calibrated standard calomel electrode.

PART II: KINETIC DATA

A. Quantum Yield of Bibenzyl Formation

The quantum yields of bibenzyl formation were measured as a function of the concentrations of the hydrogen donors. BB refers to the bibenzyl formed from the toluene. C_n is the internal standard. I_a values were obtained from valerophenone actinometry and were averages of at least two tubes per run.

Table 8. Quantum yield of bibenzyl formation for 0.05M ketone in acetonitrile with toluene, indicated C_n and conditions.

Part A: α -Trifluoroacetophenone ^a				
Toluene, M	BB/ C_{16}	[BB], $10^{-5}M$	I_a, El^{-1}	ϕ_{BB}
2.00	1.1125	168	0.0491	0.0342
1.00	1.0198	154	0.0491	0.0313
0.75	1.8543	280	0.0977	0.0286
0.50	1.6225	245	0.0977	0.0251
0.25	1.2582	190	0.0977	0.0195

^a0.002M C_{16} ; SF = 1.5100; VPC -2.

Part B: p -Methoxy- α -trifluoroacetophenone ^a				
Toluene, M	BB/ C_{20}	[BB], $10^{-5}M$	I_a, El^{-1}	ϕ_{BB}
4.00	1.0107	182	0.0853	0.0213
2.00	0.9996	180	0.1284	0.0140
1.00	0.6441	116	0.1284	0.0090
0.75	0.7497	135	0.2136	0.0063
0.50	0.5103	91.9	0.2136	0.0043

^a0.001M C_{20} ; SF = 1.8007; VPC - 2.

Table 8 (Cont.)

<u>Part C: <i>p</i>-Methyl-α-trifluoroacetophenone^a</u>				
Toluene, M	BB/C ₁₇	[BB], 10 ⁻⁵ M	I _a , El ⁻¹	ϕ_{BB}
4.00	1.0749	146	0.0244	0.0597
2.00	1.7972	244	0.0488	0.0500
1.00	1.3027	177	0.0488	0.0362
0.75	2.1722	295	0.0959	0.0307
0.50	1.8144	246	0.0959	0.0256

^a0.001M C₁₇; SF = 1.3588; VPC-2.

<u>Part D: <i>m</i>-Chloro-α-trifluoroacetophenone^a</u>				
2.00	0.7636	103	0.0164	0.0626
1.00	0.7287	98.8	0.0164	0.0599
0.75	0.6868	93.4	0.0164	0.0567
0.50	1.2100	163	0.0323	0.0505
0.25	2.1237	143	0.0323	0.0443

^a0.001M C₁₇; SF = 1.3514; VPC-2.

<u>Part E: <i>m</i>-Trifluoromethyl-α-trifluoroacetophenone^a</u>				
0.20	1.2919	174	0.0423	0.0412
0.10	1.2463	168	0.0423	0.0397
0.07	1.5963	215	0.0624	0.0345
0.05	1.4588	197	0.0624	0.0315
0.02	0.9096	122	0.0624	0.0196

^a0.001M C₁₇; SF = 1.3514; VPC-2.

<u>Part F: <i>p</i>-Trifluoromethyl-α-trifluoroacetophenone^a</u>				
0.10	1.8083 ^b	250	0.0346	0.0721
0.07	3.0968 ^c	214	0.0346	0.0617
0.05	3.7419 ^c	258	0.0510	0.0506
0.03	2.8816 ^c	199	0.0510	0.0390

^aSF = 1.3832; VPC-2.

^b0.001M C₁₇.

^c0.0005M C₁₇.

B. Quenching Studies

Two different sets of reactions were separately studied. In the reaction of trifluoroacetophenone with toluene, a series of substituted benzenes were used as quenchers to calculate the rate constants of the quenchers. On the other hand, when substituted trifluoroacetophenones were reacted with toluene, naphthalene was used as the quencher in order to figure out the k_d/k_r ratio. Concentrations of bibenzyl formation were always kept in the 5×10^{-4} - $2 \times 10^{-3} M$ region to ensure linearity in the Stern-Volmer plots.

Table 9. System with 0.05M α -trifluoroacetophenone and 0.1M toluene in acetonitrile quenching with specific quencher in indicated C_n and conditions.

<u>Part A: Anisole^a</u>		
[Quencher], M	BB/ C_{16} ^b	ϕ^0/ϕ
0.000	1.9591	
0.005	1.5190	1.2897
0.007	1.4133	1.3861
0.01	1.2070	1.6231
0.03	0.6471	3.0272

^a0.001M C_{16} ; VPC-2. ^bVPC area ratio.

<u>Part B: Benzene</u>		
0.00	2.2709	
0.50	2.2293	1.0186
1.00	2.0878	1.0876
4.00	1.5018	1.5121
7.00	1.1563	1.9639

^a0.001M C_{16} ; VPC-2. ^bVPC area ratio.

Table 9. (Cont.)

<u>Part C: Benzotrifluoride^a</u>		
[Quencher], M	BB/C ₁₇ ^b	ϕ^0/ϕ
0.0	1.5911	
0.5	1.5614	1.0190
1.0	1.5243	1.0438
5.0	1.3115	1.2131

^a0.001M C₁₇; VPC-2. ^bVPC area ratio.

<u>Part D: Benzonitrile^a</u>		
0.0	1.7569	
0.5	1.7224	1.0200
1.0	1.6801	1.0457
3.0	1.6131	1.0891
6.0	1.5000	1.1712

^a0.001M C₁₇; VPC-2. ^bVPC area ratio

<u>Part E: Chlorobenzene^a</u>		
[Quencher], M	BB/C ₁₆ ^b	ϕ^0/ϕ
0.0	2.8914	
0.2	2.6997	1.0710
0.3	2.6374	1.0963
0.5	2.5018	1.1557
1.0	2.1826	1.3247
2.0	1.7614	1.6415

^a0.001M C₁₆; VPC-2. ^bVPC area ratio.

Table 9. (Cont.)

<u>Part F: Fluorobenzene^a</u>		
[Quencher], M	BB/C ₁₇ ^b	ϕ^0/ϕ
0.0	2.0449	
0.5	1.9057	1.0730
1.0	1.8402	1.1114
3.0	1.6337	1.2516
4.0	1.4900	1.3724
5.0	1.4473	1.4129

^a0.001M C₁₇; VPC-2. ^bVPC area ratio.

Part G: p-Dimethoxybenzene^a

0.00000	1.8745	
0.00001	1.8097	1.0358
0.00004	1.6564	1.1316
0.00007	1.4850	1.2622
0.0001	1.3362	1.4028

^a0.001M C₁₇, VPC-2. ^bVPC area ratio.

Part H: p-Dichlorobenzene^a

0.00	2.0186	
0.25	1.8680	1.0806
1.00	1.4565	1.3859
1.50	1.2221	1.6517

^a0.001M C₁₇; VPC-2. ^bVPC area ratio

Table 10. System with 0.05M α -trifluoroacetophenone, 0.001M C_{20} and indicated amount of toluene in acetonitrile quenching with naphthalene.

<u>Part A: 1M Toluene</u>		
[Quencher] ,M	BB/ C_{20} ^a	ϕ^0/ϕ
0.0000	2.0116	
0.0003	1.6774	1.1992
0.0005	1.4088	1.4278
0.001	1.1631	1.7295
0.0015	0.9147	2.1991

^aVPC area ratio; VPC-2.

<u>Part B: 0.4M Toluene</u>		
0.0000	1.9824	
0.0001	1.7541	1.1301
0.0003	1.3110	1.5121
0.0005	1.1994	1.6528
0.001	0.6786	2.9213

^aVPC area ratio; VPC-2.

Table 11. System with 0.05M *p*-methoxy- α -trifluoroacetophenone, 0.001M C₂₀ and indicated amount of toluene in acetonitrile, quenching with naphthalene.

<u>Part A: 1M Toluene</u>		
[Quencher], M	BB/C ₂₀ ^a	ϕ^0/ϕ
0.000000	1.8159	
0.000005	1.5836	1.1467
0.00001	1.4217	1.2773
0.00003	1.0814	1.6781
0.00005	0.8498	2.1369

^aVPC area ratio; VPC-2.

<u>Part B: 2M Toluene</u>		
0.00000	2.6832	
0.00001	2.0718	1.2951
0.00003	1.6005	1.6764
0.00005	1.2149	2.2085
0.0001	0.8088	3.3175

^aVPC area ratio; VPC-2.

Table 12. 0.05M m-Trifluoromethyl- α -trifluoroacetophenone-0.1M toluene system in acetonitrile quenching with indicated concentration of naphthalene.^a

[Quencher] ,M	BB/C ₁₇ ^b	ϕ^0/ϕ
0.000	1.3246	
0.002	1.1843	1.1199
0.006	0.9082	1.4584
0.01	0.7581	1.7472
0.015	0.6045	2.1912

^a0.001M C₁₇; VPC-2. ^bVPC area ratio.

Table 13. 0.05M m-Chloro- α -trifluoroacetophenone- 1M toluene system in acetonitrile quenching with indicated concentration of naphthalene.^a

[Quencher] ,M	BB/C ₁₇ ^b	ϕ^0/ϕ
0.0000	2.3209	
0.0001	2.2766	1.0194
0.0005	2.1180	1.0957
0.001	1.9777	1.1735
0.002	1.6936	1.3703

^a0.001M C₁₇; VPC-2. ^bVPC area ratio.

Table 14. 0.05M *p*-Methyl- α -trifluoroacetophenone- 1M toluene system in acetonitrile quenching with indicated concentration of naphthalene.^a

[Quencher] ,M	BB/C ₁₇ ^b	ϕ_0/ϕ
0.00000	0.8750	
0.00001	0.8242	1.0616
0.00003	0.7466	1.1719
0.0001	0.5682	1.5399
0.0002	0.4168	2.0993

^a0.001M C₁₇; VPC-2. ^bVPC area ratio.

Table 15. 0.05M *p*-Trifluoromethyl- α -trifluoroacetophenone- 0.1M toluene system in acetonitrile quenching with indicated concentration of naphthalene.^a

[Quencher] ,M	BB/C ₁₇ ^b	ϕ_0/ϕ
0.000	3.1364	
0.001	2.7470	1.1417
0.004	2.3178	1.3531
0.007	1.9196	1.6338
0.01	1.6374	1.9154

^a0.001M C₁₇; VPC-2. ^bVPC area ratio.

C. Determination of Intersystem Crossing Quantum Yield

Table 16. Triplet sensitized cis-trans isomerization of perylene.^a

Ketone ^b	Sample 1 % Trans	Sample 2 % Trans	Sample 3 % Trans	Average % Trans
Acetophenone	0.0750	0.0687	0.0713	0.0717
<u>p</u> -Methoxy- α -trifluoroacetophenone	0.0689	0.0696	0.0816	0.0733
<u>m</u> -Trifluoromethyl- α -trifluoroacetophenone	0.0666	0.0713	0.0654	0.0676

^a0.200M initial cis-peryene, VPC-1. ^b 0.100M.

LIST OF REFERENCES

LIST OF REFERENCES

1. G. Ciamician and P. Silber, Ber., 33, 2911 (1900); 34, 1530 (1901).
2. P. J. Wagner and G. S. Hammond, Adv. Photochem., 5, 94 (1968).
3. G. S. Hammond and W. M. Moore, J. Am. Chem. Soc., 81, 6334 (1959).
4. C. W. Larson and H. E. O'Neal, J. Phy. Chem., 70, 2475, (1966).
5. G. S. Hammond, W. P. Baker, and W. M. Moore, J. Am. Chem. Soc., 83, 2795 (1961).
6. A. Padwa, Tetrahedron Lett., 3465 (1964).
7. S. G. Cohen and R. J. Baumgarten, J. Am. Chem. Soc., 87, 2996 (1965).
8. J. A. Howard, Adv. Free Radical Chem., 4, 49 (1971).
9. G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 84, 207 (1962).
10. P. J. Wagner, ibid., 89, 2503 (1967).
11. S. G. Cohen and H. M. Chao, ibid., 90, 165 (1968).
12. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).
13. P. J. Wagner and G. S. Hammond, Adv. Photochem., 5, 94 (1968).
14. H. L. J. Backstrom and K. Sandros, J. Chem. Phys., 23, 2197 (1955).
15. S. P. McGlynn, Molecular Spectroscopy of the Triplet State, Englewood Cliffs, N.J.: Prentice Hall, 1969. Chapters 4 and 6.

16. C. Walling and M. J. Gibian, J. Am. Chem. Soc., 87, 3361 (1965).
17. D. R. Arnold, R. L. Hinman, and A. H. Glick, Tetrahedron Lett., 1425 (1964).
18. W. R. Bergmark, B. Beckmann, and W. Lindenberger, ibid., 2259 (1971).
19. J. N. Murrell, The Theory of the Electronic Spectra of Organic Molecules, London: Methuen and Co., Ltd., 1963, pp. 206, 227.
20. S. Nagakura and J. Tanaka, J. Chem. Phys., 22, 236 (1954).
21. D. Bryce-Smith, Pure Appl. Chem., 16, 47 (1968).
22. J. Petruska, J. Chem. Phys., 34, 1120 (1961).
23. N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and Dusenbery, J. Am. Chem. Soc., 89, 5466 (1967).
24. N. C. Yang and R. Dusenbery, Molecular Photochem., 1, 159 (1969).
25. P. J. Wagner and A. E. Kemppainen, J. Am. Chem. Soc., 90, 5898 (1968).
26. N. C. Yang and R. Dusenbery, ibid., 90, 5899 (1968).
27. P. J. Wagner, A. E. Kemppainen, and H. N. Schott, ibid., 92, 5280 (1970).
28. P. J. Wagner, M. J. May, A. H. Haug, and D. R. Graber, ibid., 92, 5269 (1970).
29. P. J. Wagner, A. E. Kemppainen, and H. N. Schott, ibid., 95, 5604 (1973).
30. P. J. Wagner and T. Nakahira, ibid., 95, 8474 (1973).
31. A. Weller in, Fast Reactions and Primary Processes in Chemical Kinetics, Proceedings of the Fifth Nobel Symposium, S. Claesson, Ed., New York: Interscience, 1967, p. 413.
32. B. S. Solomon, C. Steel, and A. Weller, Chem. Commun., 927 (1969).
33. S. G. Cohen and J. I. Cohen, J. Phys. Chem., 72, 3782 (1968).

34. A. Becket and G. Porter, Trans. Faraday Soc., 59, 2038 (1963).
35. R. S. Davidson and R. Wilson, J. Chem. Soc. (B), 71 (1970).
36. S. G. Cohen and J. B. Guttenplan, J. Am. Chem. Soc., 94, 4040 (1972).
37. S. G. Cohen and J. B. Guttenplan, Tetrahedron Lett., 2163 (1972).
38. P. J. Wagner and R. A. Leavitt, J. Am. Chem. Soc., 92, 5806 (1970).
39. P. J. Wagner and R. A. Leavitt, ibid., 95, 3669 (1973).
40. N. J. Turro, Molecular Photochemistry, New York: W. A. Benjamin, Inc., 1967, p. 6.
41. P. J. Wagner in Creation and Detection of the Excited State, Vol. I, Part A., A. A. Lamola, Ed., New York: Marcel Dekker, Inc., 1971, Chapter 4.
42. J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Hesson, K. Draxi, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," U.S. Department of Commerce, National Bureau of Standards, 1969.
43. D. Rehm and A. Weller, Ber. Bunsenges. Phys. Chem., 73, 834 (1969).
44. E. S. Pysh and N. C. Yang, J. Am. Chem. Soc., 85, 2124 (1963).
45. H. Leonhardt and A. Weller, Ber. Bunsenges. Phys. Chem., 67, 791 (1963).
46. D. Rehm and A. Weller, Israel J. of Chem., 8, 259 (1970).
47. K. T. Dishan and R. Levine, J. Am. Chem. Soc., 78, 2268 (1956).
48. J. F. O'Donnell, J. T. Ayres and C. K. Mann, Anal. Chem., 37, 1161 (1965).
49. F. G. Moses, R. S. H. Liu, and B. M. Monroe, Molecular Photochem., 1, 245 (1969).

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03085 5575