CHARGE TRANSFER INTERACTIONS IN THE PHOTOREDUCTION OF PHENYL KETONES

By

Allen Edward Puchalski

A DISSERTATION

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1980

ABSTRACT

CHARGE TRANSFER INTERACTIONS IN THE PHOTOREDUCTION OF PHENYL KETONES

By

Allen Edward Puchalski

This work provides experimental results that make it possible to combine two different pathways in the photoreduction reaction into one general scheme. This scheme involves competing rate constants for the initial interaction of excited ketones with substrate, and the subsequent reactions that lead to products. The initial interactions are direct hydrogen abstraction and exciplex formation. The selectivity of the reaction is shown to be related to the competition between these modes of interaction and to the extent of charge-transfer interactions in the exciplex. The inefficiency of the reaction is discussed as a combination of exciplex decay and radical disproportionation.

The selectivity of the reaction was studied as a function of primary versus tertiary abstraction from p-cymene. For studies involving ring substitution of acetophenone, benzophenone or α,α,α-trifluoroacetophenone and for α-substitution of acetophenone a consistent pattern

emerged. This pattern showed an increase in the fraction of primary abstraction as the electron deficiency of the ketone increased. This is interpreted as the result of exciplex involvement in the reaction. This appears to be true for acetophenone as well as α,α,α-trifluoroacetophenone, even though exciplex may provide only a minor path to products for acetophenone.

The reactions of the radicals formed in the photoreduction reaction were modeled by generating the radicals independently using di-t-butyl peroxide. This resulted in almost identical product distribution for the two methods of radical formation, showing that cage reactions are unimportant in the photoreduction reaction. The formation of disproportionation products in the peroxide experiments failed to account for all of the observed inefficiency of the photoreduction of either acetophenone or α,α,α-trifluoroacetophenone by alkylbenzenes. This suggested a source of inefficiency in these reactions prior to radical formation.

The photoreduction of ketones by alcohols was shown to involve interaction of the excited ketone with the hydroxy group of the alcohol. For the reaction of acetophenone with 1-phenylethanol the deuteration of the hydroxy group led to a decrease in the rate constant and an increase in the efficiency. This shows that interaction with the proton of the hydroxy group provides a quenching mechanism

for acetophenone. Propiophenone is shown to interact with acetophenone pinacol to give propiophenone pinacol and acetophenone. This is also explained by hydrogen abstraction from the hydroxy group. The rate of hydrogen atom exchange from 1-hydroxy-1-phenylalkyl radicals to ground state ketone was also studied using the photoreduction of ketones by alcohols.

I would like to dedicate this thesis to my wife, Maureen, for her support and patient understanding. I would also like to dedicate this work to my parents, Helen and Walter Puchalski, for their constant encouragement and support.

ACKNOWLEDGEMENTS

I wish to thank Professor Peter J. Wagner for his support in conducting this research and for sharing his knowledge and experience with me. I would also like to thank the members of the Wagner research group for many informative discussions.

I would like to thank the Michigan State University Department of Chemistry for its financial support and the use of its facilities. Finally, I would like to express my gratitude to the National Science Foundation for their support through research assistantships from Dr. Peter J. Wagner's research grants.

TABLE OF CONTENTS

Page

Page

Page

LIST OF TABLES

Table Page

Table Page

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

AP	Acetophenone
APH_2	1-Phenylethanol
MFA	α-Flouroacetophenone
DFA	α,α-Difluoroacetophenone
TFA	α,α,α-Trifluoroacetophenone
$TFAH_2$	1-Phenyl-2,2,2-Trifluoroethanol
BP	Benzophenone
PP	Propiophenone
PPH_2	1-Phenylpropanol
m-F-AP	m-Fluoroacetophenone
p-F-AP	p-Fluoroacetophenone
m-CF_3-AP	m-Trifluoromethylacetophenone
p-Me-AP	p-Methylacetophenone
m-Me-TFA	m-Methyl-α,α,α-Trifluoroacetophenone
p-Me-TFA	p-Methyl-α,α,α-Trifluoroacetophenone
m-CF_3-TFA	m-Trifluoromethyl-α,α,α-Trifluoroacetophenone
p-MeO-TFA	p-Methoxy-α,α,α-Trifluoroacetophenone
p-Cl-TFA	p-Chloro-α,α,α-Trifluoroacetophenone
4,4'-Me-BP	4,4'-Dimethylbenzophenone
4,4'-MeO-BP	4,4'-Dimethoxybenzophenone
4,4'-Cl-BP	4,4'-Dichlorobenzophenone

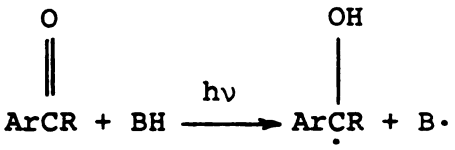
INTRODUCTION

The photoreduction reaction was first observed around the turn of the century and has periodically been the focus of intense interest ever since. This continued renewal of interest is due to an ever increasing knowledge of excited state processes and also advances in techniques which allow one to perform measurements that had previously not been possible. New theories of excited state processes can not only increase the understanding of the photoreduction reaction, but the photoreduction reaction can be a valuable tool in developing and testing these theories.

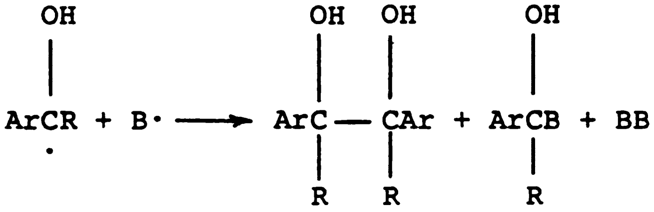
The primary goal of this research project has been to study the photoreduction reaction to see how it behaves with respect to theories of excited state behavior that are of current interest. The research focused on new ways to investigate the reaction that would result in the measurement of new parameters. These parameters could then be used to study individual steps of the reaction, leading to a more complete understanding of the overall process. The particular areas of excited state reactivity that are of current interest involve the interaction of excited molecules with ground state molecules to form excited complexes and the role of electron transfer in the formation of these complexes.

Historical Background-Early Product Studies

The first activity in the area of photoreduction started with the report of Ciamician and Silber[1] that the action of sunlight on a mixture of benzophenone and ethanol formed a precipitate identified as benzpinacol. This initial report led to the investigation of other possible hydrogen donors, such as Paternó and Chieffi's study of hydrocarbons.[2] They studied both aliphatic hydrocarbons such as pentane and decane, and alkylbenzenes such as toluene, ethylbenzene, cumene, p-xylene, diphenylmethane, and p-cymene. For the reaction of benzophenone with p-cymene, a compound that plays an important role in the work described here, the only products other than benzpinacol that were observed were unsaturated hydrocarbons and resin. However, some products incorporating the hydrogen donor were identified in other systems, such as 1,1,2,2-tetraphenylethanol from the reaction of benzophenone and diphenylmethane and 2,3-diphenylbutane from ethylbenzene. These products are indicative of the types that are expected from the photoreduction reaction. The products are formed by coupling of the two radicals produced in the initial hydrogen abstraction step:



$$\mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R} + \mathrm{BH} \xrightarrow{h\nu} \mathrm{Ar}\underset{\bullet}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}\mathrm{R} + \mathrm{B\cdot}$$

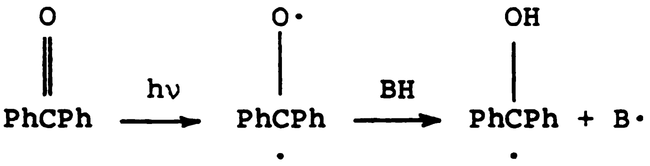


$$\mathrm{Ar}\underset{\bullet}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}\mathrm{R} + \mathrm{B\cdot} \longrightarrow \mathrm{Ar}\underset{\underset{\mathrm{R}}{|}}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}-\underset{\underset{\mathrm{R}}{|}}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}\mathrm{Ar} + \mathrm{Ar}\underset{\underset{\mathrm{R}}{|}}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}\mathrm{B} + \mathrm{BB}$$

Alcohols[3,4] and hydrocarbons[3] are not the only hydrogen donors that have been used. Work has also been done with amines,[5-11] tributylstannane,[12] ethers,[13,14] sulphides,[9,15] mercaptans,[16,17] and phenols.[18] These compounds, however, often lead to products that are difficult to analyze or that undergo further reactions and complicate analysis and kinetic studies.

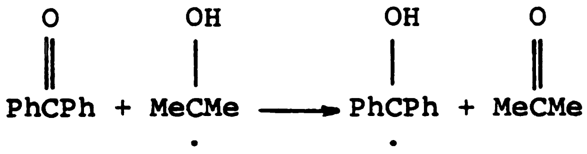
Early Mechanistic Studies

The mechanism of the reaction has been the subject of much interest. Bodenstein[19] first suggested that the absorption of light by the carbonyl produces a biradical structure which abstracts a hydrogen atom from the donor to give a pair of radicals:



$$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} \xrightarrow{h\nu} \mathrm{Ph}\underset{\bullet}{\overset{\mathrm{O\cdot}}{\overset{|}{\mathrm{C}}}}\mathrm{Ph} \xrightarrow{\mathrm{BH}} \mathrm{Ph}\underset{\bullet}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}\mathrm{Ph} + \mathrm{B\cdot}$$

The predominant or exclusive formation of pinacol derived from the ketone with little, if any, crossed pinacol and pinacol derived from the alcohol was observed in a number of studies.[1,2,20-22] Weizmann[20] suggested that this was due to the relative stability of radicals, some giving predominantly coupling products, others leading to disproportionation. Pitts et al.[21] proposed the exchange of a hydrogen atom from a hydroxy radical to ground state ketone to account for the high yield of benzpinacol and acetone when benzophenone was photoreduced by 2-propanol:



$$\mathrm{Ph}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Ph} + \mathrm{Me}\underset{\bullet}{\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}}\mathrm{Me} \longrightarrow \mathrm{Ph}\underset{\bullet}{\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}}\mathrm{Ph} + \mathrm{Me}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Me}$$

This exchange is a common reaction[23,24] but usually goes unnoticed when the donor is a hydrocarbon since the only exchange between a hydroxy radical and ketone is a degenerate one.

Another major step in the understanding of the reaction came when excited states were characterized as either singlets or triplets.[25-28] The reactivity of compounds could then be correlated with this information. Whether the excited state is n,π^* or π,π^* was shown to have a bearing on the course of the reaction.[29-32] Photoreduction and the Norrish Type II reaction both involve abstraction of a hydrogen atom and have served as valuable probes in this particular respect. Both of these probes have led to the conclusion that n,π^* triplets are normally much more reactive than π,π^* toward abstraction of hydrogen atoms. They have also shown that n,π^* triplets exhibit reactivity parallel to alkoxy radicals.[3,33-36] This has been particularly evident for the comparison of t-butoxy radicals and the photoreduction of benzophenone and acetophenone (see Table 1). Not only are the relative reactivities very similar, but the absolute rate constants for these ketones are very close to those of t-butoxy radicals. These parallels break down for excited ketones that are significantly electron deficient and are believed to react through initial formation of complexes which have strong charge-transfer character to them.[37,38] These excited state complexes, called exciplexes, do not exhibit the same trend in rate constants as alkoxy radicals. Alkoxy radicals and the triplets of acetophenone and benzophenone show reactivity patterns that correlate with carbon-hydrogen bond strength.[33-35] Rate constants for more electron deficient ketones correlate better with the ionization potentials of donors[38] than with carbon-hydrogen bond strengths.

The major evidence for an intermediate complex being formed with electron deficient ketones is the study of α,α,α-trifluoroacetophenone (TFA) with toluene-α-d_3 by

Table 1. Comparison of Rate Constants for Triplet Ketones and t-Butoxy Radicals

Substrate	$k_r (10^5 M^{-1} s^{-1})$			
	t-Butoxy Radical[a]	Benzophenone[a]	Acetophenone[b]	α,α,α-Trifluoroacetophenone[b]
Toluene	2.3	1.7	1.2	73.
Ethylbenzene	10.5	5.0	---	---
Cumene	8.7	5.5	2.8	44.
Mesitylene	8.3	9.3	---	1400.
Ethanol	11.0	5.6	---	---
2-Propanol	18.0	13.0	---	---
Benzhydrol	69.0	8.9	---	---

[a] Reference 36.

[b] Reference 38.

Wagner and Leavitt.[38] They found the rate constants were the same for the reaction of TFA with toluene and toluene-α-d_3, but the efficiency of the reaction changed significantly. This shows that the rate determining step does not involve breaking of a carbon-hydrogen bond. It also shows that there is a subsequent reaction involving carbon-hydrogen bond breaking which is in competition with a decay mode. This competition is necessary to explain the deuterium isotope effect on product formation. For the reaction of acetophenone and toluene there is a deuterium isotope effect on both rate constants and quantum yields of product formation.[38,39] The primary isotope effect on the rate constant shows that carbon-hydrogen bond breaking is involved in the rate-determining step of the reaction with acetophenone, unlike TFA. This can be interpreted as direct hydrogen abstraction. There also appears to be a deuterium isotope effect on the maximum quantum yield for the reaction of acetophenone with toluene.[38,40] This suggests that there is a pathway that competes with direct hydrogen abstraction. If there is only one type of interaction the rate constant would vary, but the maximum efficiency should not change significantly. In fact the efficiency might be expected to increase if disproportionation were the major source of inefficiency since there would be a deuterium isotope effect for back hydrogen transfer.

The exciplex proposed for the reaction of TFA with alkylbenzenes had a significant amount of charge-transfer to it. Weller[41] studied the quenching of aromatic hydrocarbons by amines, a process which is due to an electron transfer from the amine to the excited hydrocarbon. He was able to relate the rate constants to the reduction potential of the acceptor, the ionization potential of the donor, and the energy of the excited state. Other work soon followed with ketones being quenched by amines.[9,10,42,43] The ketones showed a much smaller change in quenching rate constants as a function of donor ionization potential than observed for the hydrocarbons. Both systems have been shown to reach the diffusion controlled limit for quenching with donors of low enough ionization potentials.[39,41,44,45] Amines are not the only compounds that can act as electron transfer quenchers.[9,46-48] The major requirement is that the compound be easily oxidized. Therefore, it is not surprising that alkylbenzenes can form complexes.[38] There will be a competition between complex formation and other processes, such as direct hydrogen abstraction, with the relative rates of the two processes determining which one predominates. What happens once these complexes are formed is a major concern of this research project.

The treatment of Weller[41] relates the rate constant for quenching to the change in free energy for electron transfer. To do this he assumed the change in free energy of activation was proportional to the change in free energy for the reaction and that the change in free energy of the reaction is equal to the change in either the excited state reduction potential of the acceptor, or the oxidation potential of the donor. While other workers[49,50] have suggested different equations for relating the free energy of activation to the free energy of the reaction, most of them predict similar results for a wide range of free energy changes. These relationships hold very well when the reaction is a pure endothermic electron transfer reaction. When an exciplex with only partial charge-transfer is formed, which is the rule for triplet ketones,[10] the change in free energy for reaction is no longer equal to the change in free energy for electron transfer. The relationship between free energy of exciplex formation and free energy of electron transfer for these systems depends on the contribution from charge-transfer to the stability of the exciplex.

The stability of an exciplex is due to the electronic interactions between the excited and ground state molecules involved. These electronic interactions can be described by a wavefunction which is a combination of the wavefunctions for the locally excited states and the wavefunctions for the electron transfer states.[51,52]

$$\psi_{\text{exciplex}} = a\psi_{DA^*} + b\psi_{D^+A^-} + c\psi_{D^*A} + d\psi_{D^-A^+}$$

For the exciplexes of interest here the coefficients "c" and "d" are negligible compared to "a" and "b"; therefore the wavefunction for the exciplex can be described as:

$$\psi_{exciplex} = a\psi_{DA^*} + b\psi_{D^+A^-}$$

The character of the exciplex is then determined by the relative importance of the two coefficients "a" and "b". When "a" is negligible compared to "b" the complex can be considered as a pair of ions or radical ions. These ions may diffuse apart, especially in polar solvents.[45,53-55] Because of this it is possible that many excited state electron transfer reactions proceed via exciplexes with finite lifetimes.[56] For the reactions of triplet ketones with alkylbenzenes that will be studied here, there is no evidence for formation of solvated radical ions.[54,57] It is likely that the exciplexes discussed here have a significant amount of character derived from the excited ketone (coefficient "a" in equation XV is important). The contribution from the charge transfer component (coefficient "b") is also important, but depends on the ketone and substrate. For example, there should be a much greater contribution from the charge-transfer interaction for TFA with a substrate than for acetophenone with the same substrate because of the relative excited state reduction potentials. Because of this there are two factors to take into consideration with respect to reactions occurring via exciplexes. The first factor that has to be determined is whether all of the reaction occurs through exciplex. The second is whether a change in the charge-transfer character of the exciplex influences the course of the reaction. If there are other paths for reaction besides exciplex formation systematic changes in either ketone or substrate may change the results in a predictable manner, but it may not be possible to determine which of these factors are responsible. One of the major goals of this research is to explore systems that may enable one to separate these two effects so that they can be measured independently.

Kinetics

To understand excited state reactivity it is necessary to make quantitative measurements of quantum yields, lifetimes and rate constants. This information is necessary to compare a large number of systems since chemical yields do not accurately reflect quantum yields or rates of reactions.

The quantum yield (Φ) is defined as:

$$\Phi = \frac{\text{number of molecules that react}}{\text{number of photons of light absorbed}}$$

Scheme 1 shows the reactions that are involved in the photoreduction of a ketone (K) by substrate (BH). The reaction proceeds through an intermediate which goes on to products with an efficiency α. This intermediate may be an exciplex or a pair of radicals formed from hydrogen

Scheme 1. Steps of the Photoreduction Reaction

	Reaction	Rate
I.	$K \underset{k_{d_1}}{\overset{h\nu}{\rightleftharpoons}} {}^1K^* \xrightarrow{k_{isc}} {}^3K^*$	$I_a\left(\frac{k_{isc}}{k_{isc} + k_{d_1}}\right)$
II.	${}^3K^* \xrightarrow{k_d} K$	$k_d[{}^3K^*]$
III.	${}^3K^* + Q \xrightarrow{k_q} K + {}^3Q^*$	$k_q[Q][{}^3K^*]$
IV.	${}^3K^* + BH \xrightarrow{k_r} [\text{Intermediates}]$	$k_r[BH][{}^3K^*]$
V.	$[\text{Intermediates}] \xrightarrow{\alpha} \text{Products}$	
VI.	$[\text{Intermediates}] \xrightarrow{1-\alpha} K + BH$	

abstraction. The rates for each step of the reaction are also given.

The efficiency of the reaction can be broken down into the efficiency for each step of the reaction.

1. The efficiency of triplet formation (Φ_{isc})

$$\Phi_{isc} = \frac{k_{isc}}{k_{isc} + k_{d_1}}$$

2. The efficiency of intermediate formation from triplet ketone is:

$$\frac{k_r[BH]}{k_r[BH] + k_q[Q] + k_d}$$

3. The efficiency of intermediate going on to give product is α.

The overall quantum yield is a product of these three efficiencies:

$$\text{Quantum Yield of Product} = \Phi_{Prod} = \alpha\Phi_{isc}\left(\frac{k_r[BH]}{k_r[BH] + k_d + k_q[Q]}\right) \qquad \text{(VII)}$$

Without quencher the quantum yield (Φ^0) is:

$$\Phi^0 = \alpha\Phi_{isc}\,\frac{k_r[BH]}{k_r[BH] + k_d} \qquad \text{(VIII)}$$

Dividing equation VIII by equation VII one obtains:

$$\frac{\Phi^0}{\Phi} = \frac{k_r[BH] + k_d + k_q[Q]}{k_r[BH] + k_d} = 1 + k_q[Q]\tau \qquad \text{(IX)}$$

where $\tau^{-1} = k_r[BH] + k_d$. A plot of Φ^0/Φ versus $[Q]$ gives a slope of $k_q\tau$. The value of k_q is known for triplet quenchers in various solvents;[58-60] therefore, the value of τ can be easily obtained. A plot of τ^{-1} as a function of substrate concentration ([BH]) gives an intercept of k_d and slope of k_r.

By inverting equation VIII one obtains a linear plot of $(\Phi^0)^{-1}$ versus $[BH]^{-1}$:

$$(\Phi^0)^{-1} = (\alpha\Phi_{isc})^{-1}(1 + \frac{k_d}{k_r[BH]})$$

The slope of the plot is $k_d(\alpha\Phi_{isc}k_r)^{-1}$, and the intercept is $(\alpha\Phi_{isc})^{-1}$. Dividing the slope of the intercept gives k_d/k_r. This ratio can be used as an independent check for the values of k_d and k_r obtained by quenching studies. The intercept is the maximum quantum yield, the value expected for infinite substrate concentration.

$$\Phi^{max} = \alpha\Phi_{isc}$$

The efficiency (α) of the intermediate going on to give product can be calculated from this value and the intersystem crossing yield.

The possibility of more than one type of interaction of ketone with substrate, as shown in Scheme 2, is also consistent with this kinetic derivation. The rate constant for interaction of ketone with substrate (k_r in

Scheme 2. Possible Modes of Interaction of Excited Ketone with Substrate

	Reaction	Rate
X.	$^3K^* + BH \xrightarrow{k_{ex}} {}^3K\cdots BH^*$	$k_{ex}[BH][^3K^*]$
XI.	$^3K\cdots BH^* \xrightarrow{k_{d_{ex}}} K + BH$	$k_{d_{ex}}$[Exciplex]
XII.	$^3K\cdots BH^* \xrightarrow{k_p} \overline{K\text{-}H + B\cdot}$	k_p[Exciplex]
XIII.	$^3K^* + BH \xrightarrow{k_H} \overline{K\text{-}H + B.}$	$k_H[BH][^3K^*]$
XIV.	$\overline{K\text{-}H + B\cdot} \xrightarrow{\alpha'}$ Products	
XV.	$\overline{K\text{-}H + B\cdot} \xrightarrow{1-\alpha'} K + BH$	

Scheme 1) may actually be the sum of rate constants for exciplex formation (k_{ex}) and direct hydrogen abstraction (k_H). The efficiency of the reaction would then be a function of the efficiency with which exciplex forms radicals going on to products. Unfortunately there is no easy method to measure the individual rate constants as given in Scheme 2. The rate constants for interaction of ketone with substrate reported here are the k_r values according to Scheme 1. Other methods must be used to estimate the contributions from k_H and k_{ex} to k_r.

Research Goals

The major objectives of this research were:

1. The study of the selectivity of reactions occurring from exciplexes.
2. The study of the influence of external factors, such as solvents and additives, on exciplex reactions.
3. The investigation of the initial interaction of excited state ketones with substrate. This includes direct hydrogen abstraction and exciplex formation.
4. To investigate the reactions of the radicals that are generated in the photoreduction reaction by independent methods in order to determine their contribution to the overall pattern of reactivity.

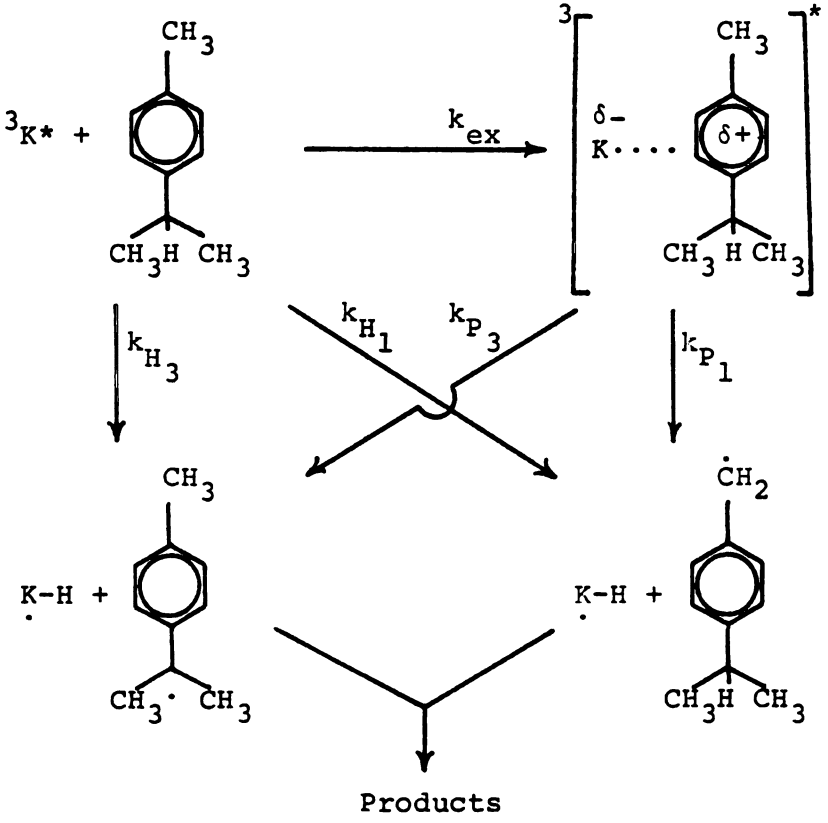
5. To coordinate the information for individual steps of the reaction into a comprehensive mechanism for the photoreduction reaction.

Approach used to Accomplish Goals

The primary system studied was the photoreduction of a series of ketones by p-cymene. This substrate was used since an exciplex involving p-cymene has two reaction pathways that give products (Scheme 3). These two pathways, transfer of primary and tertiary hydrogen atoms (or protons), can be easily monitored from the products formed. Other substrates were used when other facets of the reaction, other than exciplex selectivity, were being investigated. Ketones that react primarily, if not entirely, through exciplex formation were studied using p-cymene as substrate to investigate exciplex selectivity and to monitor the effects of solvents and additives on exciplex behavior. Ketones which are not believed to react entirely by exciplex were also investigated using p-cymene as substrate to determine if there was any evidence for exciplex formation with these ketones and if it would be possible to determine the fraction of reaction proceeding by such exciplex formation.

In addition to p-cymene and other alkylbenzenes the photoreduction of various ketones by alcohols was investigated. These experiments were performed to obtain

Scheme 3. Reaction Paths for Ketone with p-Cymene.



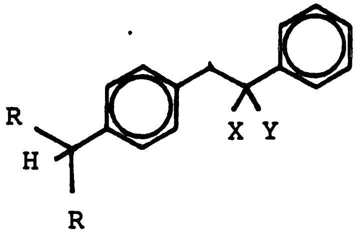
information on disproportionation between hydroxy radicals and to investigate the exchange of hydrogen atoms from hydroxy radicals to ground state ketones. Although previous attempts had been made to investigate individual aspects of the photoreduction of ketones by alcohols[21,22, 61,62] no complete description of the reaction could be formulated. One major question that remained was the extent of disproportionation that actually occurs and how it relates to reaction efficiency. Quantum efficiency studies[63] suggest disproportionation is high for acetophenone and 1-phenylethanol, while studies with optically active alcohols[20] suggest it isn't important. Since half of the radicals produced in the reaction of ketones with alkylbenzenes are hydroxy radicals their interactions play an important part in the understanding of the overall photoreduction reaction.

Other aspects of radical reactions were investigated by comparing product ratios from the photoreduction reaction to those from radicals generated independently by decomposition of di-t-butyl peroxide. Abstraction of a hydrogen from a substrate by t-butoxy radical would produce the same radical as abstraction by an excited ketone. The hydroxy radical formed from the ketone would be formed by hydrogen abstraction from the corresponding alcohol. In this way the radicals would be formed separately, not in a solvent cage, and ketone formed from the disproportionation could also be measured. In this way important information regarding relative rates of coupling and disproportionation reactions could be obtained. Although there have been numerous studies of radical-radical reactions,[64,65] they have not necessarily been aimed at the type of information that is important to understand the photoreduction reaction.

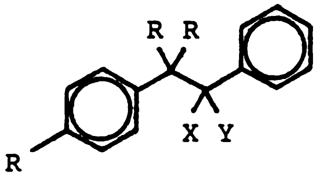
RESULTS

Product Identification

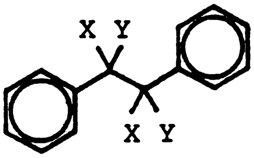
The products of photoreduction of α,α,α-trifluoroacetophenone (TFA) by p-cymene were isolated by a combination of column chromatography and sublimation. The two cross-coupled alcohols (KP and KT) and one of the diastereomeric pinacols (KK) were readily separated on an alumna column. One of the pinacol products could not be isolated in a pure form, but the infrared and n.m.r. spectra of a 50:50 mixture of the two pinacols were consistent with only pinacol product present.



KP



KT



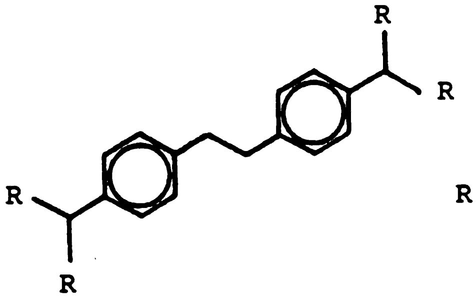
KK

R = Me

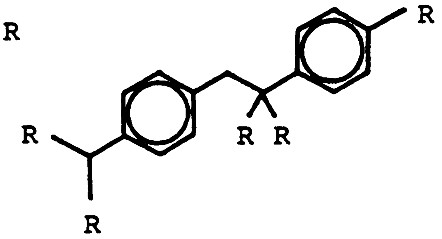
X = OH

Y = CF_3

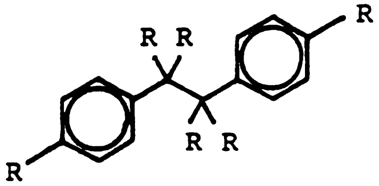
The three hydrocarbon coupling products (PP, PT and TT) were isolated by first separating them from other



PP



PT



TT

R = Me

products by column chromatography (alumina, hexane as eluting solvent), and then by subjecting them to fractional sublimation. The two symmetrically coupled products (PP and TT) sublimed more readily than the crossed (PT) product. Therefore, the two symmetrical products could be obtained by sublimation of mixtures rich in either the PP product, from photoreduction of TFA, or rich in TT product, from photoreduction of acetophenone.

The coupling products from other substrates, such as toluene, cumene, and p-xylene, were identified by comparison of gc retention times with the known compounds. The cross-coupling products from the reactions of these substrates with a variety of ketones, as well as the pinacol products, were identified either by comparison with authentic samples or by comparison to similar systems. The retention times of the cross-coupled products were consistently between the retention times of the products from the self-coupling of radicals. Which self-coupling product had the shorter retention time depended on ketone, substrate and the g.c. column used. For example, on a SE-30 column the cross-coupled alcohol had a retention time shorter than acetophenone pinacol but longer than bibenzyl. For the reaction of TFA and p-cymene the pinacol was the first product observed, followed by the two cross-coupled alcohols and finally the three hydrocarbon products. The three hydrocarbon products are an exception to this trend, with the cross-coupled product (PT) having the shortest retention time, followed by TT and PP. The hydrocarbon and pinacol products were always formed in roughly equal amounts, and their sum was usually close to the amount of cross-coupled product. However this latter situation was dependent on substrate, ketone and the solvent.

Quantum Yields

Quantum yields were determined by parallel irradiation at 313nm of degassed sample solutions and an actinometer in a merry-go-round apparatus at 25°C. Samples contained 0.1M ketone and the appropriate concentration of donor. The solvent was usually benzene, although acetonitrile was also used for some compounds. The actinometer was a 0.1M solution of valerophenone in benzene.[66] Percent conversion was kept as low as possible, usually 10% or less for systems other than p-cymene. Due to low yield of some products in the p-cymene system, it was difficult to obtain quantum yields for all products at conversion below 20%. The product to standard ratios were obtained by v.p.c. analysis.

Quenching Studies

Stern-Volmer quenching runs were performed in benzene at 366nm irradiation using napthalene as quencher. Conversion was kept below 10% for the unquenched solution. Plots were linear for the range studied, usually to Φ^0/Φ values of 3 or 4. The Φ^0/Φ values were identical for both bibenzyl and cross-coupled alcohols for all cases studied.

Quenching by amines was studied at 313nm in either benzene or acetonitrile solutions. The Stern-Volmer quenching plots were not always linear for these quenchers, and all products did not show the same quenching efficiency.

Photoreduction of Ketones by p-Cymene

Quantum yields for the three hydrocarbon coupling products (PP, PT, and TT) were determined for the photoreduction of acetophenone (AP), α,α-difluoroacetophenone

(DFA), and α,α,α-trifluoroacetophenone (TFA) with p-cymene in benzene (see Table 2). In all cases all three products gave linear plots of Φ^{-1} vs. $[\text{p-cymene}]^{-1}$ (Figures 1 through 5). For the photoreduction of TFA quantum yields for all expected products (three hydrocarbons (PP, PT, and TT), two cross-coupled alcohols (KP, KT), and pinacol products (KK)) were calculated (Table 3, Figures 6 and 7). Although at some of the lower concentrations of p-cymene there was slightly less hydrocarbon than pinacol, yields of the two products were fairly close at the higher p-cymene concentrations. The quantum yield for cross-coupled alcohols at the higher concentrations is equal to the sum of the other two products. The material balance for the TFA and the p-cymene is good (greater than 80%). The photoreduction of α-fluoroacetophenone (MFA) by p-cymene was also investigated, but the ratio of products varied with p-cymene concentration. Other results that will be presented later point to secondary radical reactions influencing the course of this reaction.

Results obtained for the reaction of TFA and p-cymene in acetonitrile solution (Table 2, Figures 8 through 11) showed a maximum quantum yield of primary radicals higher than in benzene. The products from tertiary radicals were formed in the same efficiency, however, and the result is a significant change in the ratio of tertiary products.

Table 2. Results for Reaction of Various Ketones with p-Cymene

Ketone	Slope (M^{-1})			Intercept			Intercept/Slope (M)		
	PP	PT	TT	PP	PT	TT	PP	PT	TT
AP[a]	273.0	50.5	33	200	44	32	0.73	0.87	0.97
DFA[a]	9.3	9.5	54	54	50	147	5.81	5.26	2.72
TFA[a]	12.3	24.5	125	32	65	250	2.60	2.65	2.00
TFA[b]	8.4	11.8	122	22	66	380	2.62	5.59	3.11

[a] Benzene

[b] Acetonitrile

Table 3. Maximum Quantum Yields for Reaction of TFA and p-Cymene

Solvent	Φ_{KT}^{max}	Φ_{KP}^{max}	Φ_{PP}^{max}	Φ_{PT}^{max}	Φ_{TT}^{max}	Φ_{KK}^{max}	Φ_{-K}^{max}
Benzene	0.026	0.077	0.031	0.015	0.0040	0.044	0.172
Acetonitrile	0.028	0.133	0.045	0.015	0.0026	0.038	a

[a] Not measured

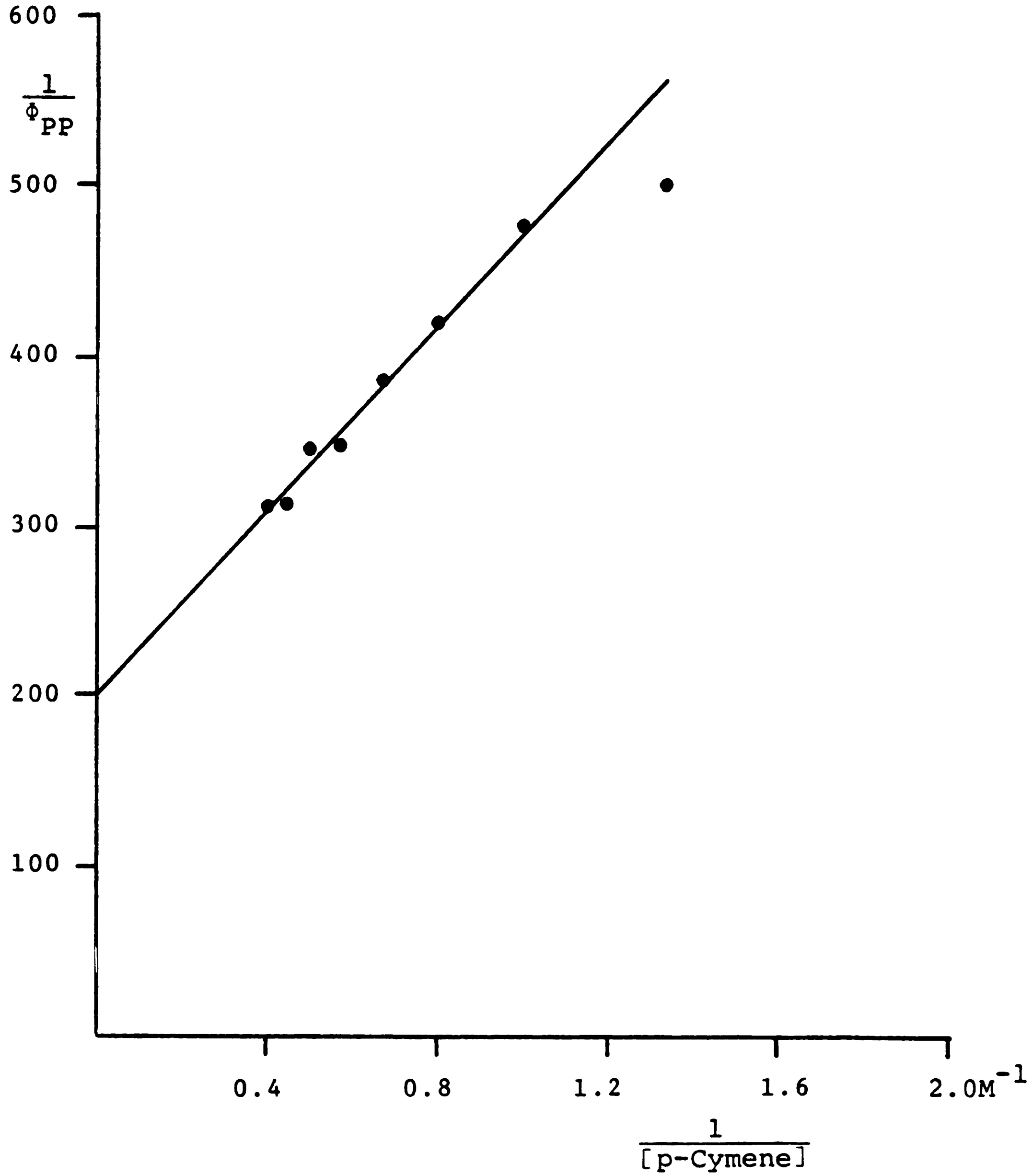


Figure 1. Results from Reaction of AP and p-Cymene, PP formation.

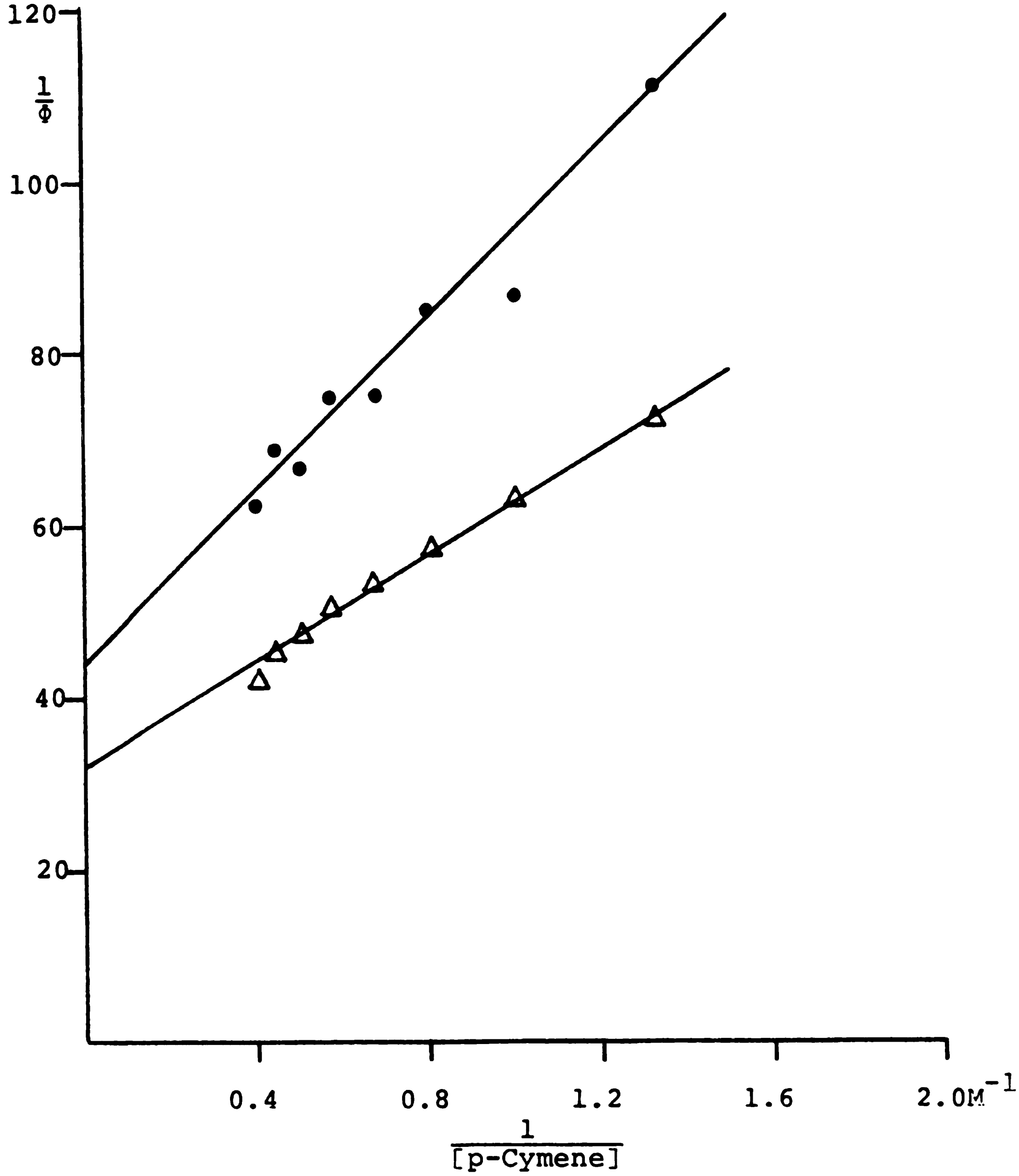


Figure 2. Results from Reaction of AP and p-Cymene, PT (●) and TT (△) formation.

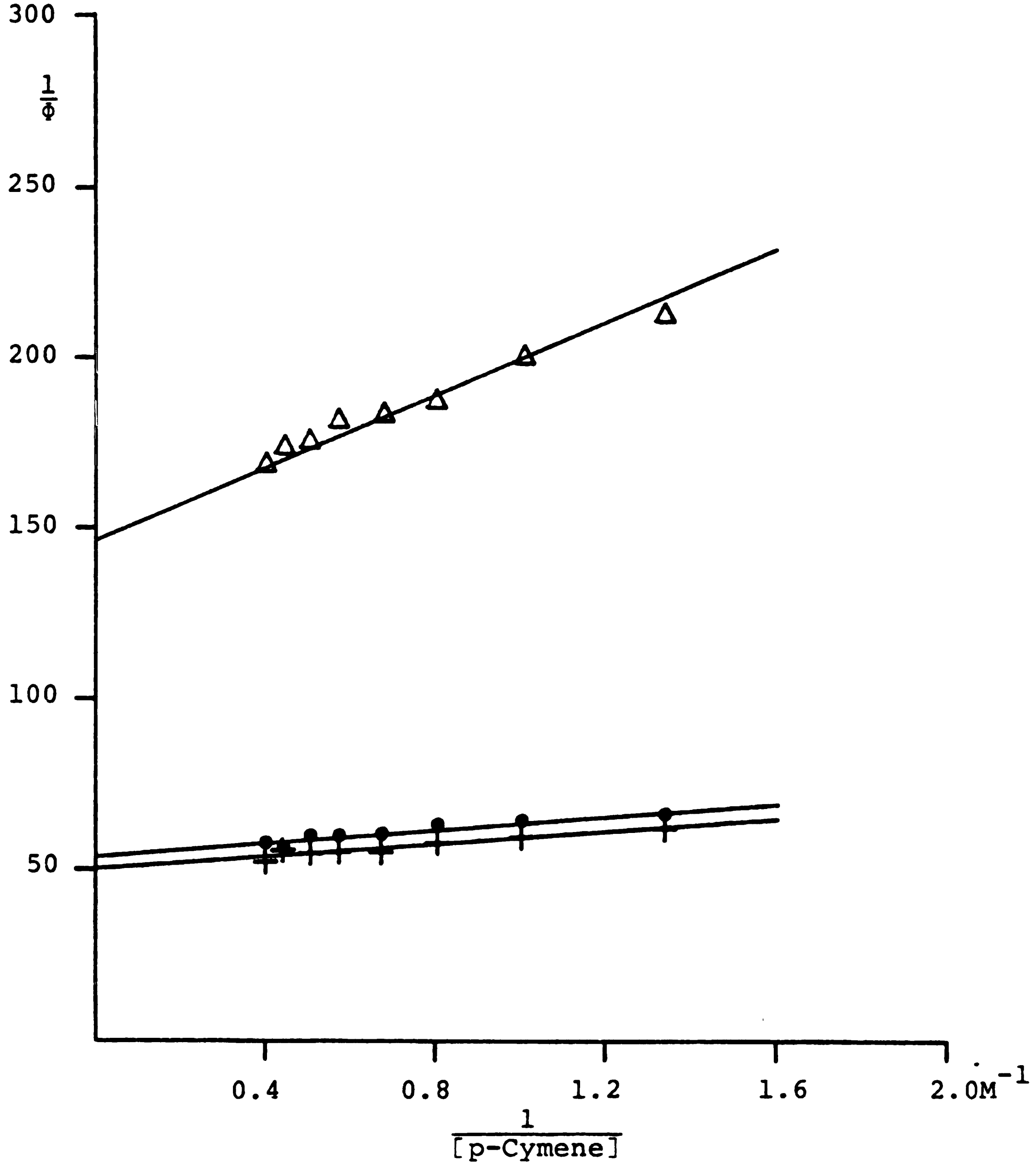


Figure 3. Results from Reaction of DFA and p-Cymene in Benzene, PP (●), PT (+), and TT (Δ) Formation.

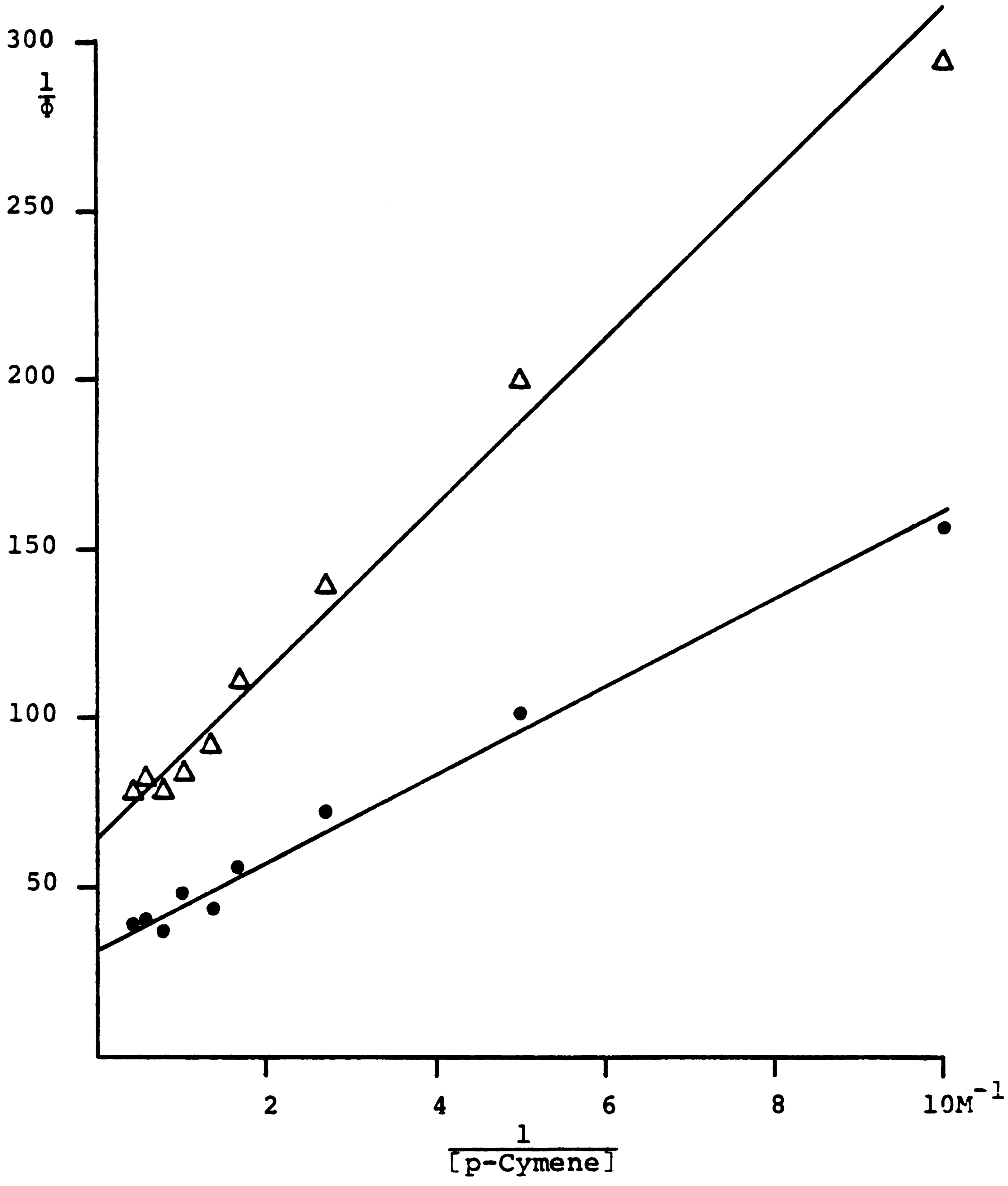


Figure 4. Results from Reaction of TFA and p-Cymene in Benzene, PP (●) and PT (△) Formation.

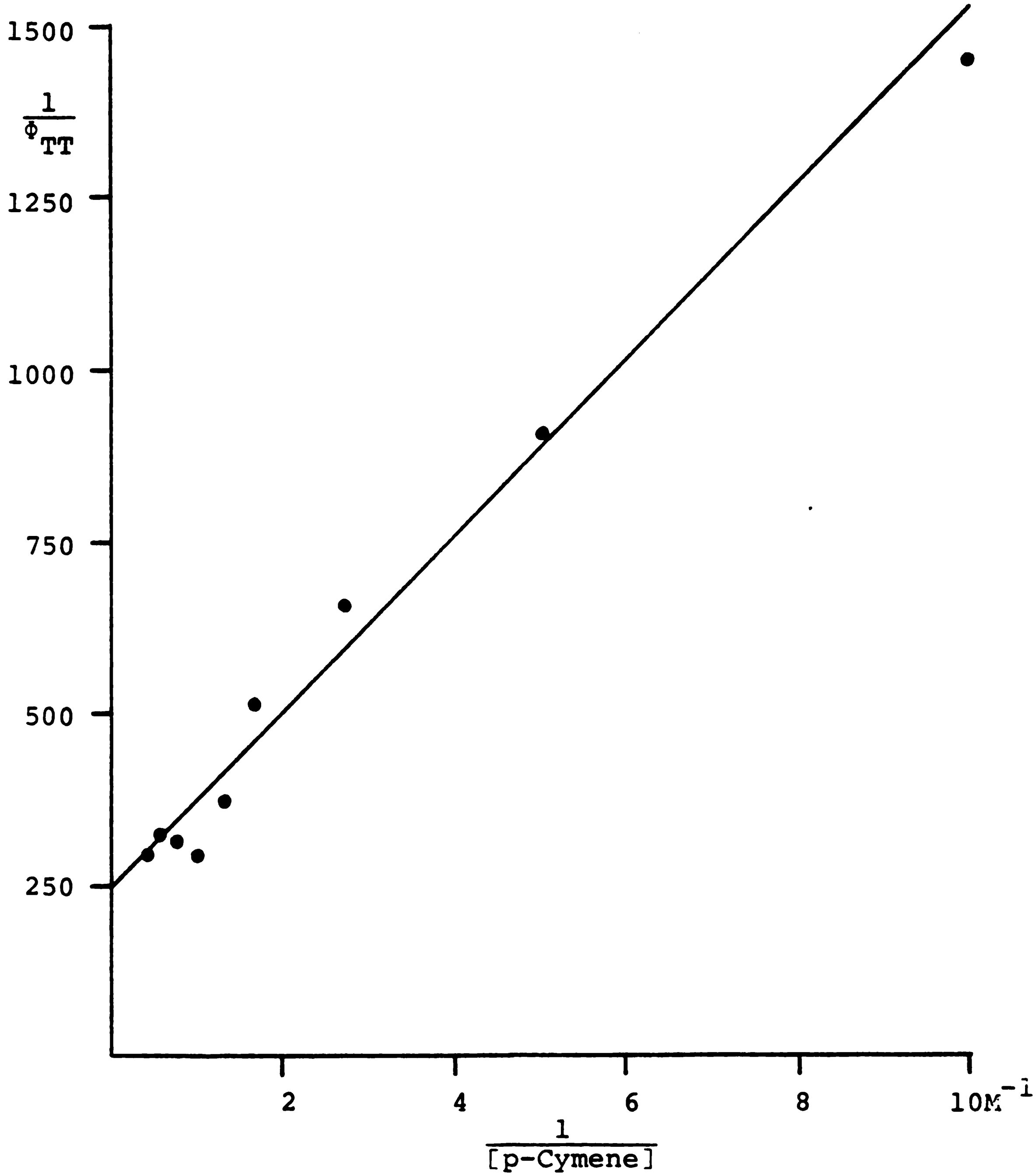


Figure 5. Results from Reaction of TFA and p-Cymene in Benzene, TT Formation.

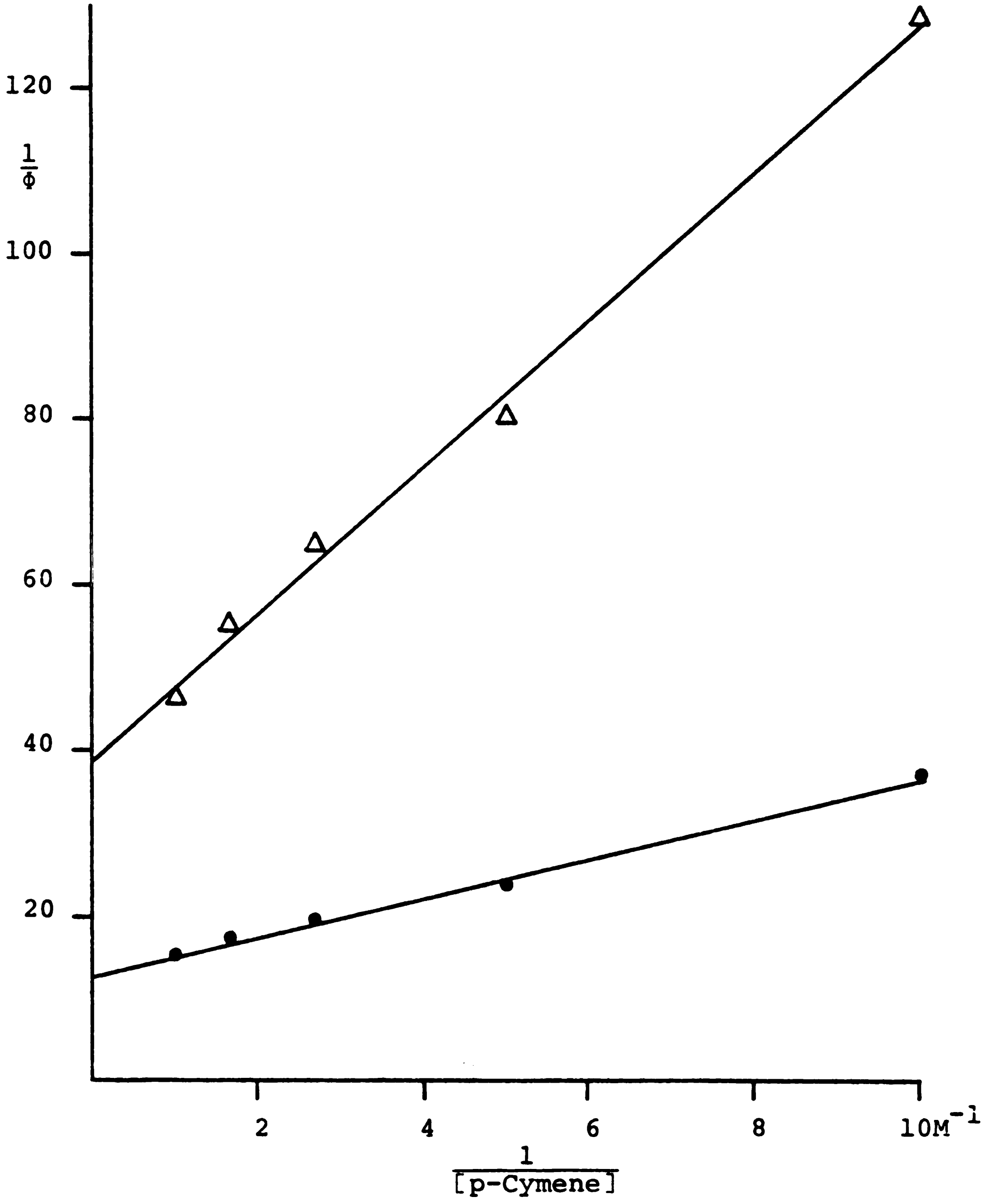


Figure 6. Results from Reaction of TFA and p-Cymene in Benzene, KP (●) and KT (Δ) Formation.

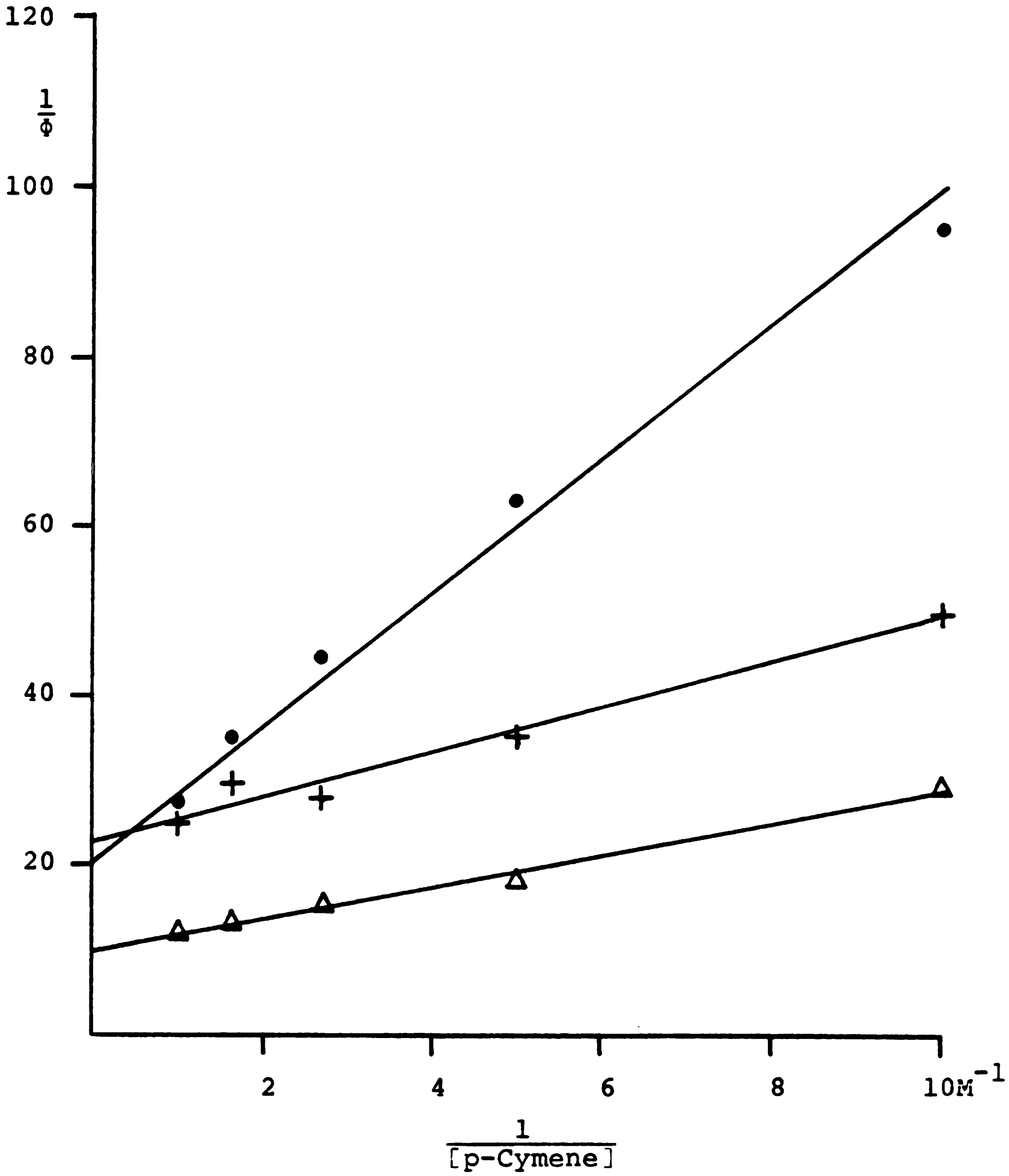


Figure 7. Results from Reaction of TFA and p-Cymene in Benzene, Formation of Pinacol (+), Hydrocarbon (●), and Cross-Coupled (Δ) Products.

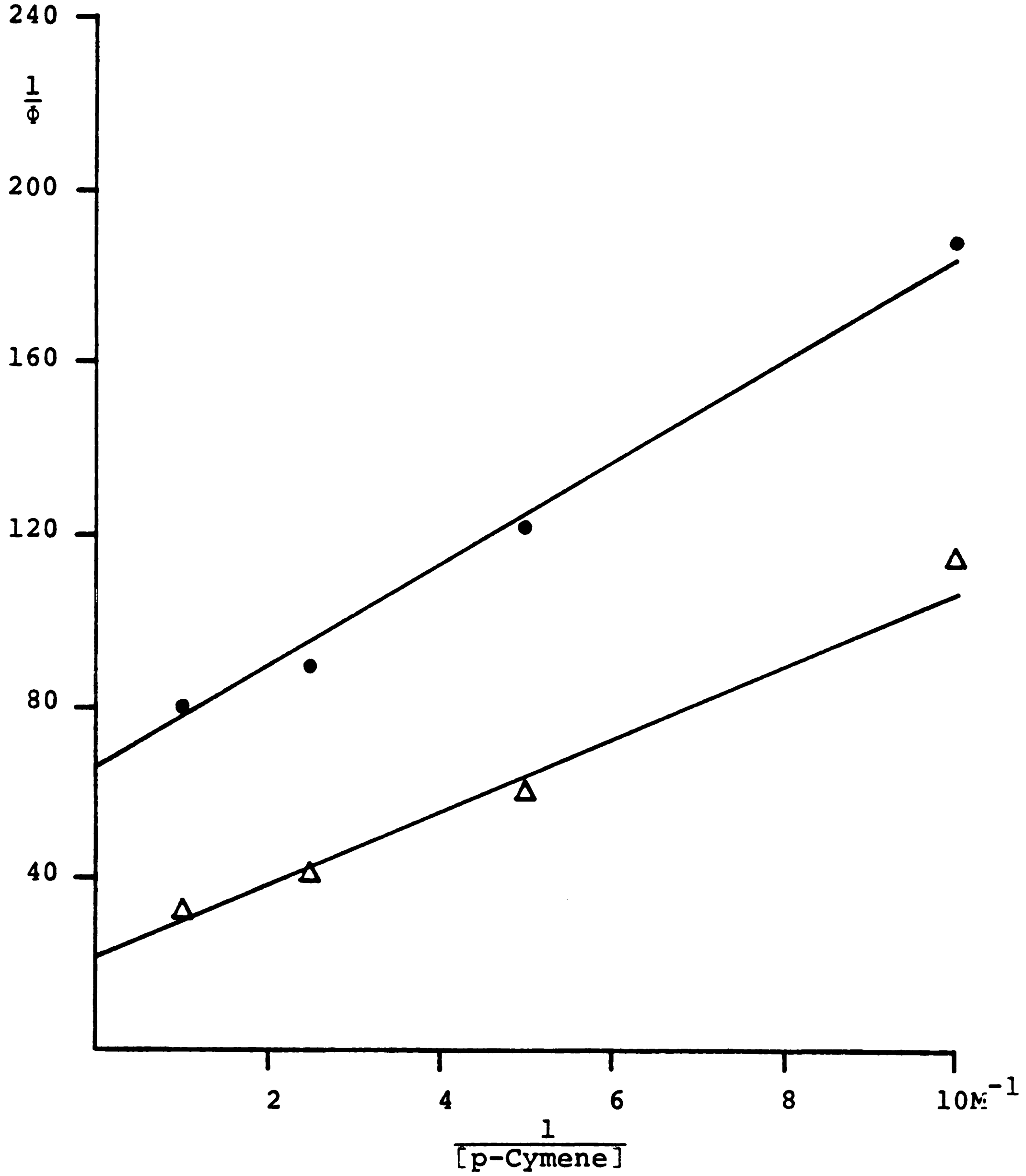


Figure 8. Results from Reaction of TFA and p-Cymene in Acetonitrile, PT (●) and PP (△) Formation.

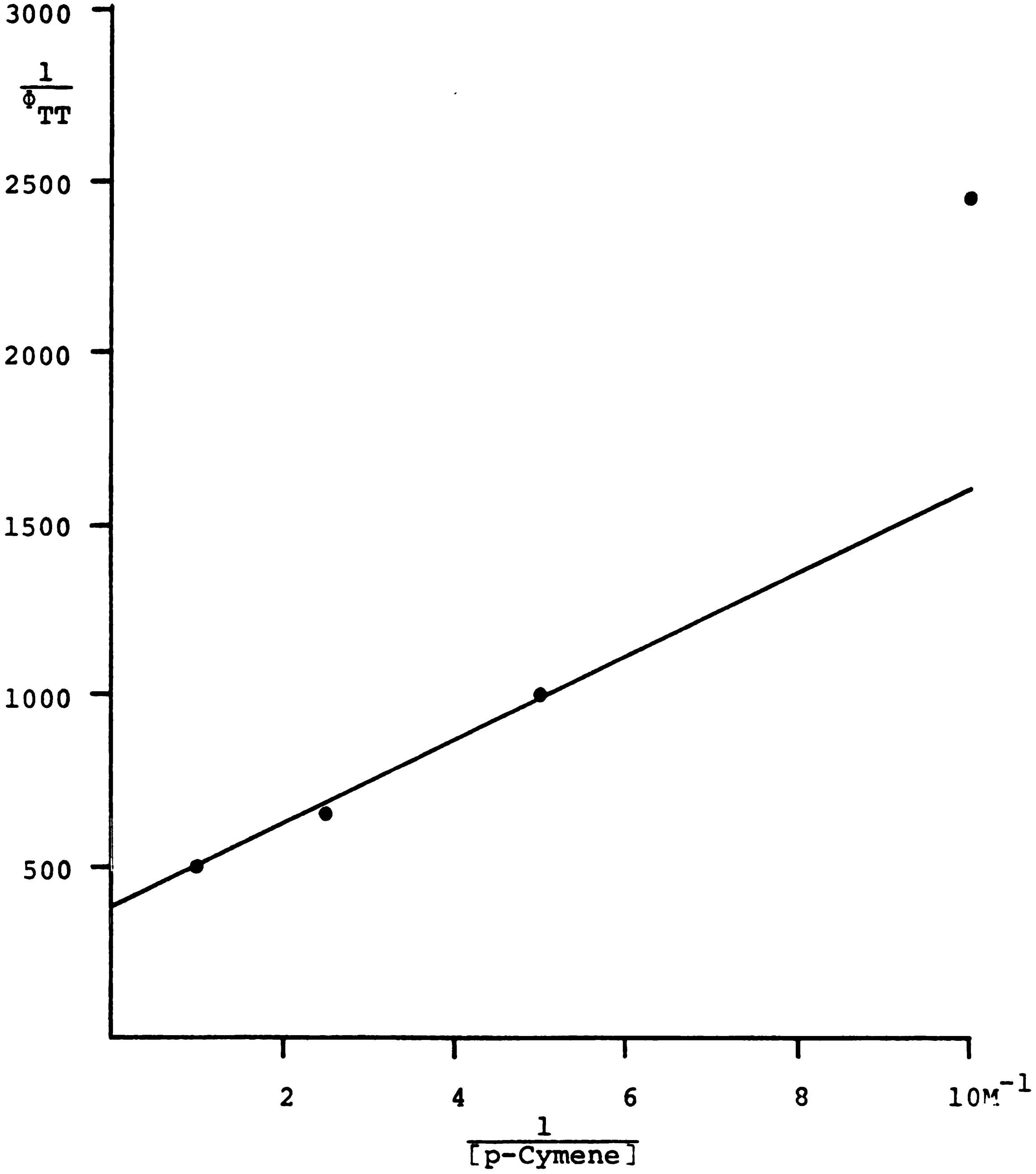


Figure 9. Results from Reaction of TFA and p-Cymene in Acetonitrile, TT Formation.

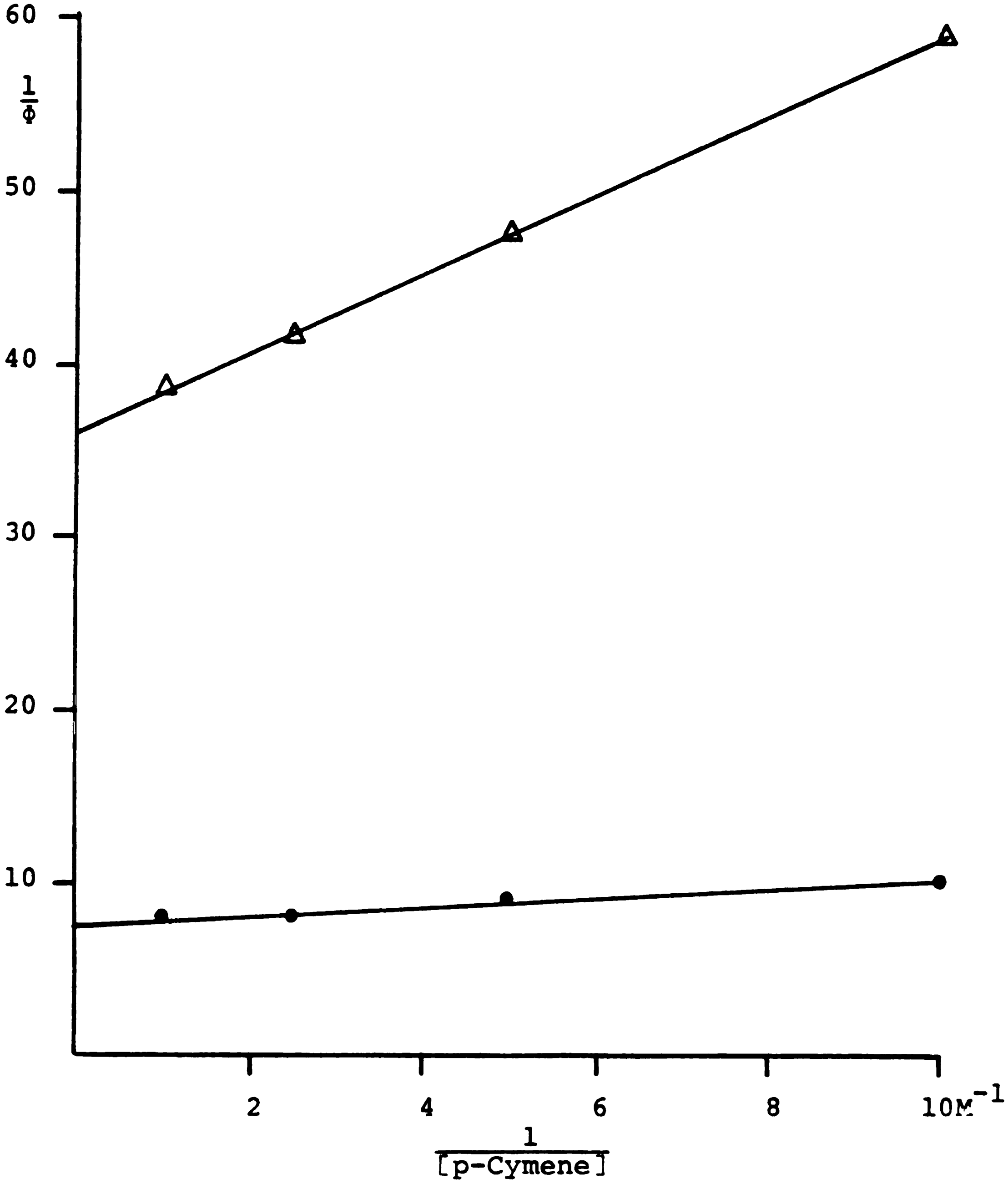


Figure 10. Results from Reaction of TFA and p-Cymene in Acetonitrile, KP (●) and KT (Δ) Formation.

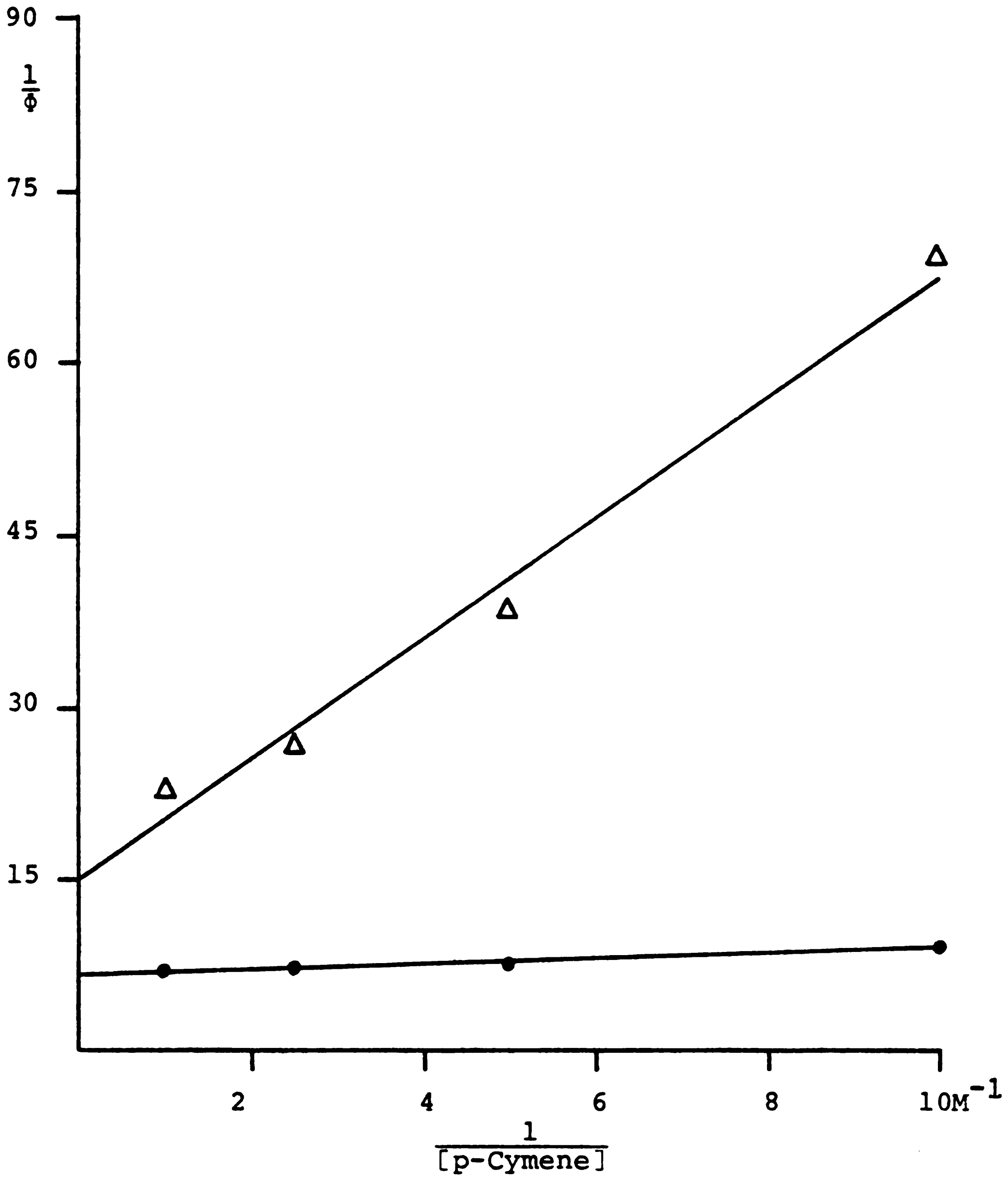


Figure 11. Results from Reaction of TFA and p-Cymene in Acetonitrile, Hydrocarbon (Δ) and Cross-Coupled (●) Product Formation.

The primary-tertiary ratios for a variety of substituted acetophenones, benzophenones and α,α,α-trifluoroacetophenones were obtained by analyzing the three hydrocarbon products. For these calculations no internal standard was used and the ratios were obtained from relative product areas. For the m-CF_3-TFA only the PP/PT ratio could be obtained due to the small amount of TT product. For a number of other ketones the PP product could not be determined either because it was a minor product or because other products such as pinacol and cross-coupled alcohols interfere with the analysis. The remaining ketones were analyzed for all three hydrocarbon products. The results are listed in Table 4.

Kinetics of Hydrogen Abstraction

Kinetic parameters were determined for AP, MFA, DFA, and TFA from quenching studies with napthalene at 366m. The lifetimes were determined from Stern-Volmer plots at several toluene concentrations for each ketone. These lifetimes are listed in Tables 5 through 8. The plots of $(\text{lifetime})^{-1}$ versus toluene concentration (Figures 12 through 15) give values for k_r and k_d from the slope and intercept, respectively. These results are given in Table 9. The ratio of k_d to k_r was also obtained from the slope divided by the intercept of a plot of $(\text{quantum yield})^{-1}$ versus $(\text{toluene concentration})^{-1}$ (Table 10).

Table 4. Results of Photoreduction of Indicated Ketone with p-Cymene in Benzene

Ketone	%PP	%PT	%TT
m-CF_3-TFA	71	29	a
m-Me-TFA	b	81	19
Benzophenone	b	45	55
4,4'-MeO-BP	b	40	60
4,4'-Me-BP	b	28	72
m-F-AP	b	48	52
m-CF_3-AP	b	50	50
p-Me-AP	b	38	62
TFA	62	30	8
p-MeO-TFA	31	45	24
p-Me-TFA	40	45	15
p-Cl-TFA	40	44	16
Propiophenone	6	41	53
Acetophenone	8	39	53
p-F-AP	20	35	45
4,4'-Cl-BP	16	42	42

[a] Minor Product

[b] PP was not analyzed, percentage is for products analyzed even though PP may be significant.

Table 5. Results of Stern-Volmer Quenching of Acetophenone

[Toluene] (M)	$k_q\tau$ (M^{-1})	τ (10^{-6}s)
0.50	6620	1.32
1.00	6000	1.20
1.50	5800	1.16
2.00	5300	1.06
2.50	4700	0.94

Table 6. Results of Stern-Volmer Quenching of α-Fluoroacetophenone

[Toluene] (M)	$k_q\tau$ (M^{-1})	τ (10^{-7}s)
0.40	2500	5.00
0.80	2050	4.10
0.94	1725	3.45
1.50	1300	2.60
1.87	1150	2.30

Table 7. Results of Stern-Volmer Quenching of α,α-Difluoroacetophenone

[Toluene] (M)	$k_q\tau$ (M^{-1})	τ (10^{-7}s)
0.50	660	1.32
1.00	524	1.05
1.50	420	0.84
2.00	364	0.73
2.50	300	0.60

Table 8. Results of Stern-Volmer Quenching of α,α,α-Trifluoroacetophenone

[Toluene] (M)	$k_q\tau$ (M^{-1})	τ (10^{-7}s)
0.50	700	1.40
1.00	480	0.96
1.50	370	0.74
2.00	300	0.60
2.50	233	0.47

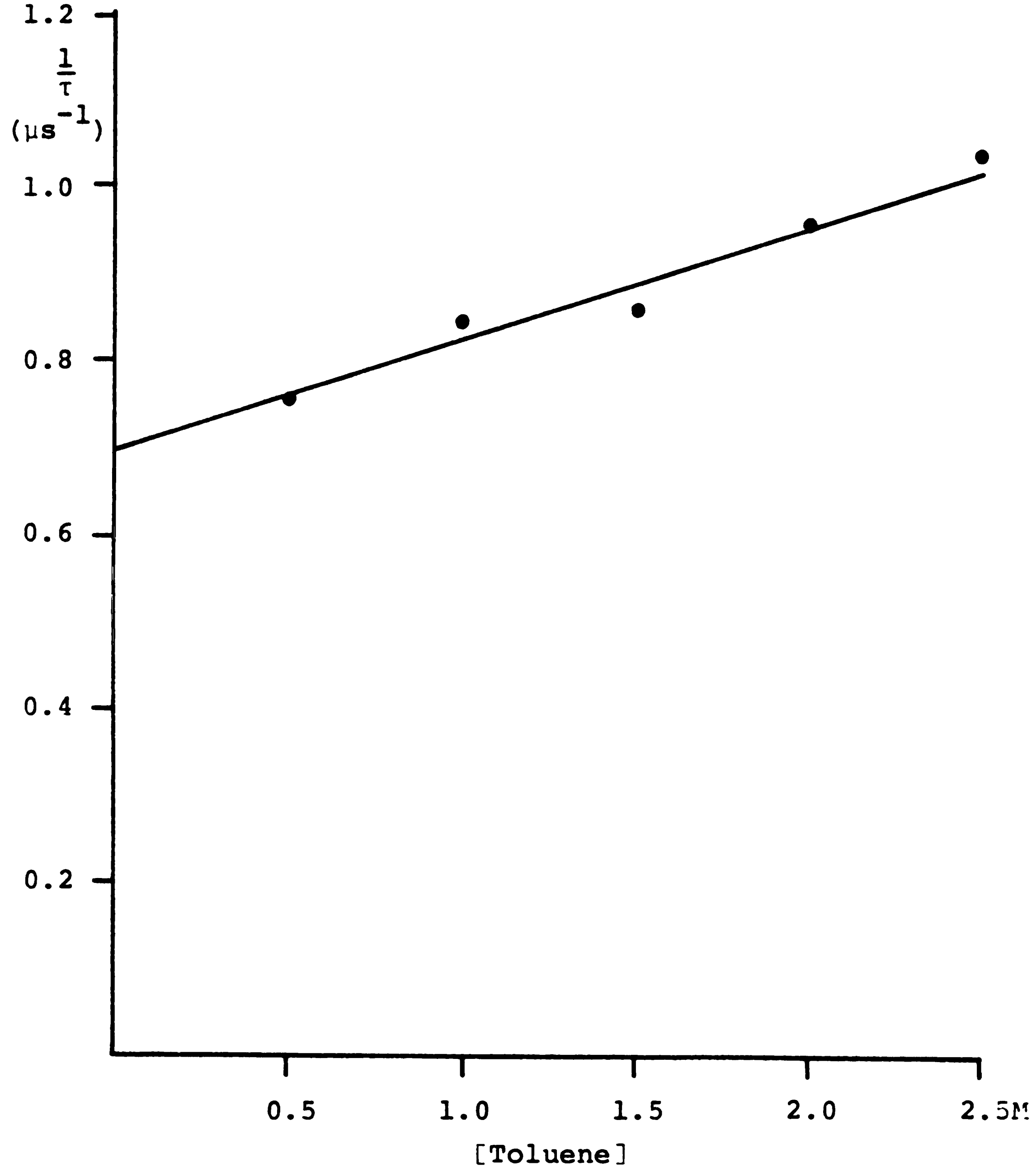


Figure 12. Lifetimes of AP as a Function of Toluene Concentration.

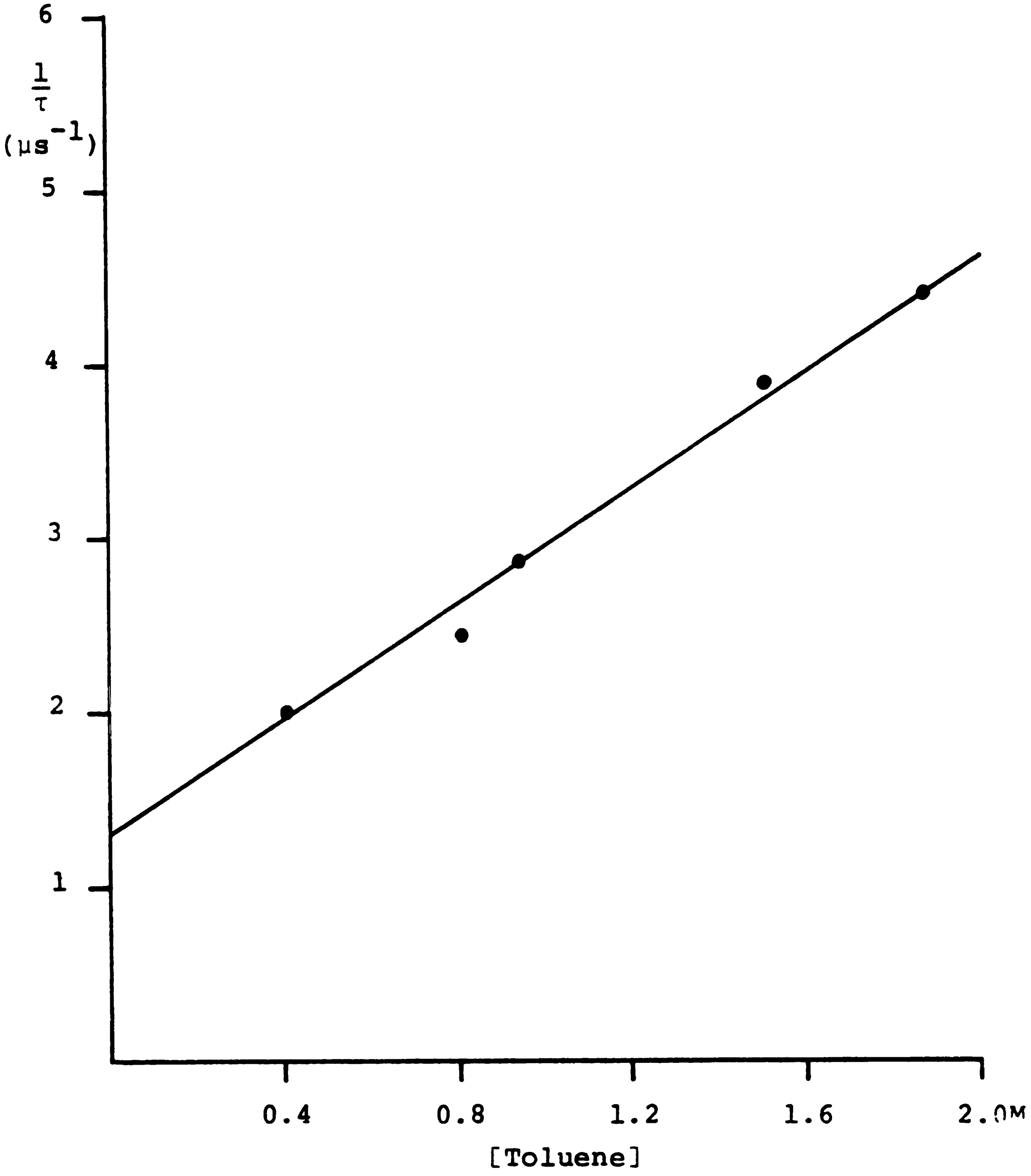


Figure 13. Lifetimes of MFA as a Function of Toluene Concentration.

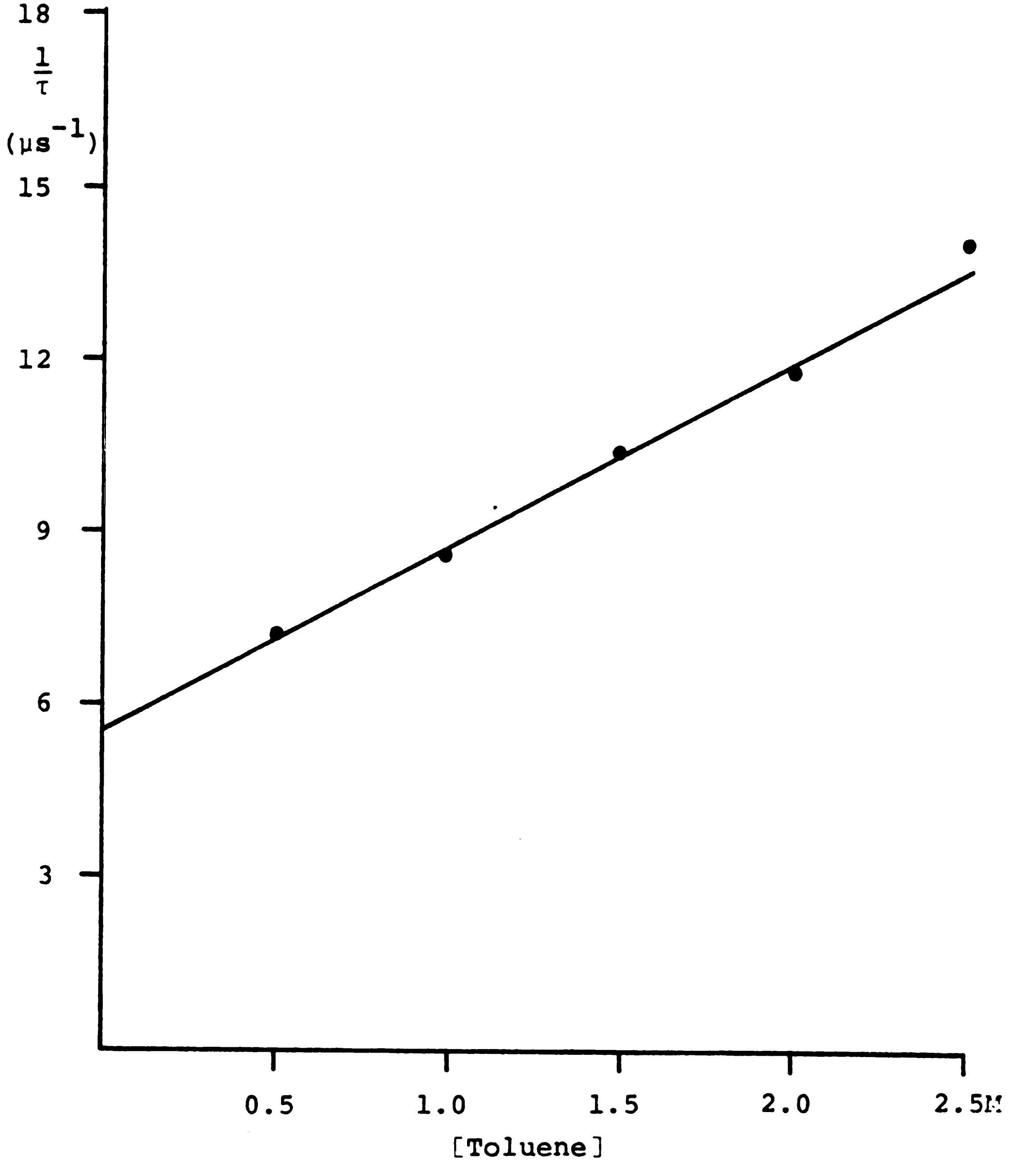


Figure 14. Lifetimes of DFA as a Function of Toluene Concentration.

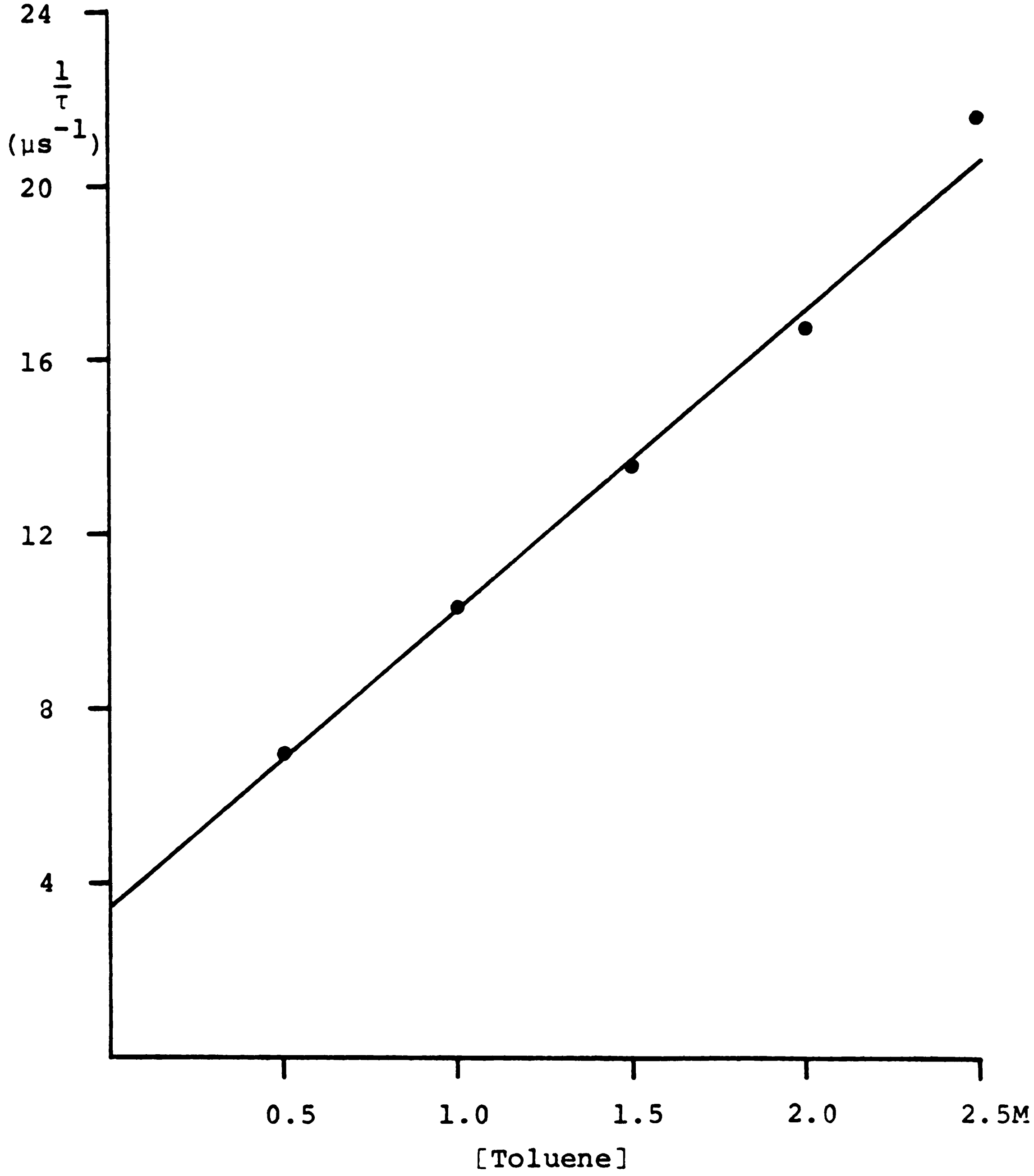


Figure 15. Lifetimes of TFA as a Function of Toluene Concentration.

Table 9. Rate Constants for Ketones from Stern-Volmer Studies

Ketone	$k_d (10^6 s^{-1})$ in Benzene	$k_r (10^6 M^{-1} s^{-1})$ with Toluene	k_d/k_r (M)
AP	0.70 (0.50)[a]	0.12 (0.12)[a]	5.83 (4.17)[a]
MFA	1.32	1.64	0.80
DFA	5.40	4.30	1.26
TFA	3.50 (7.00)[a]	6.80 (7.30)[a]	0.51 (0.96)[a]

[a] Reference 38

Table 10. Results from Φ_{BB}^{-1} versus $[\text{Toluene}]^{-1}$

Ketone	Slope (M)	Intercept	Slope/Intercept (M)
AP	45.0 (45.0)[a]	12.0 (7.7)[a]	3.75 (5.84)[a]
MFA	21.5	9.5	2.26
DFA	20.2	17.7	1.14
TFA	66.0 (22.6)[a]	13.0 (18.9)[a]	5.08 (1.20)[a]

[a] Reference 38

Hydrogen Abstraction from p-Cymene by t-Butoxy Radicals

To study the selectivity of alkoxy radicals, t-butyl hypochlorite and di-t-butyl peroxide were both used as sources of t-butoxy radicals. For the reaction of t-butyl hypochlorite, benzene solutions containing 1.0M p-cymene and varying concentrations of t-butyl hypochlorite were degassed by passing a stream of nitrogen through them; they were then irradiated at 366nm. Two products were observed by g.c., the primary chloride (1-chloromethyl-4-isopropylbenzene) and α,p-dimethylstyrene. The latter product was due to the quantitative dehydrochlorination of the tertiary chloride in the injector port to the gc. When cumene was used in place of p-cymene, both α-cumyl chloride and α-methylstyrene were observed and there was an irregular baseline between these two products that is indicative of decomposition.

The peroxide experiment was performed with 0.1M di-t-butyl peroxide and 0.6M p-cymene in benzene. The samples were degassed by three freeze-thaw cycles. The reaction was initiated by irradiation at 313nm. The products observed were the three hydrocarbon coupling products (PP, PT and TT) previously described for the photoreduction of ketones by p-cymene. The results for the t-butyl hypochlorite reaction varied with hypochlorite concentration, possibly as a result of abstraction by chlorine atoms or high concentrations of hydrogen chloride.

At low hypochlorite concentrations the primary-tertiary ratio reached a constant value, giving a ratio of 2.4 to 1 in favor of tertiary abstraction. The results from di-t-butyl peroxide show relative product formation for TT:PT:PP to be 7.5:5.9:1, corresponding to a 2.7 to 1 ratio in favor of tertiary abstraction.

Effects of Solvents on the Photoreduction Reaction

To study the effects of solvents on product distribution in the photoreduction reaction, substrates such as toluene and cumene were used in preference to p-cymene. The reason for using the simpler substrates was to reduce the number of products formed and thus to facilitate analysis. This simplification is shown to be justified for systems in which toluene and p-cymene were both used as substrates and produced similar results. The experiments were carried out using solutions of either 0.05M or 0.10M ketone and the appropriate substrate, usually 0.50M, in the solvent system indicated. Samples were irradiated at 313nm. Analysis for the coupling products was performed by g.c. in the usual manner. Self-coupling products of the radicals formed by hydrogen abstraction from the substrate are listed as BB. Pinacol products are listed as KK and cross-coupled products are listed as BK.

To compare acetonitrile and benzene as solvents for the photoreduction of TFA, the ratio of cross-coupled alcohol to bibenzyl as a function of acetonitrile concentration was looked at using toluene as the hydrogen donor. The results in Table 11 show that the ratio of cross-coupled product (BK) to bibenzyl (BB) increased when 5.0M acetonitrile was added to benzene. Increasing the acetonitrile about 5.0M had no further effect on the ratio.

The results for TFA and p-cymene are very similar to those obtained with toluene. The ratios were not obtained as a function of acetonitrile concentration in this case, but as a function of p-cymene concentration in either pure benzene or pure acetonitrile as solvent. The results are given in Table 12. The pinacol was analyzed in the p-cymene system and therefore it is also possible to look at the ratio of cross-coupled product to pinacol. The amount of product incorporating radicals derived from p-cymene and ketone can be used to obtain the relative amounts of these radicals found. It was observed that bibenzyls increase relative to cross-coupling products and the pinacols decrease relative to them as p-cymene concentration increases. This is found in both benzene and acetonitrile. It is also observed that the ratio of the two types of radicals is a function of p-cymene concentration.

In benzene solution both types of radicals decrease as p-cymene concentration decreases: however, the radicals derived from p-cymene decrease faster than the hydroxy radicals. At higher p-cymene concentrations the

Table 11. Effect of Acetonitrile on the Reaction of TFA and Toluene in Benzene

[MeCN] (M)	[BB] (10^{-3}M)	[BK] (10^{-3}M)	[BK]/[BB]
0.0	1.45	3.19	2.20
5.0	1.52	4.78	3.14
10.0	1.70	5.35	3.15
15.0	1.95	6.14	3.15

Table 12. Variation of Product Ratios[a] with p-Cymene (BH) Concentration, Reaction with TFA

[BH] (M)	Benzene				Acetonitrile			
	Φ_{BK}/Φ_{BB}	Φ_{BK}/Φ_{KK}	$\Phi_{B\cdot}$	$\Phi_{K\cdot}$	Φ_{BK}/Φ_{BB}	Φ_{BK}/Φ_{KK}	$\Phi_{B\cdot}$	$\Phi_{K\cdot}$
1.00	2.4	2.2	0.159	0.166	3.4	3.9	0.241	0.230
0.60	2.7	2.3	0.133	0.143	---	---	-----	-----
0.40	3.0	1.9	0.113	0.140	3.9	3.8	0.224	0.227
0.20	3.5	1.9	0.087	0.112	5.0	2.8	0.184	0.223
0.10	3.3	1.8	0.056	0.075	8.1	2.3	0.146	0.217

[a] BK is the sum of the two cross-coupled products (KP and KT), BB is the sum of the three hydrocarbon products (PP, PT, and TT). B· is the sum of primary and tertiary radicals found in products.

radicals are found in roughly equal amounts. In acetonitrile solution the radicals derived from p-cymene decrease as p-cymene concentration decreases, as expected, but there is very little dependence on p-cymene concentration for quantum yield of hydroxy radicals.

A comparison of the fraction of radicals that give cross-coupled product in each solvent can be made. The results show that in benzene the cross-coupled alcohols account for just over half of the products. In acetonitrile the cross-coupled alcohols account for two-thirds of the observed products.

For the photoreduction of acetophenone the solvent effect on product ratios is very similar to that found for TFA. The results in Table 13 show that for p-xylene and cumene the fraction of radicals that couple to give cross-coupled product is higher in acetonitrile than in benzene. This difference is not as significant for cumene as it is for p-xylene. Toluene was studied in t-butanol and showed results similar to cumene in acetonitrile.

Attempt to Maximize Quantum Yield of Photoreduction

The possibility that a hydrogen bonding polar solvent could be used to maximize the quantum yield by solvating radical pairs and preventing disproportionation was investigated using pyridine. The ability of pyridine to increase the quantum yield of the Norrish Type II reaction is well known.[68-70] The experiments to study the

Table 13. Product Distributions from Acetophenone and Various Substrates

Substrate	Solvent	[BB][a]	[BK][a]	[KK][a]	[B·][a]	[K·][a]
p-Xylene	MeCN	2.68	5.49	3.45	10.90	12.40
p-Xylene	Benzene	3.36	4.66	4.26	11.40	13.20
Cumene	MeCN	1.28	3.10	1.39	5.66	5.88
Cumene	Benzene	1.54	3.26	1.87	6.34	7.00
Toluene	t-BuOH	0.83	2.77	1.62	4.40	6.00
Toluene[b]	Toluene	2.03[c]	4.19[c]	2.37[c]	8.25[c]	8.93[c]
Toluene[d]	Benzene	1.00[e]	1.64[e]	----	-----	-----
p-Xylene[d]	Benzene	1.00[e]	1.32[e]	----	-----	-----
Cumene[d]	Benzene	1.00[e]	1.59[e]	----	-----	-----

[a] 10^{-3}M

[b] Reference 67

[c] Millimole of Product

[d] Reference 38

[e] Relative Product Formation

effects of pyridine were performed in the same manner as those in the previous section on solvent effects.

When pyridine was added to a benzene solution there was no substantial increase in benzyl radical formation for the photoreduction of TFA by toluene. However at concentrations of pyridine about 0.01M the ratio of cross-coupled product to bibenzyl began to increase (see Figure 16). Initially this increase was rapid and accompanied by an increase in cross-coupled product and a decrease in bibenzyl. At higher pyridine concentrations (about 1.0M) both products showed quenching by pyridine. Although a material balance was not done comparing results with and without pyridine present it seems unlikely that pyridine changes the material balance significantly. To account for the change in product ratio but not a change in benzyl radicals, while also accounting for a change in material balance, would require a much more complicated explanation than simply assuming that a polar solvent, such as pyridine or acetonitrile, increases the fraction of radicals that give cross-coupled product.

The results in acetonitrile show no change in product distribution, suggesting that both pyridine and acetonitrile have the same solvation effect on the coupling reactions. Both bibenzyl and the cross-coupled product are quenched by pyridine at almost identical rates. This quenching is expected since pyridine has an ionization

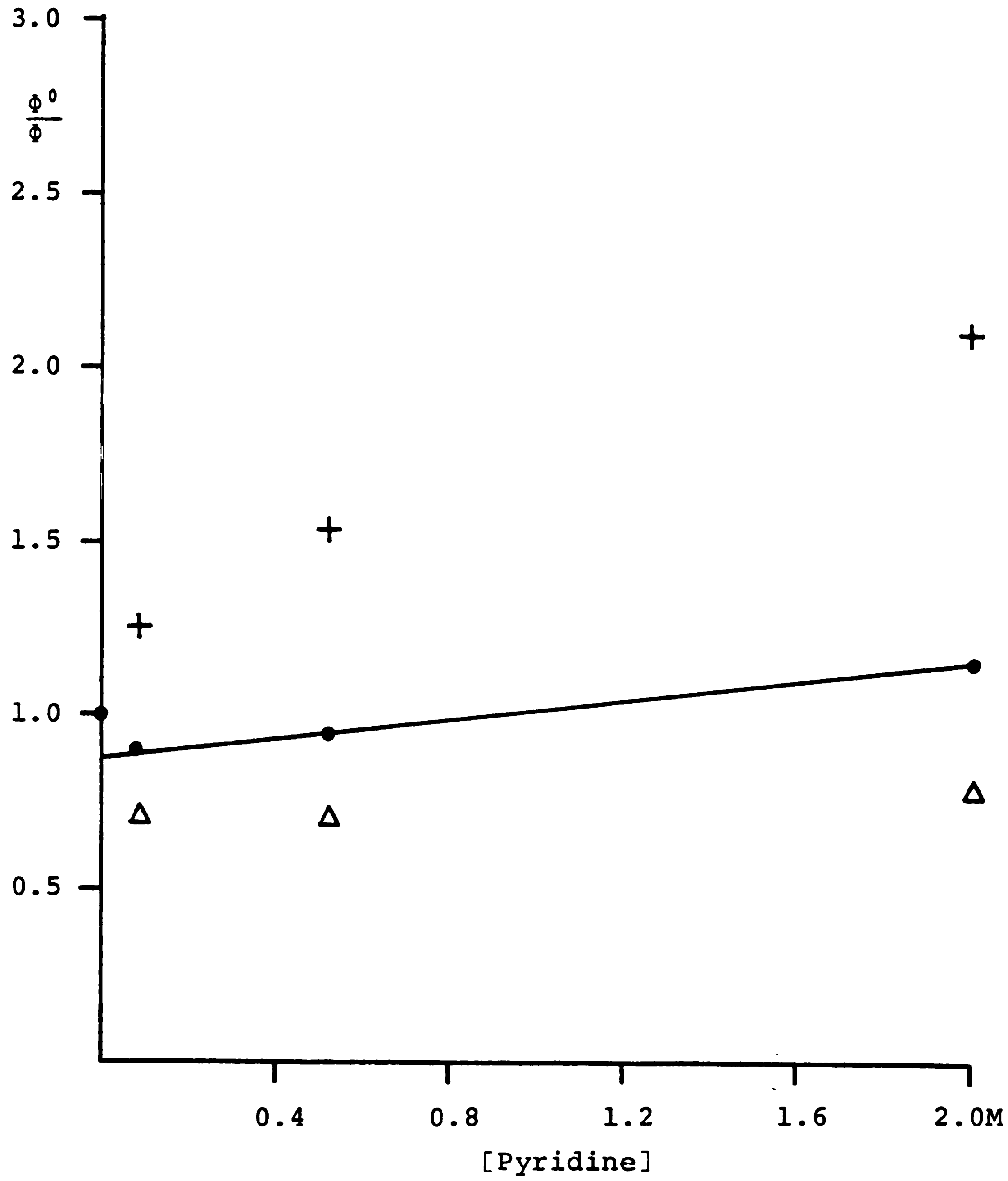


Figure 16. Effect of Pyridine on Reaction of TFA and Toluene in Benzene. Results for BB (+), BK (Δ), and B· (●).

potential comparable to benzene, which quenches by exciplex formation.[38] The results in acetonitrile are shown in Figure 17.

Effects of Charge-Transfer Quenchers

Quenching by compounds that are not capable of triplet energy transfer, but are capable of quenching by exciplex formation or electron transfer to give radical ions, was found to have a significant effect on product ratios. This effect was studied in a manner similar to the investigation of solvent effects. The quencher was added to solutions containing 0.05M ketone and substrate, usually 0.50M, in either benzene or acetonitrile. The samples were then degassed by four freeze-thaw cycles and irradiated in parallel at 313nm. Comparison of products to an internal standard by g.c. analysis provides relative product formation for different quencher concentrations.

For the photoreduction of TFA with 1.0M toluene in acetonitrile, quenching by DABCO leads to an initial increase in all three products, followed by quenching of all three products at higher DABCO concentrations (see Figure 18). At the higher DABCO concentrations bibenzyl is quenched more than the cross-coupled alcohol, although both plots are curved. When a plot of Φ^0/Φ versus DABCO concentrations is made for benzyl radicals and hydroxy radicals, instead of the three products, the results

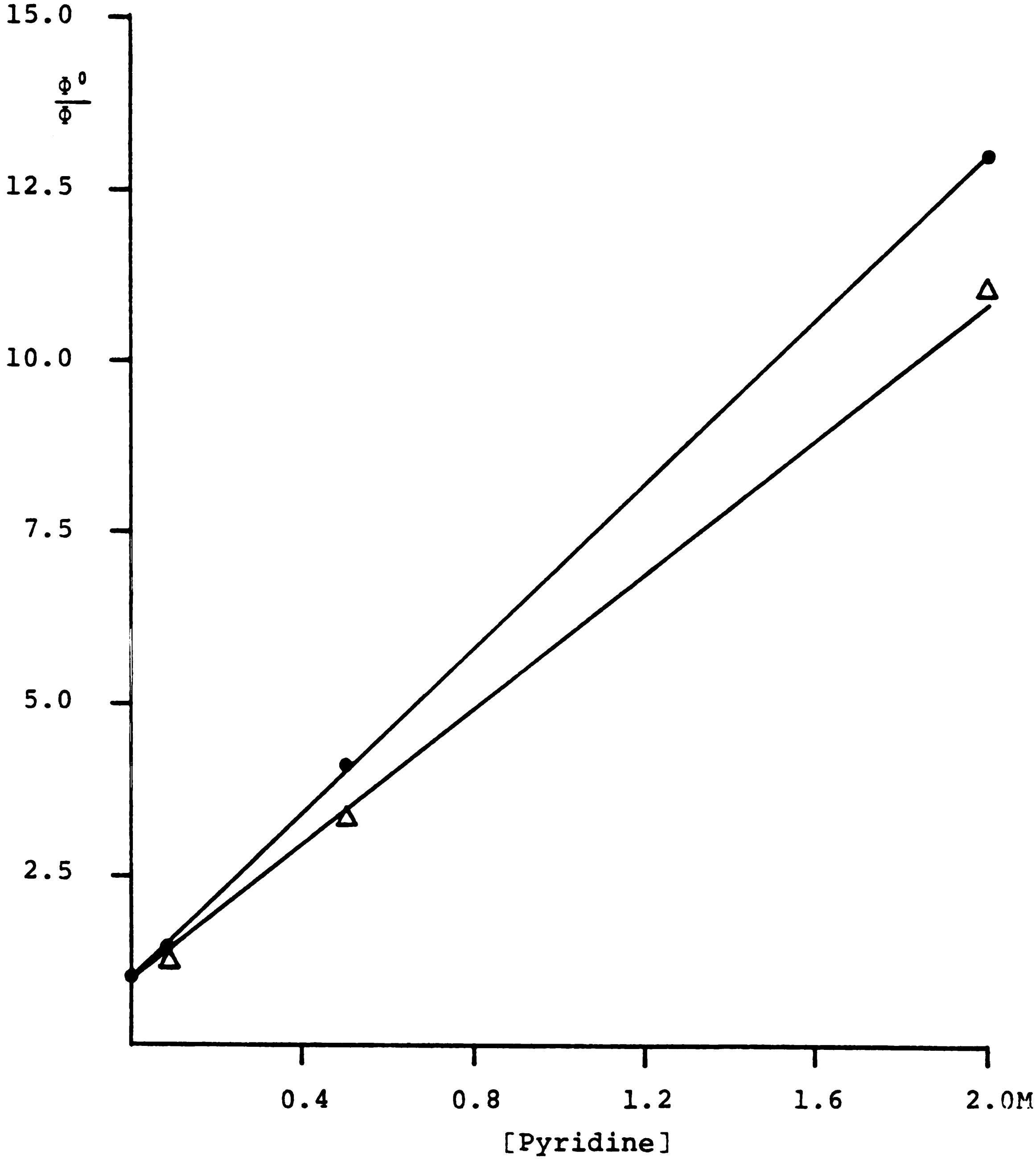


Figure 17. Pyridine Quenching of the Reaction of TFA and Toluene in Acetonitrile. Results for BB (●) and BK (Δ).

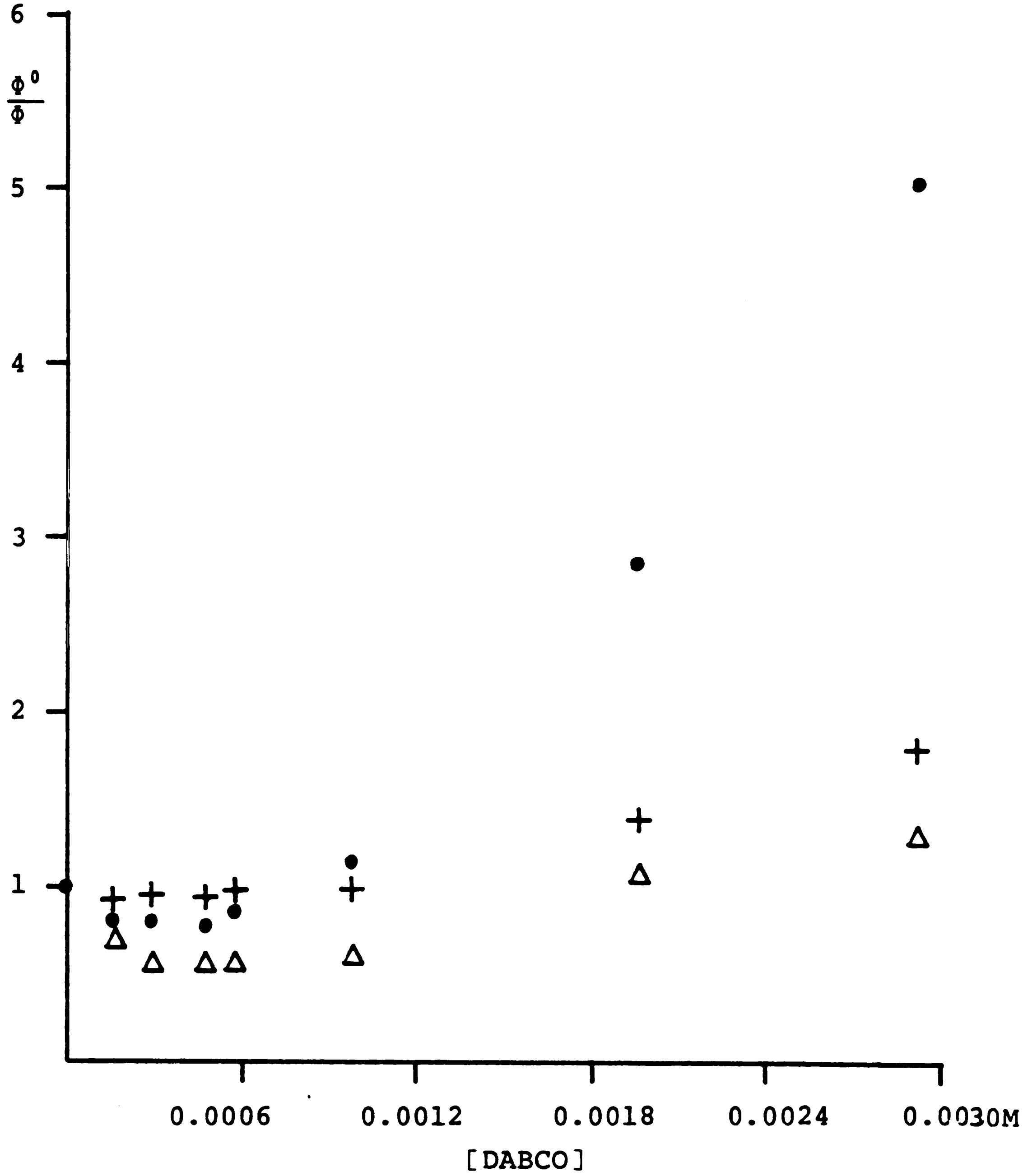


Figure 18. DABCO Quenching of the Reaction of TFA and Toluene in Acetonitrile. Results for BB (●), BK (+), and Pinacol (Δ).

are much better. Even though these plots, shown in Figure 19, initially curve below one they straighten out. Although they do not give the same slope, both plots give the same intercept (0.4) within experimental error. The values of $k_q\tau$ derived from the slope divided by intercept is $1670M^{-1}$ for benzyl radicals and $1040M^{-1}$ for hydroxy radicals.

When the experiment (0.5M toluene) is performend in benzene instead of acetonitrile there is no enhancement of benzyl radical yield. At low DABCO concentrations the bibenzyl yield is increased but the cross-coupled product is decreased, as shown in Figure 20. This leads to an overall linear quenching of benzyl radicals with an intercept of 1.0 and a $k_q\tau$ value of $410M^{-1}$.

In benzene solution the quenching of the reaction of TFA and p-cymene by DABCO is essentially the same as the reaction using toluene. Low concentrations of DABCO lead to an increase in bibenzyl coupled products (PP, PT and TT) and a corresponding decrease in cross-coupled products, as shown in Figure 21. The overall quenching of the benzylic radical formation (primary and tertiary) is linear. There is no change in primary-tertiary ratio. The plots for quenching of primary and tertiary radicals are shown in Figure 22.

The quenching of the reaction between TFA and 0.5M toluene by p-dimethoxybenzene in acetonitrile, shown

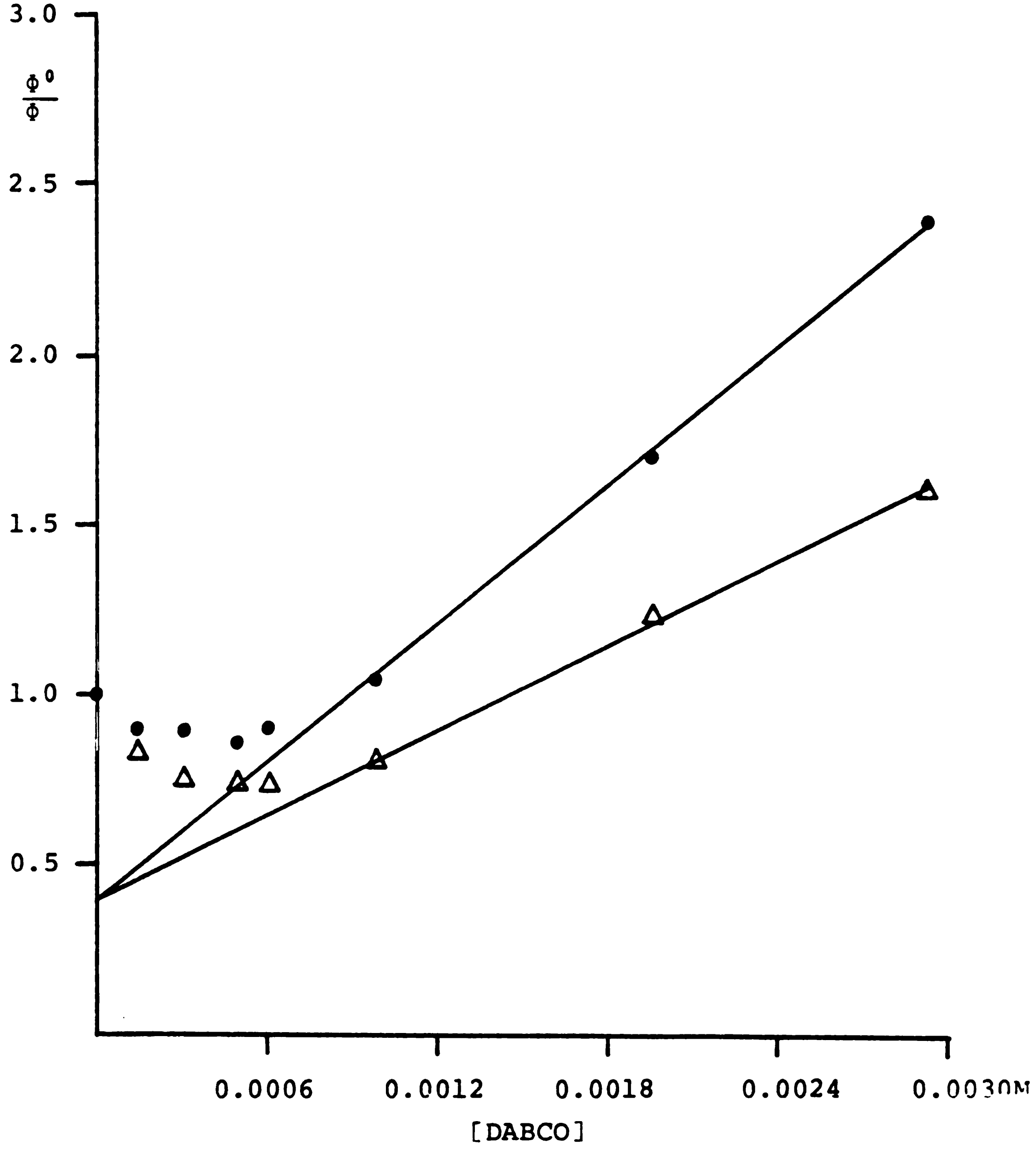


Figure 19. Effect of DABCO on the Radicals B· (●) and K· (Δ) Observed in the Reaction of TFA and Toluene in Acetonitrile.

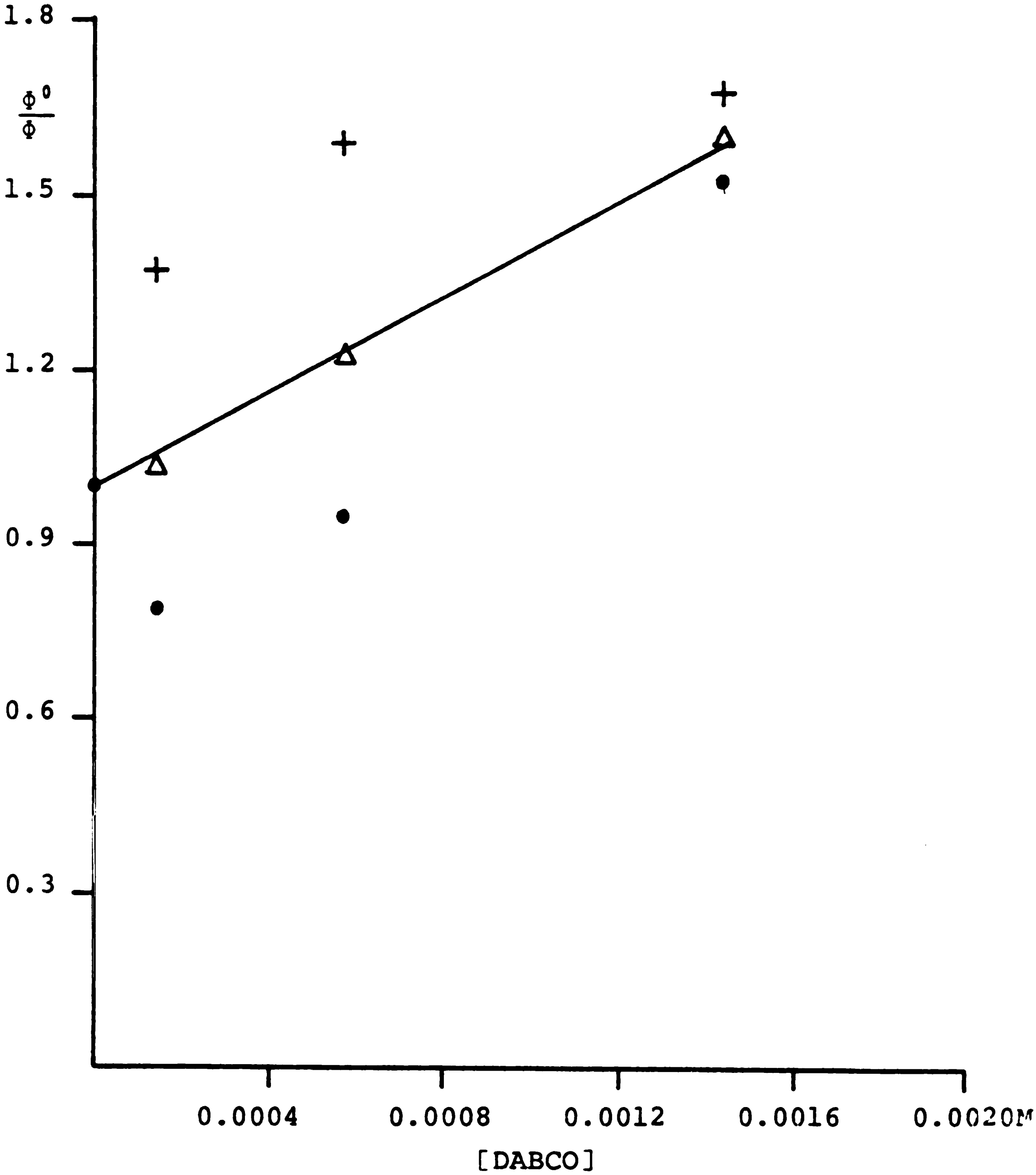


Figure 20. DABCO Quenching of the Reaction of TFA and Toluene in Benzene. Results for BB (●), BK (+), and B· (Δ).

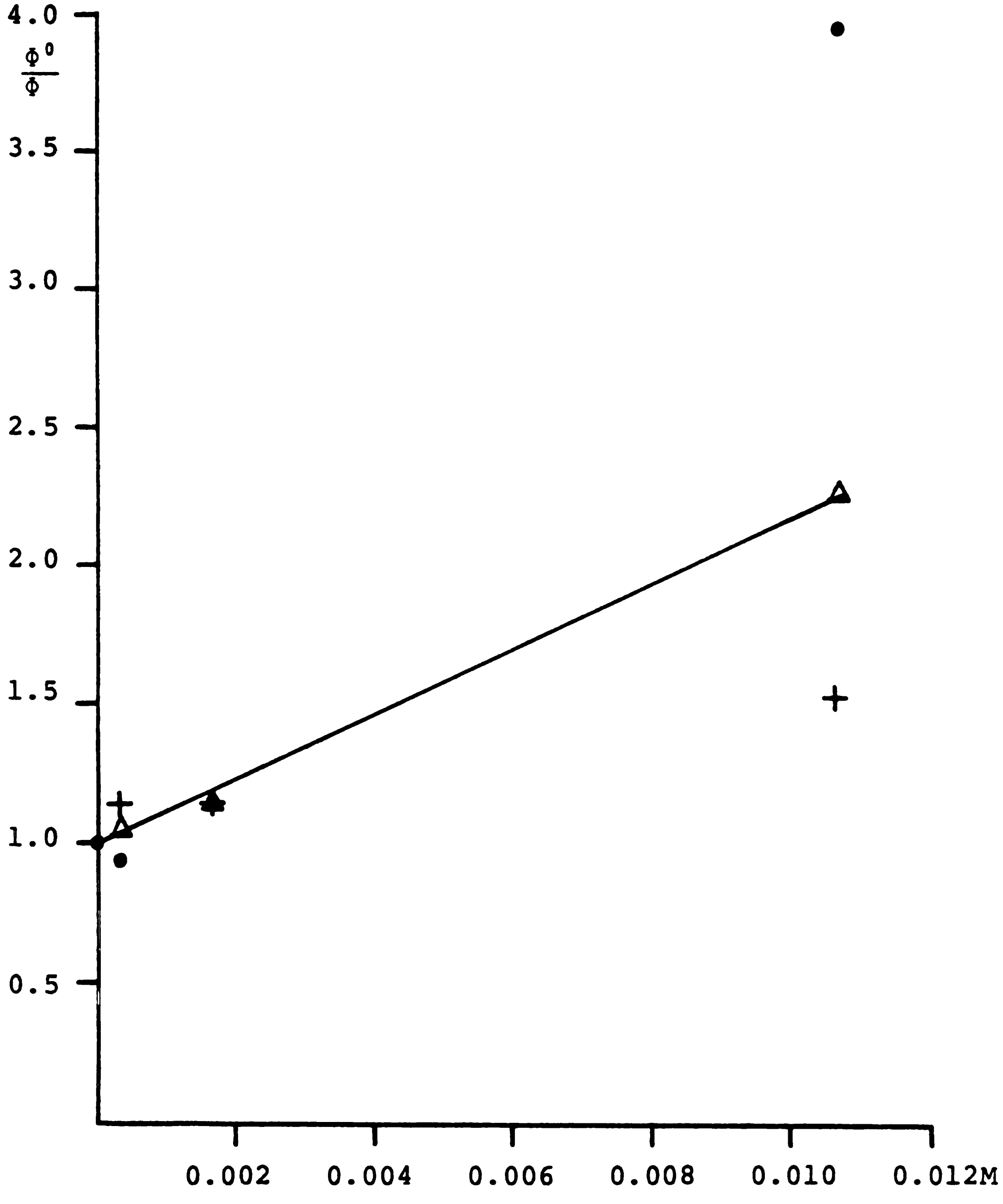


Figure 21. DABCO Quenching of the Reaction of TFA and p-Cymene in Benzene. Results for Hydrocarbon (●) and Cross-coupled (+) Products and Benzylic Radicals (Δ).

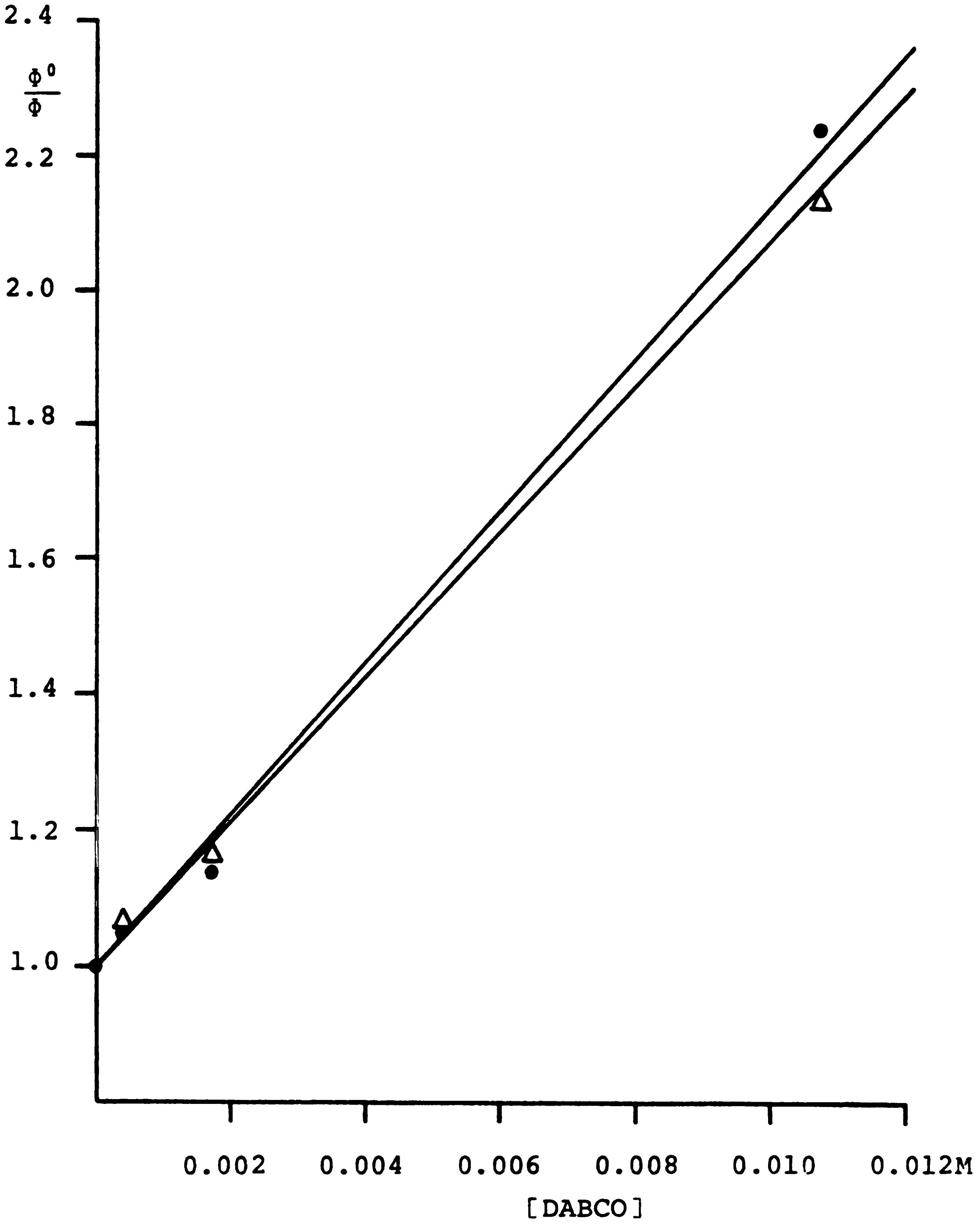


Figure 22. DABCO Quenching of the Reaction of TFA and p-Cymene in Benzene. Results for Primary (●) and Tertiary Radicals (△).

in Figure 23, did not show any of the product enhancement observed with DABCO. Instead quenching was linear for both bibenzyl and cross-coupled alcohol, both giving an intercept of one. The $k_q\tau$ value of bibenzyl was three times that of the cross-coupled product ($3040M^{-1}$ and $1000M^{-1}$ respectively). The $k_q\tau$ for benzyl radical was $1650M^{-1}$. In benzene solution p-dimethoxybenzene quenching (Figure 24) did not show such a large difference in $k_q\tau$ values for bibenzyl and cross-coupled alcohol ($722M^{-1}$ and $563M^{-1}$ respectively). The $k_q\tau$ value for benzyl radicals in benzene is $600M^{-1}$. For a comparison of ketones, the reaction of acetophenone and toluene in acetonitrile was quenched by p-dimethoxybenzene. Unfortunately both bibenzyl and cross-coupled alcohol curve above $\Phi^0/\Phi = 2$, as can be seen in Figure 25. The initial slope for both products gives a $k_q\tau$ value of $480M^{-1}$.

Effects of Acid

Since the basicity of amines may be responsible for a change in product distribution the effect of acid was also investigated. The acid used was trifluoroacetic acid, a strong acid that is soluble in both benzene and acetonitrile. To study the effect of acid on selectivity, experiments were run with 0.05M ketone and 0.50M p-cymene in either benzene or acetonitrile with varying concentrations of trifluoroacetic acid. To study the overall efficiency of the reaction, quantum yields were determined

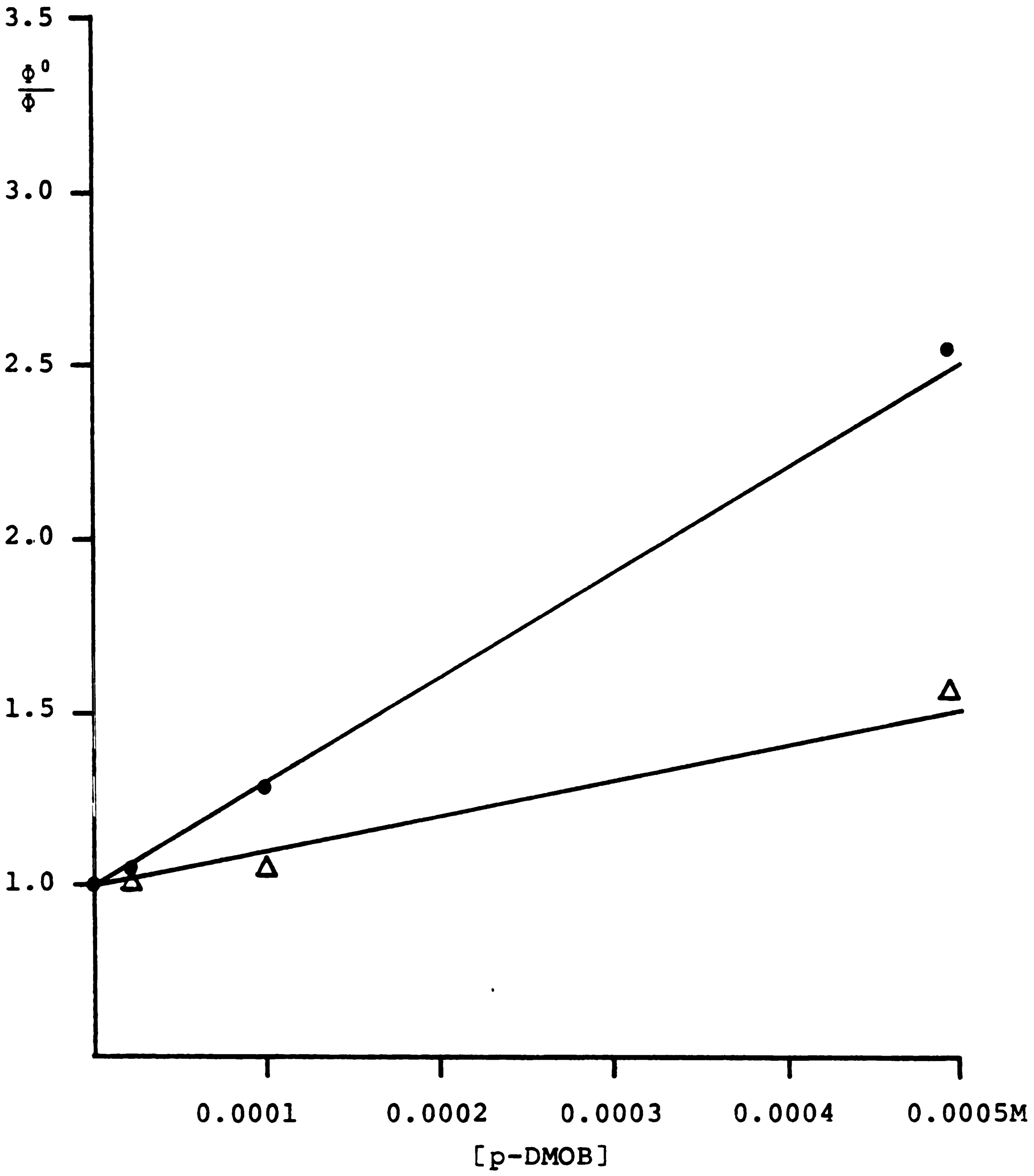


Figure 23. Quenching of the Reaction of TFA and Toluene in Acetonitrile by p-Dimethoxybenzene. Results for BB (●) and BK (Δ).

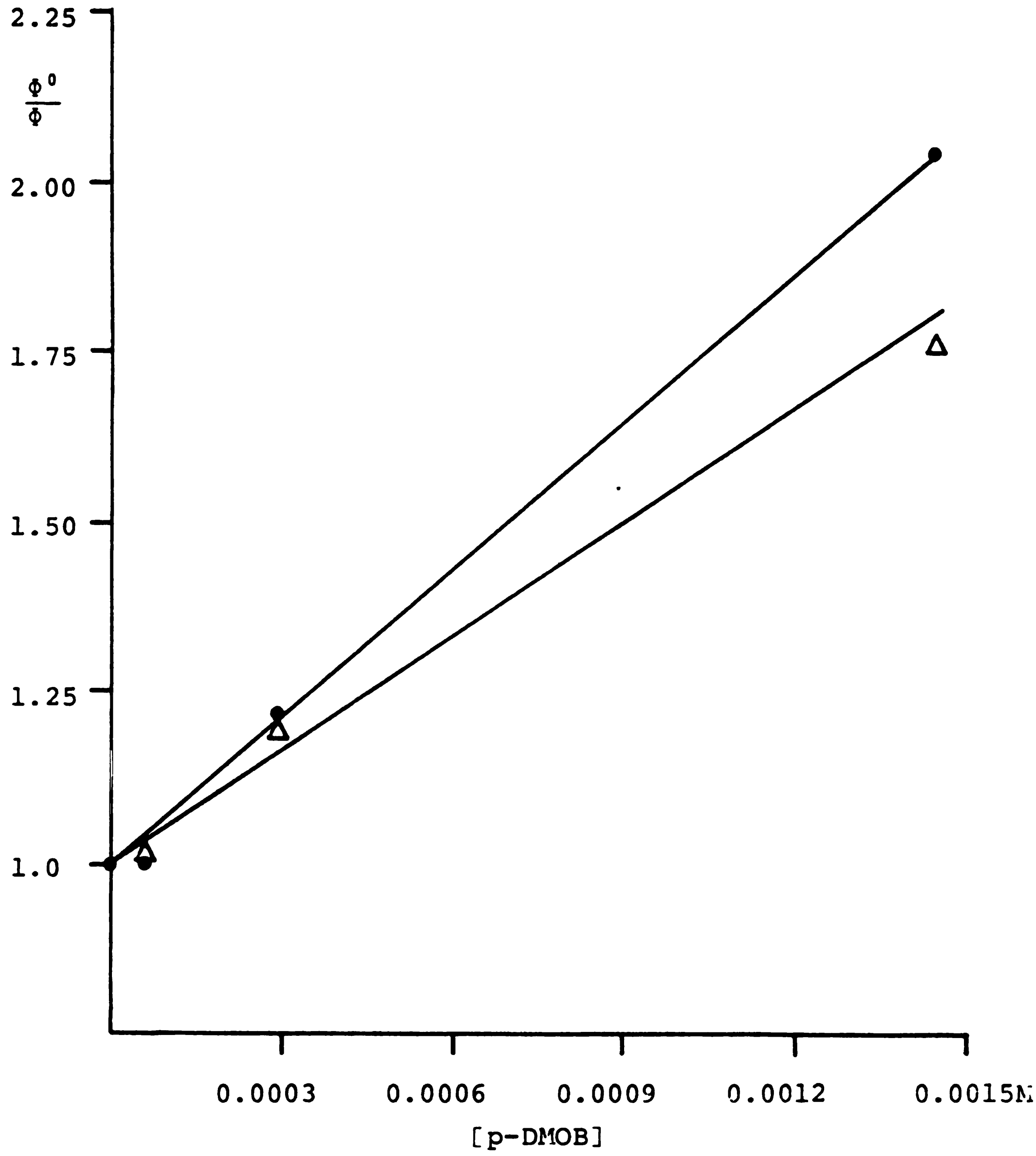


Figure 24. Quenching of the Reaction of TFA and Toluene in Benzene by p-Dimethoxybenzene. Results for BB (●) and BK (Δ).

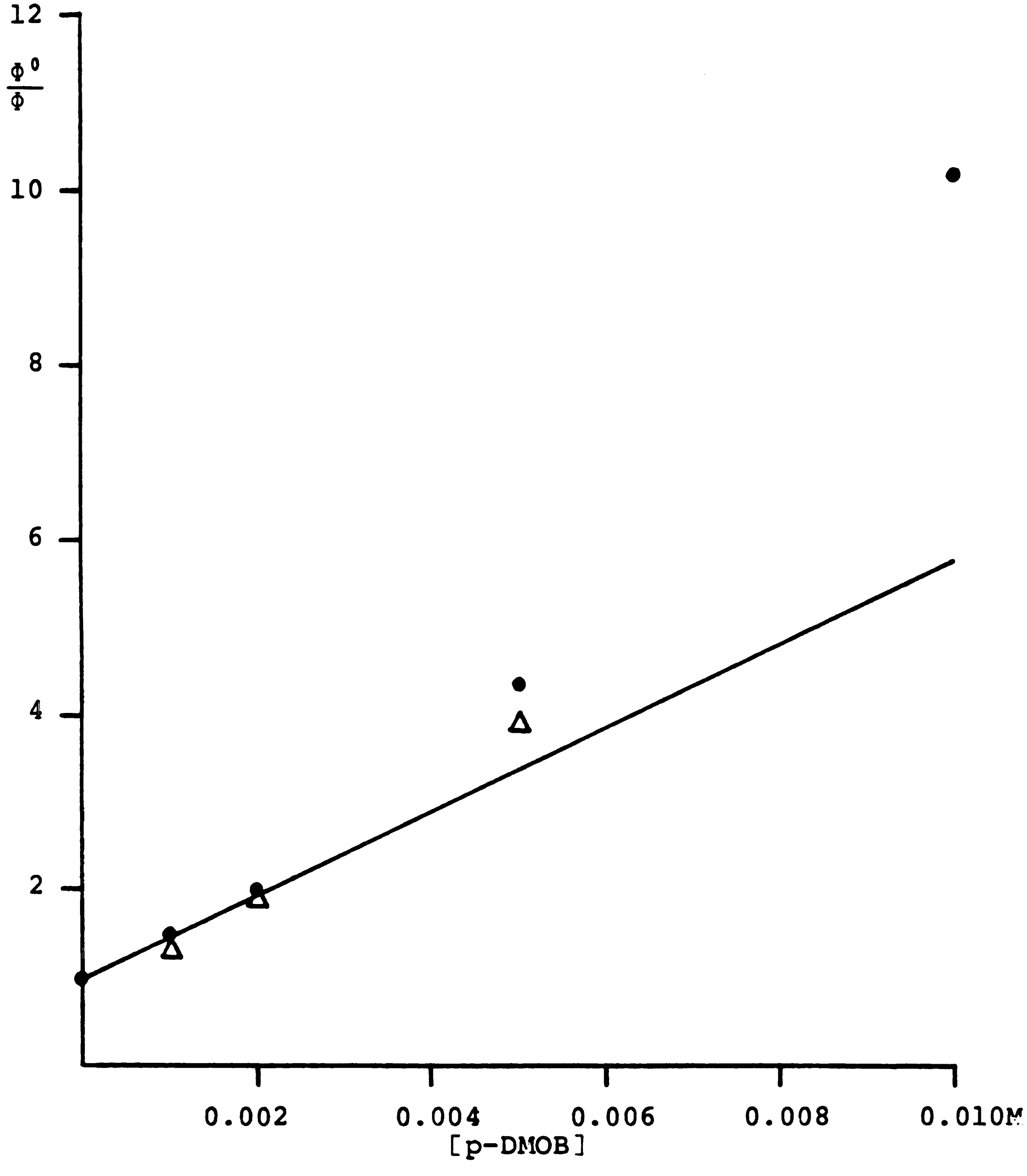


Figure 25. Quenching of the Reaction of AP and Toluene in Acetonitrile by p-Dimethoxybenzene. Results for BB (●) and BK (Δ).

for samples containing 0.10M ketone, 0.05M trifluoroacetic acid and varying concentrations of toluene in benzene.

The addition of trifluoroacetic acid to a photoreduction in benzene increases product yield, changes product distribution and also changes selectivity when p-cymene is the substrate. This occurs when either acetophenone or TFA is the ketone (see Table 14). The changes in primary-tertiary ratio for the two ketones are in opposite directions. Addition of 0.05M trifluoroacetic acid to benzene cuts the tertiary-primary ratio for acetophenone in half while doubling the same ratio of TFA. Since the tertiary-primary ratio is approximately ten times greater for acetophenone than for TFA in pure benzene, the overall result with acid is a much smaller difference in selectivity. With 0.05M acid in benzene the tertiary-primary ratio for acetophenone is slightly greater than twice what it is for TFA.

In acetonitrile TFA shows neither enhancement of products nor any change in primary-tertiary ratios when trifluoroacetic acid is added (Table 15). In both benzene and acetonitrile there is quenching of products when the acid concentration exceeds 0.05M.

To see how quantum yields varied with substrate concentration, TFA was photoreduced by varying concentrations of toluene in benzene with 0.05M trifluoroacetic acid added. The results for 1.0M to 2.5M toluene are

Table 14. Effect of Trifluoroacetic Acid (TFAA) on Products from Indicated Ketone and p-Cymene

Ketone	Solvent	[TFAA] (M)	[PT]^a	[TT]^a	[PP]^a	[KP]^a	[KT]^a	P/T
AP	Benzene	0.00	0.92	1.40	0.20	----	----	0.35
AP	Benzene	0.05	3.30	2.19	1.59	----	----	0.84
TFA	Benzene	0.00	0.83	0.12	2.00	5.7	1.7	3.80
TFA	Benzene	0.05	2.00	0.51	2.20	9.1	5.0	1.90
TFA	MeCN	0.00	1.93	0.26	4.78	16.7	3.2	5.00
TFA	MeCN	0.067	1.74	0.17	3.89	10.1	3.6	4.80

$^a10^{-3}$M

Table 15. Effect of Trifluoroacetic Acid (TFAA) on the Reaction of TFA and p-Cymene in Acetonitrile

[TFAA] (M)	[PT]^a	[PP]^a	[KP]^a	[KT]^a
0.00	0.297	0.776	2.57	0.441
0.10	0.281	0.643	2.87	0.532
0.50	0.162	0.323	1.98	0.367
1.04	0.069	0.144	1.32	0.260

$^a10^{-3}$M

shown in Table 16. The quantum yields for bibenzyl and cross-coupled alcohol are almost identical to the maximum quantum yields without acid present.

Generation of Radicals from di-t-Butyl Peroxide

Radicals were generated by irradiation of di-t-butyl peroxide at 313nm to produce t-butoxy radicals, which subsequently abstracted hydrogen atoms from substrate to produce the radicals of interest. For example benzyl radicals were formed by hydrogen abstraction from toluene and 1-phenyl-1-hydroxyethyl radicals were formed by abstraction from 1-phenylethanol. The concentrations of substrates were adjusted on the basis of rate constants for hydrogen abstraction by t-butoxy radicals so that the radicals were formed in roughly equal amounts. This means that the model system for the photoreduction of acetophenone by toluene should contain approximately ten times the concentration of toluene as of 1-phenylethanol. In this way t-butoxy radicals would abstract an equal number of hydrogen atoms from each substrate since the rate constant for abstraction from 1-phenylethanol is roughly ten times the rate constant for abstraction from toluene.[36] The samples containing the substrates and di-t-butyl peroxide in either benzene or acetonitrile were degassed by four freeze-thaw cycles. After irradiation at 313nm, analysis was performed by g.c. in the same manner as the photoreduction reaction. In addition to the three coupling

Table 16. Quantum Yields for the Reaction of TFA and Toluene with Trifluoroacetic Acid (0.05M) in Benzene

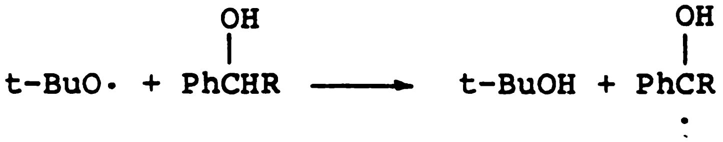
[Toluene] (M)	Φ_{BB}	Φ_{BK}	$\Phi_{B\cdot}$
1.00	0.070	0.155	0.295
1.52	0.071	0.154	0.295
2.01	0.071	0.154	0.296
2.50	0.072	0.157	0.301

products (BB, BK and KK) the formation of ketone produced by disproportionation was also monitored. Due to the hydroxy radical (K·) inducing decomposition of the peroxide,[71] the concentration of the peroxide was varied to study the relative amount of ketone formed.

Radical Formation

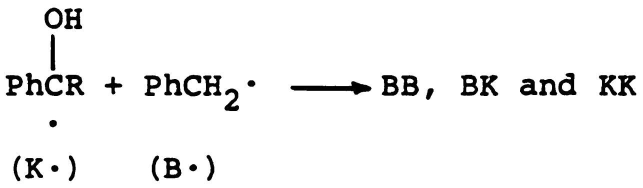
$$\text{(t-BuO)}_2 \xrightarrow{h\nu} \text{2t-BuO}\cdot$$

$$\text{t-BuO}\cdot + \text{PhCH}_3 \longrightarrow \text{t-BuOH} + \text{PhCH}_2\cdot$$



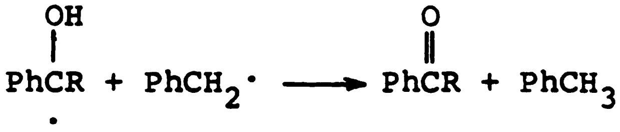
$$\text{t-BuO}\cdot + \overset{\text{OH}}{\overset{|}{\text{PhCHR}}} \longrightarrow \text{t-BuOH} + \underset{\bullet}{\overset{\text{OH}}{\overset{|}{\text{PhCR}}}}$$

Coupling



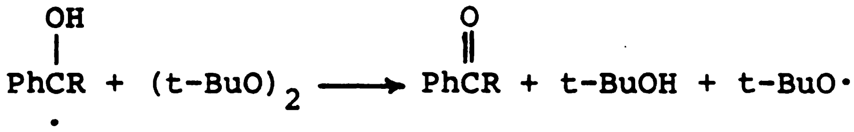
$$\underset{(\text{K}\cdot)}{\underset{\bullet}{\overset{\text{OH}}{\overset{|}{\text{PhCR}}}}} + \underset{(\text{B}\cdot)}{\text{PhCH}_2\cdot} \longrightarrow \text{BB, BK and KK}$$

Disproportionation



$$\underset{\bullet}{\overset{\text{OH}}{\overset{|}{\text{PhCR}}}} + \text{PhCH}_2\cdot \longrightarrow \overset{\text{O}}{\overset{\|}{\text{PhCR}}} + \text{PhCH}_3$$

Induced Decomposition



$$\underset{\bullet}{\overset{\text{OH}}{\overset{|}{\text{PhCR}}}} + \text{(t-BuO)}_2 \longrightarrow \overset{\text{O}}{\overset{\|}{\text{PhCR}}} + \text{t-BuOH} + \text{t-BuO}\cdot$$

The coupling and disproportionation products for benzyl and hydroxy radicals formed from toluene and

1-phenylethanol were measured in both benzene (Table 17) and acetonitrile (Table 18). In acetonitrile there was less of a dependence on peroxide concentration for formation of acetophenone. Other substrates were also studied for a direct comparison with acetophenone photoreduction. Cumene and p-xylene were studied in both benzene and acetonitrile, while toluene was studied in t-butanol also. The peroxide experiment, the results of which are shown in Table 19, were run in parallel with the photoreduction reaction, the results of which are in Table 13. There is a larger fraction of cross-coupled product formed in acetonitrile than there is in benzene and the percentage of cross-coupled product is greater for cumene than for p-xylene in either solvent.

Since there is a possibility that the substitution of fluorine on the methyl group of the ketone might effect the radical reactions, the peroxide was decomposed in benzene in the presence of 1-phenyl-2,2,2-trifluoroethanol and alkylbenzenes. The alkylbenzenes used were toluene, cumene and p-xylene. The results in Table 20 show that the relative amount of cross-coupled product is approximately the same for all three substrates. The concentration of peroxide was not varied for this study, however the amount of TFA measured for the reaction with toluene or p-xylene is only a small fraction of the amount of cross-coupled product.

Table 17. Products from the Reaction of t-Butoxy Radicals with Toluene and 1-Phenylethanol in Benzene

[Peroxide] (M)	[AP][a]	[BB][a]	[BK][a]	[KK][a]	[B·][a]	[K·][a]
0.020	0.96	1.20	2.53	3.30	4.93	9.13
0.030	2.21	1.52	2.82	3.17	5.86	9.16
0.051	2.10	1.01	1.63	1.54	3.65	4.71
0.101	4.53	1.81	2.65	2.21	6.27	7.07
0.152	7.19	2.47	3.42	2.69	8.36	8.80

[a] 10^{-3}M

Table 18. Products from the Reaction of t-Butoxy Radicals with Toluene and 1-Phenylethanol in Acetonitrile

[Peroxide] (M)	[AP][a]	[BB][a]	[BK][a]	[KK][a]	[B·][a]	[K·][a]
0.050	1.00	1.09	1.86	1.04	4.04	3.94
0.100	1.90	1.84	3.02	1.67	6.70	6.36
0.150	2.67	2.28	4.07	2.29	8.63	8.65

[a] 10^{-3}M

Table 19. Products from the Reaction of t-Butoxy Radicals with Indicated Substrate and 1-Phenylethanol

Substrate	Solvent	[BB][a]	[BK][a]	[KK][a]	[B·][a]	[K·][a]
Cumene	MeCN	5.52	9.80	3.90	20.8	17.6
Cumene	Benzene	5.03	8.36	4.90	18.4	18.2
p-Xylene	MeCN	4.87	8.26	3.69	18.1	15.7
p-Xylene	Benzene	4.09	5.64	5.26	13.8	16.2
Toluene	t-BuOH	4.05	8.50	3.27	16.7	15.1

[a] 10^{-3}M

Table 20. Products from the Reaction of t-Butoxy Radicals with Indicated Substrate and 1-Phenyl-2,2,2-Trifluoroethanol in Benzene

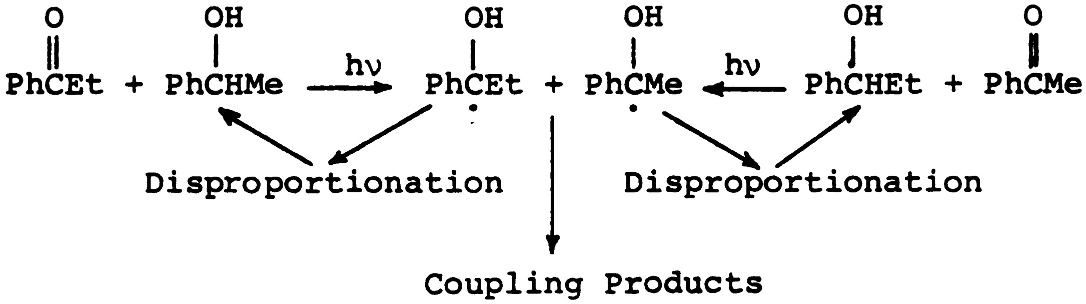
Substrate	[TFA][a]	[BB][a]	[BK][a]	[KK][a]	[B·][a]	[K·][a]
---------	2.83	----	----	2.51	----	5.02
Toluene	0.58	1.90	3.80	1.14	7.60	6.08
Cumene	1.27	0.63	2.09	1.05	3.35	4.19
p-Xylene	0.24	1.96	4.03	1.48	7.95	6.99

[a] 10^{-3}M

Photoreduction by Alcohols

The low quantum yields of acetophenone photoreduction by alcohols, such as 1-phenylethanol and 2-propanol,[63] prompted a re-examination of the interaction of excited acetophenone with alcohols in an attempt to determine the source of the inefficiency. The experiments were carried out in either benzene or acetonitrile solutions of ketone and alcohol. For maximum quantum yield studies the ketone concentration was kept constant (0.10M) and the alcohol concentration was varied. For the hydrogen exchange studies used to determine disproportionation and cage reactions the alcohol concentration was kept constant and the ketone concentration was varied. The products that were measured were the alcohol corresponding to reduction of the starting ketone, the ketone corresponding to oxidation of the starting alcohol, and the pinacols formed from the coupling of two hydroxy radicals. The product alcohol should be formed only by disproportionation, while the product ketone can be formed by disproportionation and exchange of a hydrogen from the hydroxy radical to the ground state starting ketone. This hydrogen exchange accounts for the majority of the ketone produced.

The first experiment was used to determine the extent of radical disproportionation. This was accomplished using two complementary systems. One system was the photoreduction of propiophenone by 1-phenylethanol and the other was photoreduction of acetophenone by 1-phenylpropanol. Both systems will produce the same radicals in the primary reaction and therefore disproportionation can be measured in both directions. The disproportionation products measured were



1-phenylpropanol and 1-phenylethanol. By increasing ketone concentration it is possible to make use of the exchange of hydrogen atoms from hydroxy radicals to ground state ketones to study cage coupling and the disproportionation of a particular hydroxy radical. The results of this can be clearly seen in Tables 21 and 22. The photoreduction of varying concentrations of acetophenone by 1-phenylpropanol gave the best results in regard to this. For the highest concentration of acetophenone studied (0.3M) not only is the quantum yield of 1-phenylethanol less than 3% of the quantum yield of acetophenone pinacol, but also the quantum yield of crossed pinacol is less than 1% of the total quantum yield of all pinacols formed. The experiment with propiophenone and 1-phenylethanol shows similar trends.

Table 21. Quantum Yields for the Reaction of Propiophenone (PP) and 1-Phenylethanol (APH_2)

[PP] (M)	Φ_{PPH_2}	Φ_{AP}	$\Phi_{(APH)_2}$	$\Phi_{(APH)(PPH)}$	$\Phi_{(PPH)_2}$	% Conv.
0.020	-----	-----	0.0293	0.0508	0.0189	29
0.052	0.0084	0.059	0.0127	0.0508	0.0450	17
0.145	0.0092	0.113	------	0.0309	0.0710	8
0.260	0.0110	0.125	------	0.0194	0.0750	4

[1-Phenylethanol] = 0.51M in Benzene

Table 22. Quantum Yields for the Reaction of Acetophenone (AP) and 1-Phenylpropanol $(PPH)_2$

[AP] (M)	Φ_{APH_2}	Φ_{PP}	$\Phi_{(APH)_2}$	$\Phi_{(APH)(PPH)}$	$\Phi_{(PPH)_2}$	% Conv.
0.030	0.0075	0.204	0.203	0.0415	a	69
0.060	0.0064	0.226	0.227	0.0171	a	36
0.151	0.0053	-----	0.199	0.0051	a	12
0.302	0.0027	-----	0.139	0.0011	a	4

[1-Phenylpropanol] = 0.20M in Benzene

[a] Too low to measure.

The two hydroxy radicals were also generated by using 2-propanol as the hydrogen donor and by having equal amounts of acetophenone and propiophenone in solution (Table 23). In these experiments both 1-phenylethanol and 1-phenylpropanol were measured. The ratio of pinacol products is a function of the steady-state concentration of the two hydroxy radicals and the ratio of their self-coupling rate constants. The observed ratio of acetophenone pinacol to propiophenone pinacol is approximately nine. The ratio of hydroxy radicals from acetophenone to those from propiophenone is therefore approximately three. These ratios change slightly with increased ketone concentration. The total of the disproportionation products, 1-phenylethanol and 1-phenylpropanol, account for about 3% of the products, with the other 97% being the pinacol products.

When ketones other than propiophenone were used in the above experiment, electron withdrawing groups increased the fraction of hydroxy radicals formed from that ketone relative to hydroxy radicals formed from acetophenone. Electron donating groups had the opposite effect. Thus when a solution equimolar in acetophenone and p-methoxyacetophenone was photoreduced by 2-propanol in benzene, the only product observed was acetophenone pinacol. When acetophenone and m-trifluoromethylacetophenone were used the acetophenone pinacol accounted for less than 4%

Table 23. Results for Reaction of Acetophenone (AP) and Propiophenone (PP) with 2-Propanol in Benzene

Run[a]	$\Phi_{(APH)_2}$	$\Phi_{(APH)(PPH)}$	$\Phi_{(PPH)_2}$	Φ_{APH_2}	Φ_{PPH_2}
1	0.169	0.116	0.0178	0.0075	0.0031
2	0.172	0.104	0.0142	0.0066	0.0022

[a] Run 1: [AP] = [PP] = 0.05M, [2-Propanol] = 0.50M.

Run 2: [AP] = [PP] = 0.10M, [2-Propanol] = 1.00M.

of the products. These and other results are shown in Table 24.

The quantum yields for pinacol formation were measured to obtain maximum quantum yields to compare to the amount of disproportionation. The results obtained for acetophenone and 1-phenylethanol in benzene ($\Phi^{max} = 0.59$, Figure 26) agree well with the value of 0.55 reported by Cohen.[63] For TFA and 1-phenylethanol the measured quantum yields are lower than with acetophenone, but the slope is much greater and leads to a maximum quantum yield at least as high as acetophenone and possibly near one (Figure 27). One problem with both systems is a decrease in quantum yields when the alcohol concentration is too high. This prevents the use of concentrations higher than 0.5M when extrapolating to infinite concentration.[63]

To see if the hydroxy proton has any effect on the efficiency of the reaction a comparison was made between undeuterated alcohol (O-h) and the alcohol deuterated on the oxygen (O-d). The deuterated alcohol was 65% deuterated. In benzene there were minor differences between the two compounds but not large enough to be significant. In acetonitrile however, there was a significant increase in maximum quantum yield for the deuterated alcohol. The slopes of the double reciprocal plots for the two alcohols were the same, as shown in Figure 28.

Table 24. Results for Reaction of Acetophenone (AP) and Indicated Ketone (K) with 2-Propanol in Benzene

Ketone	Pinacols (%)		
	$(APH)_2$	(APH)(KH)	$(KH)_2$
p-MeO-AP	100.0	----	----
p-Me-AP	68.7	28.7	2.6
m-Me-AP	39.0	52.0	9.0
PP	58.0	36.4	5.6
m-CF_3-AP	3.5	22.5	74.0
TFA	----	----	100.0
m-CF_3-TFA	----	----	100.0

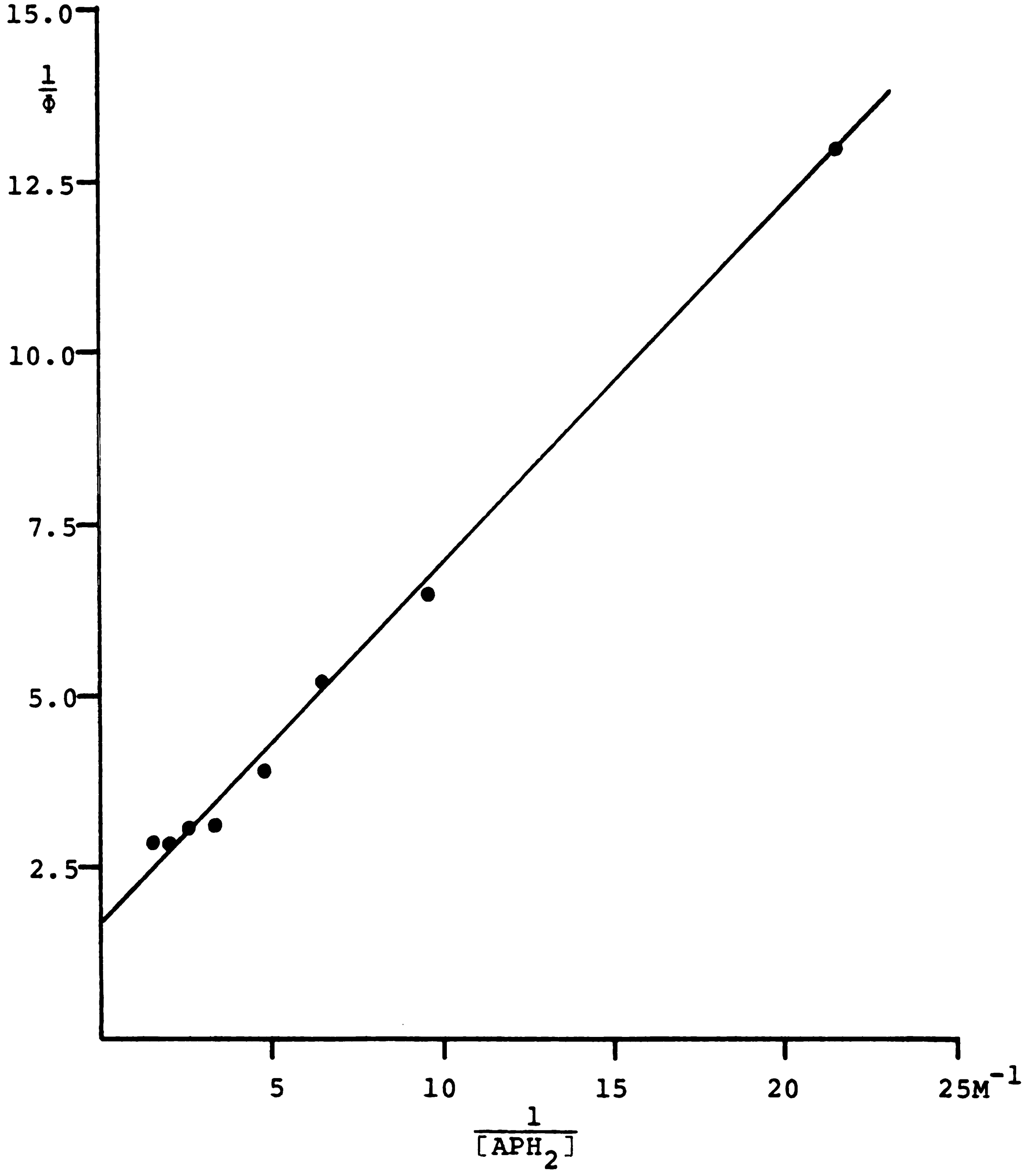


Figure 26. Results from Reaction of AP and 1-Phenylethanol in Benzene, Formation of Pinacol.

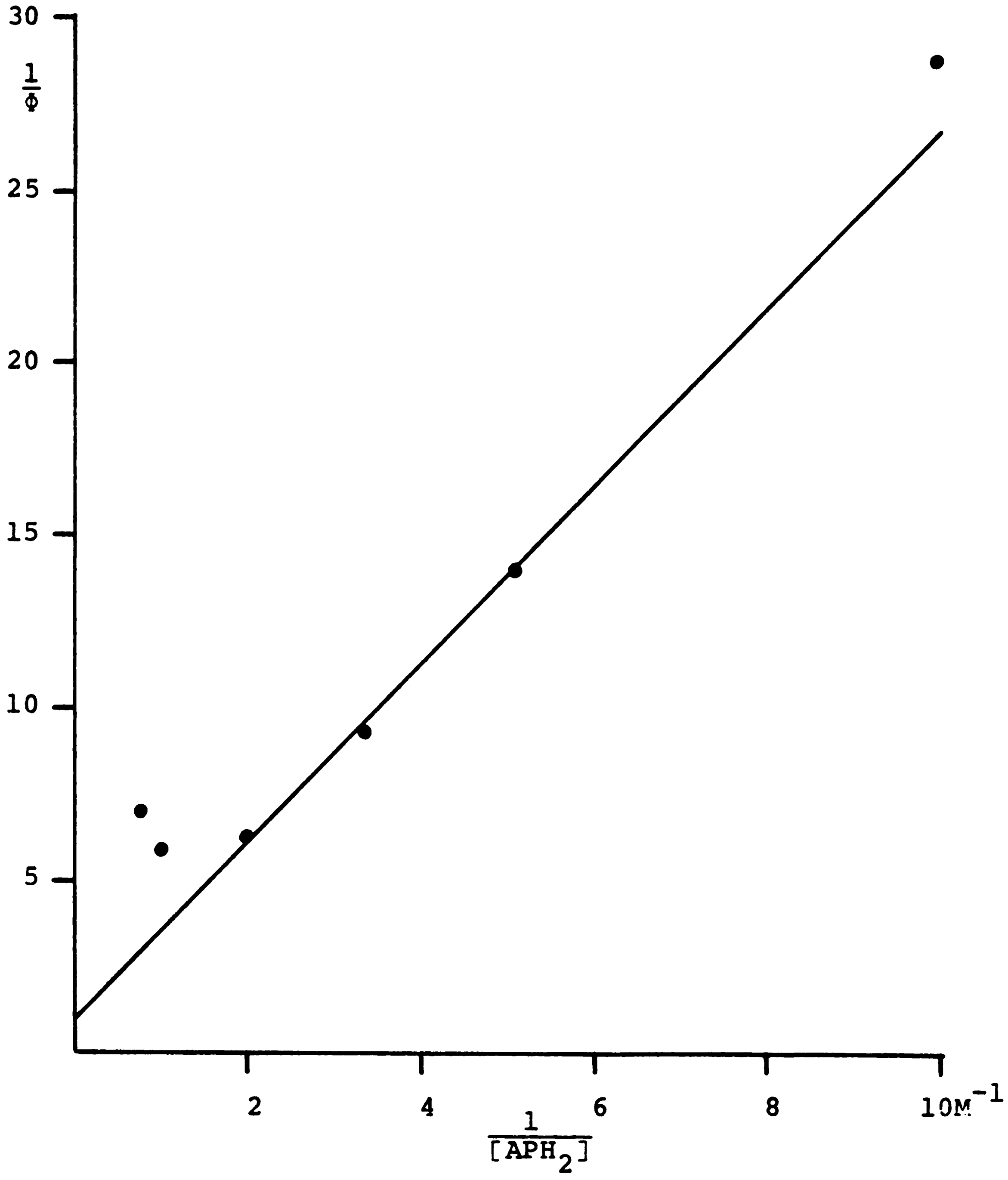


Figure 27. Results from Reaction of TFA and 1-Phenylethanol in Benzene, Formation of TFA Pinacol.

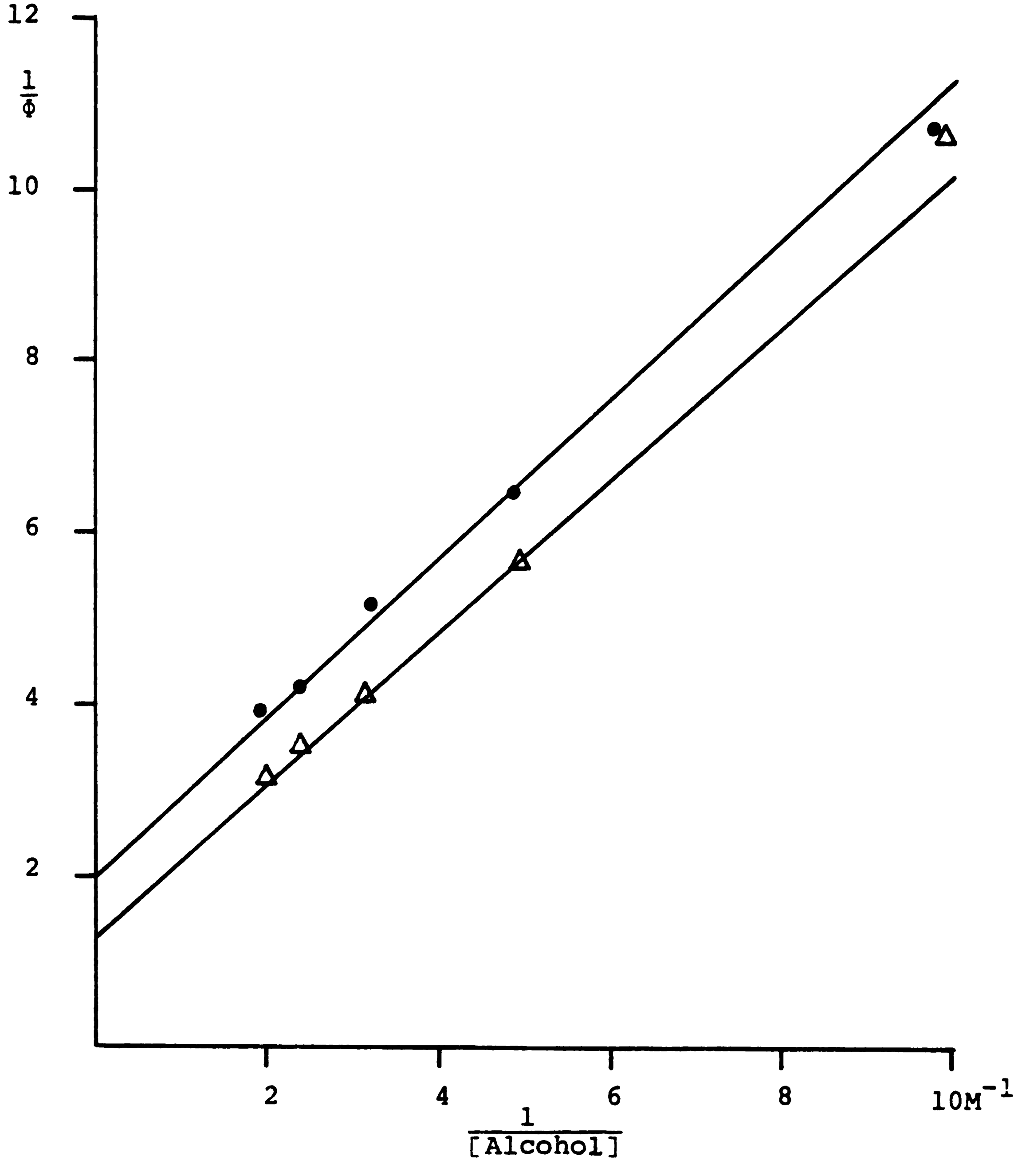


Figure 28. Pinacol Formation from the Reaction of AP with Deuterated (Δ) and Undeuterated (●) 1-Phenylethanol.

Propiophenone was irradiated in benzene with 0.10M of either 1-phenylethanol or the pinacol of acetophenone (Table 25). The concentration of propiophenone was varied to study the change in product distribution. The reaction with 1-phenylethanol went to high conversion since it was irradiated in parallel with the less efficient pinacol reaction. The crossed pinacol could not be measured in the acetophenone pinacol experiment because of the large acetophenone pinacol peak. The results for the 1-phenylethanol experiment clearly shows a shift toward propiophenone pinacol at higher ketone concentration, although the high conversion probably has some effect on the ratios. The results for the acetophenone pinacol experiment suggest that there is a shift toward more propiophenone pinacol at higher ketone concentrations in this case too, although not as pronounced. The total quantum yield for pinacol formation for the photoreduction of propiophenone by 1-phenylethanol can be estimated to be close to 20%. Based on this, the photoreduction of propiophenone by acetophenone pinacol gives quantum yields of 2 to 3% for propiophenone pinacol formation and 6 to 8% for formation of acetophenone. These quantum yields are for 0.10M of the respective substrates, and not the maximum quantum yields.

The photoreduction of α-fluoroacetophenone (MFA) by 2-propanol was investigated to see if MFA pinacol

Table 25. Results for the Reaction of Propiophenone (PP) with Acetophenone Pinacol ($(APH)_2$) or 1-Phenylethanol (APH_2)

Reactants			Products				% Conv.
[PP]	[APH_2]	[$(APH)_2$]	[AP][a]	[$(APH)_2$][a]	[(APH)(PPH)][a]	[$(PPH)_2$][a]	
0.020	0.102	-----	0.93	2.56	5.86	4.31	74
0.099	0.102	-----	12.30	----	4.27	10.50	26
0.020	-----	0.099	4.86	----	----	1.49	25
0.049	-----	0.099	6.44	----	----	2.31	13
0.099	-----	0.099	6.11	----	----	2.33	6

[a] 10^{-3} M

could be observed. The reaction of MFA with toluene produced bibenzyl, acetophenone and an unidentified compound that is probably the cross-coupled alcohol. This latter compound was produced in smaller quantities than either bibenzyl or acetophenone. It could not be determined if fluorine was lost as a fluorine atom or as fluoride ion, and whether it occurred in the initial photoreduction or after formation of the hydroxy radical. Since the hydroxy radical could be formed by hydrogen transfer when 2-propanol is the substrate, whether MFA pinacol is formed or not could be useful in answering this question. The quantum yields for acetophenone formation are high and extrapolate to a maximum quantum yield of 3.3 (see Figure 29). A quantum yield greater than two suggests a chain reaction other than just hydrogen exchange. In addition, only a minor long retention time product was observed. This product could be MFA pinacol or 1,2-dibenzoylethane. The latter produce could be formed from loss of a fluorine atom from the ketone and subsequent coupling of the radicals. Whatever this product is, it is clearly a minor product compared to acetophenone.

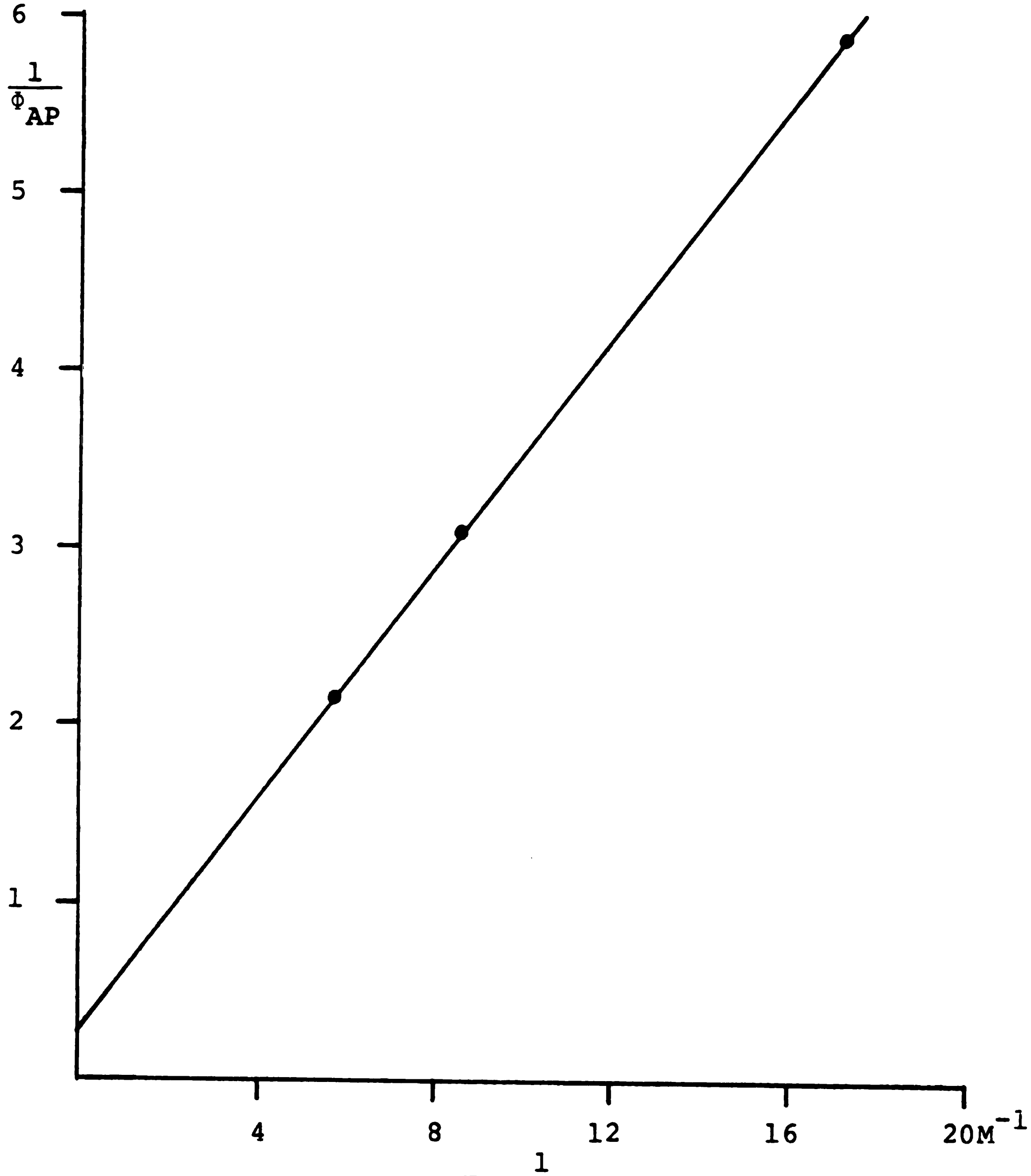


Figure 29. Acetophenone Formation from the Reaction of α-Fluoroacetophenone and 2-Propanol.

DISCUSSION

Selectivity of the Photoreduction Reaction

Comparing primary-tertiary ratios for systematically substituted ketones shows that electron withdrawing groups decrease, and electron donating groups increase, preference for tertiary hydrogen abstraction from p-cymene. This effect is observed for acetophenone substituted in the α-position (Table 26) and for ring substituted acetophenones, benzophenones and α,α,α-trifluoroacetophenones (Table 27). A literature report for benzophenone and p-cymene gives a result favoring tertiary over primary with a ratio of 3.8 to 1.[72] While this is higher than obtained here (2.4 to 1), the conditions were not given and could account for the difference.

For the sequence of acetophenone substituted by fluorine in the α-position (AP, DFA, and TFA) the rate constants increase as primary preference increases (see Table 28). This can be interpreted as a decrease in selectivity corresponding to an increase in reactivity. The results for TFA, a very reactive ketone, give a ratio of primary to tertiary products of 3.4 to 1. This corresponds to a primary to tertiary preference of 1.1 to 1 per hydrogen

Table 26. Effects of α-Substitution on Primary-Tertiary Ratio

Ketone	Tertiary : Primary
Propiophenone	2.7 : 1.0
Acetophenone	2.8 : 1.0
α,α-Difluoroacetophenone	1.0 : 1.8
α,α,α-Trifluoroacetophenone	1.0 : 3.4

Table 27. Effects of Ring Substitution on Primary-Tertiary Ratio

Ketone	Tertiary : Primary
Benzophenones	
4,4'-Me-BP	5.2 : 1.0
4,4'-MeO-BP	3.0 : 1.0
BP	2.4 : 1.0
4,4'-Cl-BP	1.7 : 1.0
Acetophenones	
p-Me-AP	3.3 : 1.0
AP	2.8 : 1.0
m-F-AP	2.3 : 1.0
M-CF_3-AP	1.9 : 1.0
p-F-AP	1.7 : 1.0
α,α,α-Trifluoroacetophenones	
p-MeO-TFA	1.0 : 1.1
p-Me-TFA	1.0 : 1.7
m-Me-TFA	1.0 : 2.1
TFA	1.0 : 3.4
m-CF_3-TFA	1.0 : 4.7

Table 28. Rate Constants for Photoreduction

Ketone	Substrate	k_d/k_r (M)	k_r ($10^6 M^{-1} s^{-1}$)	Φ_{BB}^{max}
AP	Toluene	3.75	0.12	0.083
AP	p-Cymene	0.94	0.48	0.058[a]
AP	APH_2[b]	0.31	1.46	0.590[c]
MFA	Toluene	2.26	1.64	0.105
MFA	2-Propanol	1.08	3.43	3.300[d]
DFA	Toluene	1.14	4.30	0.056
DFA	p-Cymene	0.20	24.50	0.045[a]
TFA	Toluene	5.08	6.80	0.077
TFA	p-Cymene	0.42	82.20	0.051[a]
TFA	APH_2[b]	2.57	13.4	1.000[c]

[a] Sum of PP, PT and TT

[b] APH_2 is 1-Phenylethanol

[c] Quantum yield for pinacol of the ketone

[d] Acetophenone formation

and can be interpreted as lacking any selectivity. Other results suggest selectivity is not directly related to reactivity. A primary to tertiary preference of 4.9 to 1 is obtained for m-trifluoromethyl-α,α,α-trifluoroacetophenone. This is a per hydrogen preference to 1.6 to 1 for primary product. This is large enough to be considered a definite preference and not just a lack of selectivity. This suggests that there is a change in selectivity with electron-withdrawing substituents, not a decrease in selectivity related to an increase in reactivity as mentioned above. The selectivity for ketones without electron-withdrawing groups is in favor of tertiary hydrogens, which would be expected on the basis of bond strength. The rate constants for these ketones show a primary deuterium isotope effect,[38,39] which is expected for a reaction involving carbon-hydrogen bond cleavage in the rate determining step. For significantly electron deficient ketones, the selectivity is in favor of the primary hydrogens. The rate determining step in the reaction has been shown to be formation of an exciplex.[38] It is possible to conclude that electron-withdrawing substituents increase the likelihood of exciplex formation, and that reaction via exciplexes show a preference for abstraction of primary hydrogens. The magnitude of this primary preference depends on the extent of charge transfer in the exciplex. For example the rate determining step for the reaction of TFA and toluene is exciplex formation.[38,40] Since m-CF_3-TFA is more electron deficient and reacts faster than TFA with toluene[73] it is likely that it too reacts entirely via exciplex formation with toluene. If both of these ketones react with toluene solely by exciplex formation it is likely that they also react with p-cymene entirely by exciplex formation, yet their selectivities are different (3.4 to 1 for TFA versus 4.9 to 1 for m-CF_3-TFA). A direct hydrogen abstraction pathway would be in competition with exciplex formation.

Since p-cymene is extremely sensitive to substituent effects it could prove to be useful in determining the fraction of reaction proceeding through an exciplex and the amount of charge transfer in a particular exciplex. To do this, however, the change in ratio due to extent of charge transfer has to be separated from the change in ratio due to percent of reaction proceeding through exciplex. To illustrate the difficulty of separating these effects and to underscore the utility of the p-cymene system it is informative to compare rate constants and selectivities for acetophenone and p-MeO-TFA. The rate constant for interaction with toluene is larger for acetophenone ($k_r = 1.9 \times 10^5 M^{-1}s^{-1}$ in acetonitrile[74]) than for p-MeO-TFA ($k_r = 5.1 \times 10^4 M^{-1}s^{-1}$ in acetonitrile[73]). Yet acetophenone shows greater preference for tertiary abstraction, 2.8 to 1 versus 1 to 1.1 for p-MeO-TFA. Based on rate constants alone very little could have been said as to whether an exciplex was involved in this reaction or not. The para methoxy group changes excited state reduction potential, thereby decreasing the rate constant for exciplex formation. It also changes the lowest triplet state from n,π^* for TFA to π,π^* for p-MeO-TFA,[73] which decreases the rate constant for any direct hydrogen abstraction. Therefore, this is a case where a substituent slows down both pathways, possibly by comparable amounts. The primary-tertiary ratio for p-MeO-TFA is a third of the ratio of TFA, yet the rate constants for reaction with toluene differ by a factor of 200. It is not possible to determine how much of the change in selectivity is due to a change in exciplex selectivity and how much may be due to some direct hydrogen abstraction.

A number of systems can be used as models for the behavior of the photoreduction reaction. The reaction of t-butoxy radicals with p-cymene was used as a model for direct Hydrogen abstraction. Both n,π^* triplet states and t-butoxy radicals have an unpaired electron in a nonbonding orbital on oxygen. This half-filled orbital is responsible for direct hydrogen abstraction. The tertiary-primary preferences for reaction of p-cymene with acetophenone (2.8 to 1) and benzophenone (2.4 to 1) are very close to the results for t-butoxy radicals (2.7 to 1). Rate constants are also very similar for these three compounds (Table 1). This shows that t-butoxy radicals are a good model for the triplets of acetophenone and benzophenone, but does not necessarily mean that all products come from direct hydrogen abstraction. Since the effects of substituents suggest that there is some exciplex formation with acetophenone and benzophenone, it is possible that t-butoxy radicals can also form a complex with p-cymene. However this complex may not be as important for product formation as it is for explaining quantum inefficiency for acetophenone and benzophenone.

Oxidation by cobalt (III) acetate can be used as a model for the two step reaction where electron transfer is followed by proton transfer, the former step being rate determining. Onopchenko and Schulz[75] showed that the methyl hydrogens are preferred over the isopropyl hydrogen by nine to one for this reaction. Addition of lithium chloride changes this to a 3.2 to 1 preference for the tertiary hydrogens. The electrochemical oxidation of p-cymene in methanol shows oxidation of the tertiary center to be approximately twice that of the primary center.[76] However the effect of supporting electrolyte and base would have to be carefully investigated since they should both affect the deprotonation of the radical cation.[77] This is clearly evident from the effect lithium chloride had on the oxidation by cobalt mentioned above.

Some photochemical systems that are believed to proceed by electron transfer show similar preference for primary hydrogens. In the photoreduction of esters by p-cymene[78] there appears to be a primary preference. However, the products observed suggest there may be some secondary reactions occurring making it difficult to determine exact ratios. Cohen[8] has looked at the photoreduction of benzophenone by tertiary amines and studied the products of oxidation of the amines to find a preference for primary or secondary proton transfer over tertiary proton transfer. Thus for N,N-dimethyl-2-butylamine there is more than twelve times more formaldehyde from oxidation of the methyl group than 2-butanone from oxidation of the 2-butyl group. This corresponds to a greater than 2 to 1 preference for the methyl protons when corrected for the number of hydrogens on each group. Similarly there is more than two times more acetaldehyde than acetone formed from the reaction of benzophenone with diisopropylethylamine. For the reaction of excited stilbene with amines the product ratio appears to depend on the statistical number of each type of hydrogen except for a few cases where a definite preference for primary versus tertiary hydrogen transfer (20 to 1 corrected for the number of hydrogens) is observed.[79] This large primary preference was attributed to steric effects. Davidson[5] studied the disappearance of benzophenone when photoreduced by amines with N-methyl or N-benzyl groups and found a greater disappearance for the N-methyl amines. This is not as useful as Cohen's study, however, since the two groups were not present in the same amine. This would be similar to comparing quantum yields of photoreduction by toluene and cumene instead of the primary and tertiary hydrogens of p-cymene.

Mechanistic Implications of Selectivity

The above results are consistent with the argument that charge transfer in the exciplex leads to greater reactivity of the primary hydrogen. The results also support a competition between direct hydrogen abstraction and exciplex formation for the photoreduction of acetophenone by alkybenzenes. The rate constants for acetophenone photoreduction show interactions with 1-phenylethanol to be greater than with toluene, cumene and p-xylene. This is consistent with direct hydrogen abstraction dependent on carbon-hydrogen bond strengths. Because of relative bond strengths and ionization potentials the alkylbenzenes should show smaller rate constants for direct hydrogen abstraction and larger rate constants for exciplex formation than 1-phenylethanol. Therefore, it is possible that there is some exciplex formation between acetophenone and alkylbenzenes, although deuterium isotope effects rule out all products coming from an irreversibly formed exciplex.

One way to describe the competition between pathways would be to construct a three dimensional energy diagram as in Figure 30. The Z-axis would be potential energy, the X-axis would be the movement of the hydrogen atom, and the Y-axis would be a measure of electron transfer from the substrate to the ketone. The origin would be the encounter between ketone and substrate with no complexation (Point A). Moving in the direction of charge transfer one would go from point A over a transition state for exciplex formation (Point B) to the exciplex (Point C). Moving in the direction of hydrogen transfer from point A one would proceed up in energy to the transition state for direct hydrogen abstraction (Point D) and then down to the radical pair (Point G). From the exciplex (Point C) one could proceed up in energy toward point F, which is the transition state for transfer of a hydrogen (or proton) from the exciplex. This path combines movement along the axis for charge separation as well as the hydrogen transfer axis. This is in keeping with the transfer of a proton, which would neutralize the charge separation and lead to the same radical pair as direct abstraction.

The two reaction paths can now be described by this diagram. Direct hydrogen abstraction is represented by the path A-D-G, and reaction via exciplex is described by path A-B-C-F-G. The relative energies of B and D determine whether an exciplex will be formed or not. If an exciplex is formed the relative energy of points B and F

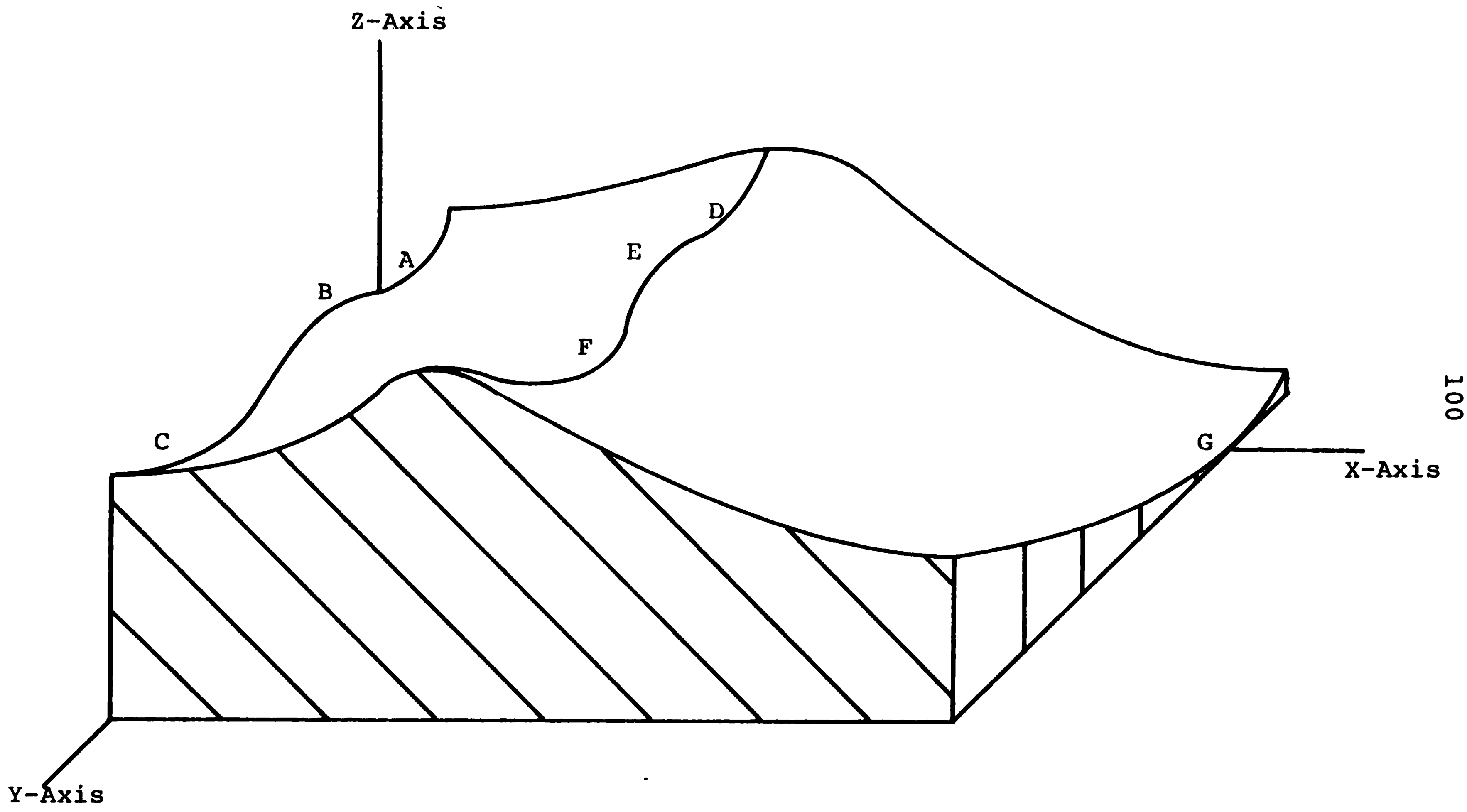


Figure 30. Potential Energy Diagram for the Photoreduction Reaction.

determine if it will be formed reversibly. For TFA and toluene all reaction proceeds via an irreversibly formed exciplex. This means that for TFA and toluene point F is lower than point B which, in turn, is lower than point D. In addition to reaction through point F and reversal of exciplex formation the exciplex has another path not shown. That path is decay to ground state reactants and leads to much of the inefficiency in photochemical reactions proceeding through exciplex formation. It is possible that there are systems where points B and F are significantly higher in energy than the barrier for radiationless decay of the exciplex and points B and D are comparable in energy. For this case product formation would be primarily by direct hydrogen abstraction even though there would be comparable amounts of direct hydrogen abstraction and exciplex formation. The exciplex would mainly be a quenching reaction contributing little to product formation. Such a situation may be occurring in the reaction of acetophenone with alkylbenzenes.

The selectivity results from p-cymene suggest that point D is higher for a primary hydrogen abstraction than for a tertiary hydrogen abstraction, while the opposite seems to be true for point F. The extent of charge transfer in the exciplex would change the position of point C along the Y-axis and would also be expected to change the energies of points B, C, and F while points A and D should be unaffected. The relative energies of point F for primary and tertiary abstraction may also be affected. These changes would have a significant effect on the course of the reaction. An increase in charge separation corresponding to a decrease in the energy of points B and C would lead to an increase in the rate of exciplex formation. This is consistent with the observed relationship between rate constant for exciplex formation and ΔG for electron transfer. An increase in charge transfer may also lower the energies of the transition state for reaction from exciplex (Point F) and the barrier for radiationless decay. There is no evidence for either of these changing very much, however.

The reaction of TFA and 1-phenylethanol is an interesting situation. The rate constant for this reaction is comparable to that of the reaction of TFA and toluene, even though toluene would be expected to be more reactive toward exciplex formation. This suggests that TFA may be reacting partially via direct hydrogen abstraction with 1-phenylethanol.

The above interpretations, suggesting that acetophenone can form exciplexes with alkylbenzenes and TFA can react with 1-phenylethanol by direct hydrogen abstraction, are not unreasonable. Most reactions that proceed through more than one mechanism have cases where only one mechanism is predominant as well as cases where the mechanisms are in competition. Determining when only one mechanism is operating is a major step in understanding reactions that occur by more than one mechanism. The results discussed here have laid the foundation for investigating competing pathways in the photoreduction reaction.

Solvent Effects on Selectivity

The increase in primary preference in acetonitrile compared to benzene is large enough to be of interest, but does not suggest a major change in mechanism. The difference in maximum quantum yields for photoreduction of TFA by p-cymene in benzene and acetonitrile are not large enough to suggest a major interaction of solvent with the exciplex. The increase in primary preference can be attributed to a combination of more charge-transfer in the exciplex, due to a polar solvent, and a decrease in disproportionation of radicals.

The change in selectivity when trifluoroacetic acid is added to benzene but not acetonitrile suggests the acid is reacting with the ketone-benzene exciplex. The formation of an exciplex is the main path for radiationless decay (k_d) for TFA in benzene.[38] If acid reacts with this exciplex to form another intermediate it is possible that this intermediate can react with p-cymene with a different selectivity than the triplet ketone. The reaction of trifluoroacetic acid with a TFA-benzene exciplex was suggested by Bryce-Smith[80] to explain the addition of TFA to benzene to form 1,1-diphenyl-2,2,2-trifluoroethanol. The protonation of an exciplex by a protic solvent has also been suggested for an intramolecular exciplex formation.[81] The lack of dependence of quantum yield on substrate concentration for the reaction of TFA with toluene in benzene with 0.05M trifluoroacetic acid further supports this mechanism. The slope divided by the intercept of the double reciprocal plot, which is equal to k_d/k_r, is close to zero. Therefore k_r should be much greater than k_d. This means that either k_r has increased dramatically or k_d has decreased. Lifetimes obtained from quenching studies indicate that neither has changed, however. The reaction of acid with the TFA-benzene exciplex to form another reactive intermediate which can react with toluene can be used to explain these results. This means that reaction with benzene, which had been the major component of k_d, leads to reaction. This effectively reduces the k_d and increases the k_r, leading to a very small ratio of k_d/k_r from the double reciprocal plot. However the rate constants for reaction of triplet ketone with benzene and toluene do not change, and therefore the lifetimes of ketone are the same with and without acid present. Further information is needed to determine the nature of the intermediate formed when acid interacts with the TFA-benzene exciplex. It is also interesting to note that maximum quantum yields are the same whether acid is present or not, although the selectivity of product formation with p-cymene changes noticeably. The former result suggests a common intermediate while the latter suggests different intermediates.

Fate of Radicals

Comparison of the coupling products from radicals generated from the photoreduction reaction to those formed by abstraction by t-butoxy radicals show no significant differences. Since the photoreduction reaction produces radicals in-cage and peroxide decomposition can only produce them out-of-cage, there must not be a significant cage reaction occurring in the photoreduction reaction.

A correction for different amounts of the two radicals was made by assuming equal rate constants for the three coupling reactions. This method predicts half of the products to be cross-coupled product and the other half equally divided between the two self-coupling products (BB:BK:KK equal to 1:2:1) when the two types of radicals are formed in equal amounts. When there are unequal amounts of benzyl radicals (B·) and hydroxy radicals (K·) the cross-coupled product concentration is predicted as follows:

$$[\mathrm{BK}]_{\mathrm{predicted}} = \frac{[\mathrm{B}\cdot][\mathrm{K}\cdot]}{[\mathrm{B}\cdot] + [\mathrm{K}\cdot]}$$

The concentrations of B· and K· are calculated from the observed coupling products. Comparing the experimentally observed values to the predicted values shows no significant difference between coupling ratios from photoreduction and peroxide initiated reaction (Table 29). This comparison also shows that the ratio is a function of the particular radicals involved and the solvent used. Changing relative ratios of the two types of radicals does not appear to change the ratio of BK observed to BK predicted.

The amount of ketone formed from hydroxy radicals in the peroxide reaction gives an upper limit to the amount of disproportionation occurring. To calculate the amount of disproportionation it was assumed that all the ketone measured was a result of disproportionation between a hydroxy radical and a benzyl radical. This neglect of any disproportionation between two hydroxy radicals is justified on the basis of the results of the photoreduction of acetophenone by various alcohols, which resulted in only 3% disproportionation compared to 97% coupling. The oxidation of hydroxy radicals by peroxide is also ignored even though it is not negligible. To relate these results to the photoreduction reaction the fraction of ketones to cross-coupled product was used in conjunction with the product distribution for the coupling products to calculate the maximum fraction of hydroxy radicals that can be expected to disproportionate (Tables 30 and 31). This value (K• Disprop./K• Formed) is the maximum inefficiency that can be expected in the photoreduction reaction as a result of radical disproportionation.

Table 29. Product Coupling Ratios-Photoreduction versus Peroxide Induced Reaction

Substrate	Solvent	Reaction	[K]/[B]	$\frac{[BK]([B] + [K])}{[B] \times [K]}$
p-Xylene	Benzene	Ketone	1.16	0.76
p-Xylene	Benzene	Peroxide	1.17	0.75
Cumene	Benzene	Ketone	1.10	0.98
Cumene	Benzene	Peroxide	0.99	0.92
p-Xylene	MeCN	Ketone	1.14	0.95
p-Xylene	MeCN	Peroxide	0.87	0.99
Cumene	MeCN	Ketone	1.04	1.07
Cumene	MeCN	Peroxide	0.85	1.03
Toluene	t-BuOH	Ketone	1.36	1.09
Toluene	t-BuOH	Peroxide	0.90	1.07

Table 30. Disproportionation Results from Peroxide Experiments, Acetophenone and Toluene

[Peroxide] (M)	Solvent	$\frac{[AP]}{[AP] + [BK]}$	$\frac{K\cdot Disprop.}{K\cdot Formed}$
0.020	Benzene	0.28	0.14
0.030	Benzene	0.44	0.25
0.051	Benzene	0.56	0.35
0.101	Benzene	0.63	0.42
0.152	Benzene	0.68	0.48
0.050	MeCN	0.35	0.21
0.100	MeCN	0.39	0.24
0.150	MeCN	0.40	0.25

Unfortunately the di-t-butylperoxide oxidizes the hydroxy radicals from 1-phenylethanol very rapidly in benzene. This results in a large amount of acetophenone formed from this reaction in addition to the acetophenone formed from disproportionation. Conversions have to be kept very low to prevent competitive absorption of light by acetophenone. When low peroxide concentrations are used this causes difficulties in analyzing for acetophenone. Because of this, results in benzene are not as useful as the results in acetonitrile. However, it does appear as if disproportionation is responsible for less than 25% of the reaction in acetonitrile and less than 35% of the reaction in benzene. Since the photoreduction of acetophenone by toluene is less than 50% efficient in benzene these results suggest pathways for inefficiency other than disproportionation. The most likely source of this inefficiency is exciplex formation.

For the reaction of peroxide with 1-phenyl-2,2,2-trifluoroethanol and either toluene or p-xylene (Table 31) the amount of ketone (TFA) formed is very small. Apparently this hydroxy radical is not oxidized as rapidly as the one formed from 1-phenylethanol. The maximum amount of inefficiency expected from disproportionation is less than 15%. The inefficiency observed for the photoreduction of TFA by toluene and p-xylene is greater than 70%.[38] Since the photoreduction of TFA by toluene and p-xylene proceed

Table 31. Disproportionation Results from Peroxide Experiments, $TFAH_2$ in Benzene

Substrate	$\frac{[TFA]}{[TFA] + [BK]}$	$\frac{K\cdot Disprop.}{K\cdot Formed}$
Toluene	0.13	0.08
Cumene	0.38	0.25
p-Xylene	0.06	0.03

entirely by exciplex formation, this inefficiency is easily explained by decay of the exciplex to ground state reactants.

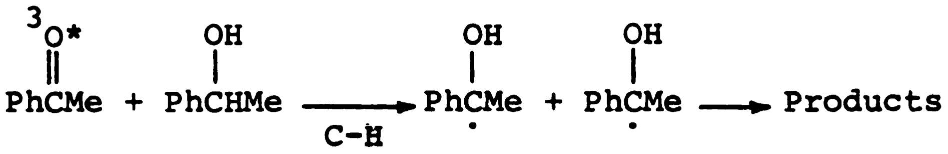
Photoreduction by Alcohols

The minor amounts of 1-phenylethanol and 2,3-diphenyl-2,3,-pentanediol formed when 0.3M acetophenone is photoreduced by 1-phenylpropanol to give almost entirely acetophenone pinacol is inconsistent with in-cage coupling or significant disproportionation. The fraction of in-cage coupling has to be less than the fraction of 2,3-diphenyl-2,3-pentanediol found. Since this product accounts for less than 1% of the products there cannot be significant in-cage coupling. Since the 1-phenylethanol accounts for only 3% of the products and the acetophenone pinacol accounts for roughly 97%, disproportionation must not be responsible for the greater than 40% inefficiency observed in the photoreduction of acetophenone by 1-phenylethanol. The results of the complementary experiment using propiophenone and 1-phenylethanol lead to the same conclusion. The photoreduction of TFA by 1-phenylethanol is more efficient than the photoreduction of acetophenone. Since the TFA should be expected to result in more exciplex formation it is unlikely that exciplex decay is the cause of the inefficiency for acetophenone.

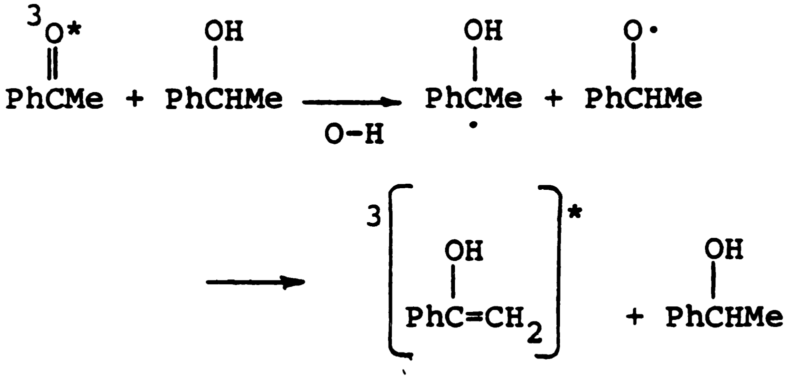
In addition to information on disproportionation and cage reactions, these experiments also provide a method of estimating the rate constant for exchange of a hydrogen from a hydroxy radical to a ground state ketone. It is possible to calculate the steady state concentration of hydroxy radicals if the rate constant for coupling, the light intensity, and the quantum yield for reaction are known. The rate of formation of radicals is the quantum yields times the light intensity. The rate of disappearance is the rate constant for coupling times the radical concentration squared. For the hydroxy radicals from the reaction of acetophenone and 1-phenylethanol the rate constant for coupling in benzene is $2 \times 10^{9} M^{-1} s^{-1}$.[82] The light intensity is approximately 0.008E/l.hr. for these experiments, and the quantum yields for reaction are approximately 0.20. This gives a steady-state concentration of hydroxy radicals of approximately 1.5×10^{-8}M. In the acetophenone and 1-phenylpropanol experiment about 80% of the radicals from the alcohol have exchanged when the acetophenone concentration is 0.03M. This means that at this concentration exchange is four times faster than coupling. Using the rate constants for coupling and the steady state concentration of radicals the rate constant for exchange can be estimated to be approximately $4000 M^{-1} s^{-1}$. The exchange in the opposite direction when propiophenone is photoreduced by 1-phenylethanol is slower, with a rate constant on the order of $10^{3} M^{-1} s^{-1}$. These rate constants are considerably slower than the rate constant of $2.75 \times 10^{8} M^{-1} s^{-1}$ for the exchange of a hydrogen atom from

2-hydroxy-2-propyl radicals to benzophenone in the photoreduction of bezophenone by 2-propanol.[83] This is not surprising since the system studied here involves almost isoenergetic radicals, while the radicals involved in the photoreduction of benzophenone by 2-propanol are not as close in energy. A better example is the degenerate exchange of a hydrogen from a hydroxybenzyl radical to benzaldehyde. The rate constant for this exchange was determined from CIDNP experiments[84] to be $8 \times 10^4 M^{-1}s^{-1}$. The fact that the exchange is slower for the ketones and alcohols used here allows the measurement of the exchange by chemical methods such as product studies. For faster exchange the reactions have to be studied by physical methods such as flash photolysis and CIDNP.[83]

The comparison of 1-phenylethanol and 1-phenylethanol-O-d as the substrate for photoreduction of acetophenone in acetonitrile suggests the hydroxy proton influences the reaction. Even though the 1-phenylethanol-O-d used was only 65% deuterated, the increase in maximum quantum yield was significant. The deuterated alcohol showed a maximum quantum yield of 0.71 compared to 0.49 for the undeuterated alcohol, a 45% increase. The exact cause of the interaction is not clear, but it may involve interaction with the α-protons of acetophenone. Both benzophenone and TFA are photoreduced by alcohols more efficiently than is acetophenone. Neither TFA nor benzophenone have α-protons. It is possible that the triplet enol of acetophenone is formed when acetophenone interacts with alcohols. This reaction may occur by initial abstraction of the hydroxyl proton since deuteration increases the efficiency of the reaction.



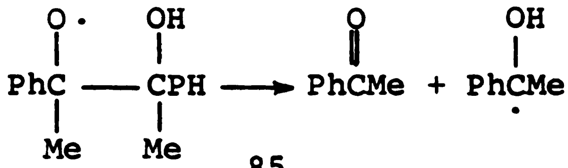
$$\mathrm{Ph}\overset{{}^{3}\mathrm{O}^{*}}{\overset{\|}{\mathrm{C}}}\mathrm{Me} + \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HMe} \xrightarrow[\text{C-H}]{} \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\underset{\bullet}{\mathrm{C}}}}\mathrm{Me} + \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\underset{\bullet}{\mathrm{C}}}}\mathrm{Me} \longrightarrow \text{Products}$$



$$\mathrm{Ph}\overset{{}^{3}\mathrm{O}^{*}}{\overset{\|}{\mathrm{C}}}\mathrm{Me} + \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HMe} \xrightarrow[\text{O-H}]{} \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\underset{\bullet}{\mathrm{C}}}}\mathrm{Me} + \mathrm{Ph}\overset{\mathrm{O}\bullet}{\overset{|}{\mathrm{C}}}\mathrm{HMe}$$

$$\longrightarrow {}^{3}\left[\mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}{=}\mathrm{CH}_2\right]^{*} + \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HMe}$$

The reaction of propiophenone and the pinacol of acetophenone to give propiophenone pinacol and acetophenone supports the possibility of hydrogen abstraction of a hydroxyl proton. In this case the alkoxy radical that is formed can cleave to give ketone and a hydroxy radical. Decomposition of pinacols by ketones was observed by Schonberg and Mustafa,[85] who attributed it to sensitized bond cleavage instead of a hydrogen abstraction mechanism.

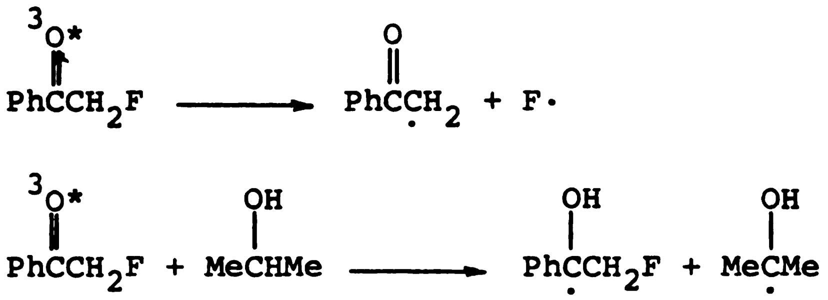


$$\mathrm{Ph}\overset{\mathrm{O}\bullet}{\overset{|}{\underset{\substack{|\\ \mathrm{Me}}}{\mathrm{C}}}} - \overset{\mathrm{OH}}{\overset{|}{\underset{\substack{|\\ \mathrm{Me}}}{\mathrm{C}}}}\mathrm{PH} \longrightarrow \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Me} + \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\underset{\bullet}{\mathrm{C}}}}\mathrm{Me}$$

The reaction has also been studied by CIDNP for the benzophenone-benzpinacol reaction.[83]

The results for the reaction of α-fluoroacetophenone (MFA) and 2-propanol suggests a chain mechanism involving abstraction of a hydrogen, exchange of hydrogens to ground state MFA from 2-hydroxy-2-propyl radicals, loss of fluorine atoms from the hydroxy radicals of MFA, and hydrogen abstraction from 2-propanol by the fluorine atoms. The loss of fluorine atoms and their abstraction of hydrogen from 2-propanol is necessary to account for the high maximum quantum yield (3.3) of acetophenone. If fluorine were lost from the hydroxy radical to give the enol of acetophenone but did not abstract hydrogen from 2-propanol, the maximum quantum yield should be less than two. Loss of fluorine from the excited state, a process which is common for α-chloro and α-bromo ketones, with subsequent hydrogen abstraction from 2-propanol by fluorine, followed by disproportionation of the resulting radicals, could also give acetophenone. This mechanism would give at best a maximum quantum yield of one, however. Loss of fluorine from a radical would not normally be expected and was not observed for the difluoro and trifluoro ketones. The concentration effect observed for selectivity with p-cymene could be due to a change in the amount of abstraction by fluorine. At higher p-cymene concentration there would be higher radical concentration, and therefore

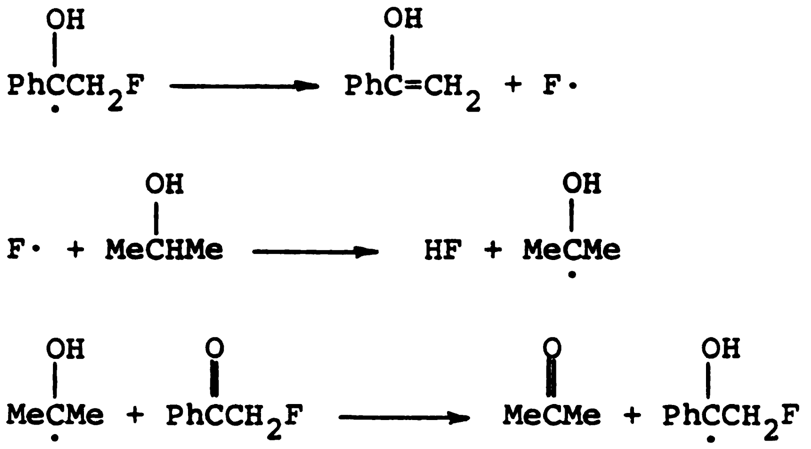
Primary Photoreactions (Initiation)



$$\mathrm{Ph\overset{{}^{3}O^{*}}{\overset{\|}{C}}CH_2F} \longrightarrow \mathrm{Ph\overset{O}{\overset{\|}{\underset{\bullet}{C}}}H_2} + \mathrm{F\cdot}$$

$$\mathrm{Ph\overset{{}^{3}O^{*}}{\overset{\|}{C}}CH_2F} + \mathrm{Me\overset{OH}{\overset{|}{C}}HMe} \longrightarrow \mathrm{Ph\overset{OH}{\overset{|}{\underset{\bullet}{C}}}CH_2F} + \mathrm{Me\overset{OH}{\overset{|}{\underset{\bullet}{C}}}Me}$$

Secondary Radical Reactions (Chain Propagation Steps)

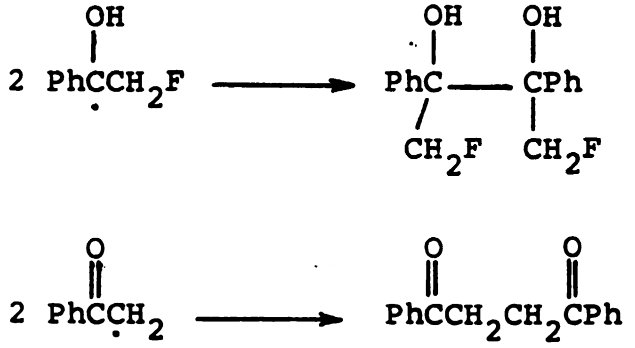


$$\mathrm{Ph\overset{OH}{\overset{|}{\underset{\bullet}{C}}}CH_2F} \longrightarrow \mathrm{Ph\overset{OH}{\overset{|}{C}}{=}CH_2} + \mathrm{F\cdot}$$

$$\mathrm{F\cdot} + \mathrm{Me\overset{OH}{\overset{|}{C}}HMe} \longrightarrow \mathrm{HF} + \mathrm{Me\overset{OH}{\overset{|}{\underset{\bullet}{C}}}Me}$$

$$\mathrm{Me\overset{OH}{\overset{|}{\underset{\bullet}{C}}}Me} + \mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2F} \longrightarrow \mathrm{Me\overset{O}{\overset{\|}{C}}Me} + \mathrm{Ph\overset{OH}{\overset{|}{\underset{\bullet}{C}}}CH_2F}$$

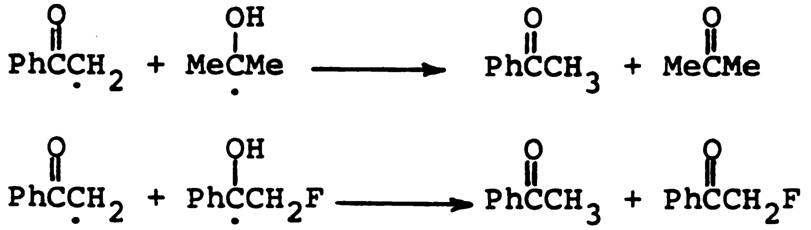
Radical Coupling



$$2\ \mathrm{Ph\overset{OH}{\overset{|}{\underset{\bullet}{C}}}CH_2F} \longrightarrow \mathrm{Ph\overset{OH}{\overset{|}{\underset{\underset{CH_2F}{/}}{C}}}{-}\overset{OH}{\overset{|}{\underset{\underset{CH_2F}{|}}{C}}}Ph}$$

$$2\ \mathrm{Ph\overset{O}{\overset{\|}{\underset{\bullet}{C}}}H_2} \longrightarrow \mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}Ph}$$

Disproportionation



$$\mathrm{Ph\overset{O}{\overset{\|}{\underset{\bullet}{C}}}H_2} + \mathrm{Me\overset{OH}{\overset{|}{\underset{\bullet}{C}}}Me} \longrightarrow \mathrm{Ph\overset{O}{\overset{\|}{C}}CH_3} + \mathrm{Me\overset{O}{\overset{\|}{C}}Me}$$

$$\mathrm{Ph\overset{O}{\overset{\|}{\underset{\bullet}{C}}}H_2} + \mathrm{Ph\overset{OH}{\overset{|}{\underset{\bullet}{C}}}CH_2F} \longrightarrow \mathrm{Ph\overset{O}{\overset{\|}{C}}CH_3} + \mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2F}$$

bimolecular coupling of the hydroxy radicals could more effectively compete with the unimolecular loss of fluorine.

Charge-Transfer Quenchers

Quenching of the reaction of TFA and toluene by DABCO or p-dimethoxybenzene led to rate constants for quenching that are all within a factor of two of diffusion controlled (Table 32). Although there may be changes in product ratios and plots for particular products may curve, it is possible to get rate constants by looking at total formation of a particular radical. This is necessary because the ratio of hydroxy radicals to benzyl radicals increases with increased quenching, causing a significant difference in quenching of bibenzyl versus cross-coupled alcohol. By looking at quenching of total benzyl radicals this effect can be corrected for. The increased product formation observed at low DABCO concentrations in acetonitrile, leading to an intercept of 0.4 with TFA and 1.0M toluene, depends on both solvent and the basicity of the amine. In benzene the product ratio changes, but there is no product enhancement. When p-dimethoxybenzene is the quencher there is no product enhancement in either benzene or acetonitrile. The reason for the product enhancement could be due to DABCO reacting with either the exciplex or the triplet ketone before exciplex formation. Reaction of DABCO with the radicals would not be expected to have such a large effect

Table 32. Rate Constants for Charge Transfer Quenching of TFA and Toluene

Quencher	Solvent	[Toluene] (M)	$\tau(10^{-7}s)$	B·		K·	
				$k_q\tau(M^{-1})$	$k_q(10^9M^{-1}s^{-1})$	$k_q\tau(M^{-1})$	$k_q(10^9M^{-1}s^{-1})$
DABCO	MeCN	1.00	0.80	1670	20.80	1040	12.9
DABCO	Benzene	0.50	1.40	410	2.39	----	----
p-DMB[a]	MeCN	0.50	1.41	1650	11.70	----	----
p-DMB[a]	Benzene	0.50	1.40	600	4.29	----	----

[a] p-Dimethoxybenzene

since the only way to enhance products after radicals are formed is to prevent disproportionation. Evidence from the t-butyl peroxide experiment shows that there is not enough disproportionation to account for the observed increase.

CONCLUSION

The results of the research reported here have led to several important conclusions regarding the photoreduction reaction. The main questions dealt with were the inefficiency of the photoreduction reaction and the selectivity of the reaction as it relates to exciplex formation.

The first of these, reaction inefficiency, had been interpreted as a result of either disproportionation of radicals or decay of exciplex. The former was believed to be responsible for the inefficiency of acetophenone photoreduction and both were believed to be responsible for the inefficiency of TFA photoreduction. It is now apparent that disproportionation cannot account for all of the inefficiency of acetophenone photoreduction. Evidence points to exciplex interactions as being responsible for some of the inefficiency of acetophenone reacting with alkylbenzenes such as toluene and p-xylene. The inefficiency of acetophenone reacting with 1-phenylethanol involves interaction with the hydroxyl proton of the alcohol and may also involve the α-hydrogens of acetophenone.

The primary-tertiary ratio for hydrogen abstraction from p-cymene was shown to be sensitive to substitution on the ketone. As the tendency for charge-transfer interactions increased, so did the fraction of primary radicals formed. The fact that the three hydrocarbon coupling products formed in this reaction are relatively easy to analyze will make this system an extremely valuable probe for further work related to exciplexes.

This work has led to a greater understanding of excited state processes. It has served to clarify some important questions involving the individual steps of the photoreduction, such as the initial interactions of excited ketone with substrate and the reactivity of exciplexes. Moreover, it has led to new ways of looking at the photoreduction reaction and has provided a framework of comprehensive experiments that can be used to separate the many facets of the reaction.

Suggestions for Further Investigation

There are a number of aspects of the photoreduction reaction that need further investigation. Some of the most important involve breaking the reaction into its component steps. It is obvious that the photoreduction reaction can no longer be treated as a one step reaction. The reaction can be viewed as consisting of two separate sets of reactions, one set leading to the formation of radicals and the other consisting of the reactions of the radicals. Each of these two parts is comprised of a number of competing reactions. The formation of radicals is a function of rate constants for direct hydrogen abstraction, exciplex formation, reaction from exciplex, and decay from exciplex. Radical reactions involve self-coupling and cross-coupling rate constants, as well as the partitioning between coupling and disproportionation. Radical-solvent reactions may also be important in some cases. The following are some suggestions for work that could lead to a better understanding of the photoreduction reaction.

The radical reactions can be further investigated using peroxide initiation to generate radicals of interest in different solvents and with different additives present. To correct for both induced decomposition of peroxide by hydroxy radicals and secondary reaction of ketone formed during the reaction it will be necessary to perform a number of extrapolations. To correct for secondary reactions of ketone formed during the reaction, the product formation will have to be studied as a function of conversion. Extrapolation to zero conversion will give the product distribution resulting from primary reactions. Obtaining these results for a number of peroxide concentrations would allow extrapolation of the product ratio to zero peroxide concentration. This would give the fraction of ketone formed, and therefore the amount of disproportionation, in the absence of induced decomposition.

Extrapolation can also be used with the photoreduction reaction to determine which step of the reaction is affected by additives. If an additive or solvent interacts with the excited ketone before the ketone reacts with substrate, an extrapolation to infinite substrate would give the same result with and without the additive. This type of extrapolation was used to show that the maximum quantum yield for TFA and toluene in benzene is the same whether trifluoroacetic acid is present or not, even though there are significant differences for low toluene concentrations. A similar study could be done to see if the primary-tertiary ratio for abstraction from p-cymene changes as a function of p-cymene concentration. If the ratio extrapolates to the same value for infinite p-cymene in benzene with and without acid present, it would suggest that the observed effect is due to reaction of acid with some species before exciplex formation. If the additive reacts with the exciplex or radicals, there should be little or no variation with substrate concentration. Studies of this type could be done with solvents and charge-transfer quenchers, as well as with the trifluoroacetic acid studies mentioned above.

The possibility of finding systems that react only by direct hydrogen abstraction should be investigated. Such systems should have easily abstractable hydrogens to maximize exciplex formation. Compounds such as 2-propanol and 1-phenylethanol could be useful for such studies. Ring substituents on 1-phenylethanol could lead to information concerning direct hydrogen abstraction versus exciplex formation as well as abstraction of hydrogen bonded to carbon versus oxygen. For the reaction of TFA with substituted 1-phenylethanols the rate constant for reaction could be compared to ionization potentials or values to see how the reaction compares to substituted toluenes. For the reaction of acetophenone with 1-phenylethanols the maximum efficiency could be studied as a function of substituents. If substituents have a negligible effect on abstraction of the hydroxyl proton the efficiency should be related to the reactivity of the α-hydrogen, which should be affected by substituents. If necessary, yields of disproportionation products and the deuterium isotope effect on product formation could also be studied for these reactions.

Using donors other than p-cymene that can react to give different products might offer new insights into the reaction, or at least expand the range of ketones that can be investigated. Changing one or both of the methyl groups on the isopropyl group of p-cymene to other groups, such as methoxy or trifluoromethyl, could be tried. Such methods could be used to change the carbon-hydrogen strength, the acidity of the proton in the radical cation, or adjust the ionization potential of the donor. Setting up a competition between an alkyl group and an alcohol might show if proton loss is affected by hydroxy groups.

Other miscellaneous work could be done to investigate the different effects of deuterium on rate constants and efficiencies. This would be extremely useful for systems which react by both direct hydrogen abstraction and exciplex formation. The reaction of ketones with hydroxyl protons could also be studied by using pinacols as substrates and calculating rate constants and maximum quantum yields.

EXPERIMENTAL

Preparation and Purification of Chemicals

Solvents

Acetonitrile: (Fisher) was distilled rapidly (approximately 500ml per hour) from potassium permanganate. Enough sulfuric acid was added to the distillate to make it slightly acidic.[86] The acetonitrile was then decanted from the ammonium salts and distilled through a column packed with glass helices (BP = 81.0°C), only the middle 75% being retained.

Benzene: (Mallinckrodt) was purified by stirring over concentrated sulfuric acid. The sulfuric acid was changed every twenty-four hours until it remained clear for two consecutive washings. The benzene was then washed several times with water, several times with saturated sodium bicarbonate solution, and two final times with water. The benzene was pre-dried with sodium sulfate and distilled from phosphorus pentoxide through a column packed with glass helices. The first 10% and the last 20% were discarded. BP = 80.0°C.

t-Butanol: (Baker) was purified by R.A. Bartoszek.

Pyridine: (Mallinckrodt) was purified by distillation from barium oxide by Dr. M.J. Lindstrom.

Trifluoroacetic Acid: (Baker) was used as received.

Internal Standards

The internal standards were purified by various members of the Dr. P.J. Wagner research group as follows:

Undecane (C11): (Aldrich) was purified in the same manner as benzene and distilled under reduced pressure.

Tetradecane (C14): (Columbia Organics) was purified in the same manner as undecane.

Pentadecane (C15): (Chemical Samples) was purified in the same manner as undecane.

Hexadecane (C16): (Aldrich) was purified in the same manner as undecane.

Heptadecane (C17): (Chemical Samples) was purified in the same manner as undecane.

Octadecane (C18): (Aldrich) was washed with concentrated sulfuric acid and recrystallized from ethanol.

Nonadecane (C19): (Chemical Samples) was purified by recrystallization from ethanol.

Heneicosane (C21): (Chemical Samples) was purified by recrystallization from ethanol.

Docosane (C22): (Aldrich) was purified in the same manner as heneicosane.

Quenchers

Napthalene: (Matheson Coleman and Bell) was purified by several recrystallizations from ethanol, m.p. 79.5-80.5°C.

DABCO: (Aldrich) was purified by Dr. M.J. Thomas by recrystallization from ethanol followed by sublimation.

p-Dimethoxybenzene: (Aldrich) was purified by recrystallization from ethanol, m.p. 56.5-58.0°C.

Hydrogen Donors

Toluene: (Mallinckrodt) was purified in the same manner as benzene with the exception that the toluene was kept in an ice bath while being washed with sulfuric acid to prevent sulfonation of the ring. BP = 110°C.

p-Cymene: (Aldrich) was purified in the same manner as toluene. BP = 176°C.

p-Xylene: (Mallinckrodt) was purified by Dr. R.A. Leavitt in the same manner as toluene.

Cumene: (Aldrich) was purified by Dr. R.A. Leavitt in the same manner as toluene.

1-Phenylethanol: (Aldrich) was purified by stirring over sodium borohydride to reduce acetophenone, then washed with water and distilled under reduced pressure. G.C. purity showed less than 0.01% acetophenone present. BP = 95°C (15mm).

1-Phenylethanol-O-d: was synthesized by stirring 1-phenylethanol over several portions of D_2O. After drying and distilling under reduced pressure a comparison of O-H stretch ($3400cm^{-1}$) and O-D stretch ($2500cm^{-1}$) showed 65% deuteration.

1-Phenylpropanol: was synthesized from propiophenone by sodium borohydride reduction in absolute ethanol. After being washed with water and dried over sodium sulfate, the alcohol was distilled under reduced pressure. BP = 118°C (16mm). G.C. purity check showed less than 0.01% ketone and approximately 0.01% 1-phenylethanol. IR 3350, 3030, 2970 1490cm^{-1}.

1-Phenyl-2,2,2-Trifluoroethanol: was synthesized from α,α,α-trifluoroacetophenone by sodium borohydride reduction in absolute ethanol. It was purified in the same manner as 1-phenylpropanol. BP = 117° (25mm). G.C. purity showed less than 0.01% of either ketone or the hydrated ketone. IR 3400, 3040, 1455, 800cm^{-1}; ^{1}H-NMR δ3.1 (s, 1H), 4.8 (quartet, 1H, J = 7Hz), 7.3 (m, 5H); ^{19}F-NMR δ78.4 (d, J = 7Hz).

Reactants

Valerophenone: was prepared by E.J. Seibert by Freidel-Crafts acylation of benzene by valeryl chloride. After work-up with cracked ice and concentrated hydrochloric acid, the crude product was dried and distilled under reduced pressure. BP = 105-110°C (2mm).

Acetophenone: (Mallinckrodt) was passed through alumina and then purified by spinning band distillation under reduced pressure. BP = 105°C (17mm).

p-Fluoroacetophenone: (Aldrich) was purified by Dr. M.J. Thomas by distillation under reduced pressure.

m-Fluoroacetophenone: (Aldrich) was purified by Dr. M.J. Thomas by distillation under reduced pressure.

m-Trifluoromethylacetophenone: (Pierce) was purified by Dr. M.J. Thomas by distillation under reduced pressure.

p-Methoxyacetophenone: (Aldrich) was purified by Dr. H.N. Schott by recrystallization from ethanol.

p-Methylacetophenone: (Matheson Coleman and Bell) was purified by E.G. Harris by distillation under reduced pressure.

Benzophenone: (Eastman) was purified by Dr. P.J. Wagner by recrystallization from ethanol.

4,4'-Dimethoxybenzophenone: (Aldrich) was purified by Dr. P.J. Wagner by recrystallization from ethanol.

4,4'-Dichlorobenzophenone: (Aldrich) was purified by Dr. P.J. Wagner by recrystallication from ethanol.

α,α,α-Trifluoroacetophenone: (Aldrich) was purified by spinning band distillation under reduced pressure. BP = 70° (25mm).

m-Trifluoromethyl-TFA: was prepared and purified by H. Lam.[73]

p-Methyl-TFA: was prepared and purified by H. Lam.[73]

p-Methoxy-TFA: was prepared and purified by H. Lam.[73]

m-Methyl-TFA: was prepared and purified by H. Lam.[73]

p-Chloro-TFA: was prepared and purified by H. Lam.[73]

α,α-Difluoroacetophenone: was synthesized by heating and vigorously stirring a mixture of 24g (.127 mole) of α,α-dichloroacetophenone and 48g (.83 mole) of dry potassium fluoride (flame dried, ground to a fine powder, and stored in an oven at 140°C) in 200ml of dry glycerin. The flask containing the glycerine was heated to 60°C in an oil bath before addition of the reactants. After the reactants were added a vacuum was applied and the mixture was steadily heated, rising to 150°C after 1.5 hours. During this time the product was distilled out of the mixture through a short-path distilling head. The yield was 28%. The crude product was dissolved in ether and washed with water to remove glycerin. The ether layer was then dried over sodium sulfate and evaporated. The ketone was then purified by spinning band distillation under reduced pressure. BP = 60°C (4mm); H-NMR ($CDCl_3$) $\delta 6.2$ (t, 1H, J = 54Hz), 7.5 (m, 3H), 7.9 (m, 2H); IR (neat) 3060, 1705, 1601, 1150cm^{-1}; ^{19}F-NMR $\delta 122.3$ (d, J = 54Hz).

α-Fluoroacetophenone: was synthesized by heating and vigorously stirring a mixture of 25g (.126 mole) phenacyl bromide and 25g (.43 mole) of dry potassium fluoride (flame dried, ground to a fine powder, and stored in an oven at 140°C) in 170ml of dry glycerin. The flask containing the glycerin was heated to 60°C in an oil bath before addition of the reactants. After the reactants were added a vacuum was applied and the mixture was steadily heated, rising to 130° after 30 minutes. During this time the product was distilled out of the mixture through a short-path distilling head. The yield was 52%. The crude product was dissolved in ether and washed with water to remove glycerin. The ether layer was then dried over sodium sulfate and evaporated. The ketone was then purified by spinning band distillation under reduced pressure. BP = 103°C (5mm): ^{1}H-NMR δ5.5 (d, 2H, J = 48Hz), 7.5 (m, 3H), 7.8 (m, 2H); IR 3070, 2940, 1715, 1450cm^{-1}; ^{19}F-NMR δ231 (t, J = 48Hz).

Di-t-butyl Peroxide: (Aldrich) was used as received.

t-Butyl Hypochlorite: was synthesized[87] by adding a mixture of 37ml of t-butanol and 24.5ml of glacial acetic acid to 500ml of stirred Home Gem Bleach (5% NaOCl) which had been cooled to 10°C. When the temperature ceased rising the ice bath was removed and the mixture allowed to stand for one minute before removing the lower aqueous (total reaction time was four minutes). The yellow oil was washed with 10% sodium bicarbonate, then water, then dried over calcium chloride and filtered to yield pure t-butyl hypochlorite.

Identification of Photoproducts

Where authentic samples were available the expected photoproducts were identified by comparison of retention times on at least two different g.c. columns. Other products were identified by isolation and identification.

The products from a preparative irradiation of TFA with p-cymene in benzene were separated by column chromatography. After removal of the solvent from the irradiation mixture the oily residue was absorbed on alumina and placed on top of an alumina column. Elution with hexane resulted in four fractions. The first contained a mixture of the three hydrocarbon products (PP, PT, and TT). The second and third fraction contained the tertiary (KT) and primary (KP) cross-coupled products, respectively. The fourth fraction, which eluted only after chloroform was added to the solvent, contained one of the two diastereomeric TFA pinacols. The mixture of hydrocarbon products was rich in PP and contained very little TT. Sublimation of this mixture provided pure PP, which sublimed more readily than PT. The di-tertiary product (TT) was also sublimed more readily than PT, and was separated from a mixture rich in TT from a preparative irradiation of acetophenone and p-cymene. The unsymmetrical hydrocarbon (PT) was then obtained from the combined residues of the two sublimations.

Bibenzyl: (Aldrich) was used as received.

Bixylyl: (Aldrich) was used as received.

Dicumyl: (Columbia Organics) was used as received.

Acetophenone Pinacol: was synthesized and purified by Dr. M.J. Thomas.

α,α,α-Trifluoroacetophenone Pinacol: m.p. 154-156°C; ^{1}H-NMR ($CDCl_3$) δ3.5 (s, 2H), 7.1 (m, 10H); m/e 350 (M^+); ^{19}F-NMR ($CDCl_3$) δ69.6 (s).

1,2-Diphenyl-3-propanol: was synthesized by addition of benzylmagnesium chloride to acetophenone followed by the usual Grignard work-up. m.p. 49-50°C; ^{1}H-NMR ($CDCl_3$) δ1.5 (s, 3H), 2.0 (s, 1H), 3.0 (s, 2H), 7.0 (m, 5H), 7.1 (m, 5H); m/e 195 (M^+-OH).

1,1,1-Trifluoro-2-phenyl-3-methyl-3-(4-methylphenyl)-2-butanol (KT): ^{1}H-NMR ($CDCl_3$) δ1.3 (s, 3H), 1.6 (s, 3H), 2.3 (s, 3H), 2.6 (s, 1H), 7.0 (2, 4H), 7.3 (m, 5H); IR (neat) 3560, 3990, 1145cm^{-1}; m/e 175 (M^+-175); ^{19}F-NMR δ67.2 (s).

1,1,1-Trifluoro-2-phenyl-3-(4-isopropylphenyl)-2-propanol (KP): ^{1}H-NMR ($CDCl_3$) δ1.1 (d, 6H), 2.4 (s, 1H), 2.7 (septet, 1H), 3.3 (s, 2H), 6.8 (d, 4H), 7.1 (m, 5H); IR (neat) 3540, 2945, 1150, 820cm^{-1}; m/e 308 (M^+); ^{19}F-NMR δ78.2 (s).

1,2-Bis-(4-isopropylphenyl)-ethane (PP): ^{1}H-NMR ($CDCl_3$) δ1.1 (d, 12H), 2.8 (s, 4H), 2.9 (septet, 2H), 7.0 (s, 8H); m/e 266 (M^+).

<u>1-(4-isopropylphenyl)-2-(4-methylphenyl)-2-methylpropane (PT)</u>: ^{1}H-NMR ($CDCl_3$) δ1.1 (d, 6H), 1.3 (s, 6H), 2.3 (s, 3H), 2.8 (s, 2H), 2.9 (septet, 1H), 6.9 (s, 4H), 7.0 (s, 4H); m/e 266 (M^+).

<u>2,3-Bis-(4-methylphenyl)-2,3-dimethylbutane (TT)</u>: m.p. 156-158°C: ^{1}H-NMR ($CDCl_3$) δ1.2 (s, 12H), 2.3 (s, 6H), 6.9 (s, 8H); m/e 266 (M^+).

Techniques

Glassware

All solutions were prepared with class A volumetric flasks and pipets. The volumetric ware was cleaned by soaking in hot distilled water containing 5% concentrated ammonium hydroxide solution for a minimum of twelve hours. This was followed by rinsing and soaking in hot water, changing the water several times over a period of at least three days. Pyrex culture tubes used for irradiation were cleaned in the same manner. Syringes used for transfering solutions from volumetric flasks to culture tubes were cleaned in a manner similar to the volumetric ware except that a solution of Alconox Laboratory Glassware Cleaner was used instead of ammonium hydroxide solution. All glassware was dried in an oven at 140°C used only for analytical glassware to avoid contamination.

The Pyrex culture tubes (13 × 100mm) were drawn out by heating near the top so that a narrow constriction (approximately 3 × 50mm was formed 30mm from the top of the tube.

Preparation of Samples

Solutions were made by weighing samples directly into volumetric flasks and diluting to the mark or by pipetting from a stock solution made in the above manner into volumetric flasks and then diluting. The latter method was used when a number of solutions were needed with the same component, such as an internal standard. A 3.4ml aliquot of these solutions were then added to the constricted culture tubes by means of a 5cc syringe.

Degassing Procedure

The tubes prepared above were then attached to a vacuum line capable of 10^{-4} Torr by means of size 00 one-holed rubber stoppers fitted to a manifold containing twelve stopcocks. The solutions were frozen in liquid nitrogen and the stopcocks opened. After pumping on the samples for twenty minutes the stopcocks were closed and the solutions allowed to warm to room temperature until completely thawed. The freeze-pump-thaw cycle was repeated three more times, after which the tubes were sealed using a torch while the samples were frozen.

Irradiation Procedure

All quantum yield and quenching studies were performed by parallel irradiation of samples and actinometer on a merry-go-round apparatus. The light source was a Hanovia medium-pressure mercury lamp with either the 313nm or 366nm region isolated by means of a chemical or glass filter respectively. The chemical filter was a 0.0002M potassium chromate solution buffered by 1% potassium carbonate. The glass filter was a Corning No. 7-83 filter. The entire apparatus, merry-go-round and light source with filter, was immersed in a constant temperature bath at 25°C.

Preparative irradiations were performed in a photochemical immersion well. The light was filtered by a pyrex sleeve surrounding the lamp. The well had a capacity of 150ml of solution and was fitted with a condenser to prevent loss of solvent. A stream of dry nitrogen was passed through the solution through a frit at the bottom of the well.

Analysis

All analyses were done by gas chromatography on either a Varian Aerograph model 1200 or a Varian Aerograph model 1400 gas chromatograph, both employing flame ionization detectors. Peak areas were measured using an Infotronics model CRS 309 digital integrator. Samples of 0.3 microliters were injected directly onto the column using a 1.0 microliter Hamilton syringe. All analytical columns were 1/8 inch diameter aluminum tubing. The carrier gas (nitrogen) was kept at a constant flow of 30ml/minute for all columns. The column used for each analysis is listed in each table according to the following designation:

Column A: 8ft, 4.6% QF-1 on chromosorb G

Column B: 5ft, 5% SE-30 on chromosorb W

Column C: 6ft, 5% Apiezon L on chromosorb G

The temperature for each analysis is also listed in each table.

Calculations of Quantum Yields

The amount of light absorbed (I_a in einstein/liter) was determined by valerophenone actinometer. A benzene solution containing 0.10M valerophenone and a standard (hexadecane) was irradiated in parallel with the samples to be analyzed. The acetophenone concentration was calculated using the following equation:

$$\text{acetophenone} = \text{SF} \times \text{standard} \times \frac{\text{peak area of acetophenone}}{\text{peak area of standard}}$$

where SF is the standardization factor determined from the relative g.c. peak areas of the two compounds with known concentrations. For acetophenone and hexadecane the standardization factor was calculated to be 2.43. The standardization factors for other compounds and standards are given in the appropriate tables in the Appendix.

From the concentration of acetophenone and the quantum yield of acetophenone formation ($\Phi_{AP} = 0.33$ in benzene for 0.1M valerophenone)[88] the amount of light absorbed can be calculated.

$$I_a = \text{light absorbed} = \frac{\text{acetophenone}}{(0.33)}$$

The concentration of the photoproducts of the reaction in equation were determined using appropriate standards and their standardization factors. Dividing these concentrations by the light absorbed results in the quantum yield for product.

$$\Phi = \text{quantum yield} = \frac{\text{Product}}{I_a}$$

<u>Sample Calculation</u>

Actinometer: 0.10M valerophenone
0.0108M hexadecane (C16)
SF = 2.43

$$\frac{\text{area of acetophenone}}{\text{area of hexadecane}} = 0.469$$

$$[\text{acetophenone}] = \text{SF} \times [\text{C16}] \times \frac{\text{area of AP}}{\text{area of C16}}$$

$$[\text{acetophenone}] = (2.43) \times (0.0108) \times (0.469) = 0.0123\text{M}$$

$$I_a = \text{light absorbed} = \frac{0.0123}{0.33} = 0.0373 \text{ E/l}$$

Sample: 0.10M TFA
1.0M toluene
0.0226M tetradecane (C14)
SF = 1.03 for bibenzyl (BB) and tetradecane

$$\frac{\text{area of bibenzyl}}{\text{area of tetradecane}} = 0.205$$

$$[\text{bibenzyl}] = \text{SF} \times [\text{C14}] \times \frac{\text{area of BB}}{\text{area of C14}}$$

$$[\text{BB}] = (1.03) \times (0.00226) \times (0.205) = 0.000477\text{M}$$

$$\Phi_{BB} = \frac{[\text{BB}]}{I_a} = \frac{0.000477}{0.0373} = 0.0128$$

LIST OF REFERENCES

LIST OF REFERENCES

1. G. Ciamician and P. Silber, Chem. Ber., 33, 2911 (1900); G. Ciamician and P. Silber, ibid., 34, 1530 (1901).

2. E. Paterno and G. Chieffi, Gazz. Chem. Ital., 39, II, 415 (1909); E. Paterno and G. Chieffi, ibid., 40, II, 321 (1910).

3. J.C. Scaiano, J. Photochem., 2, 81 (1973/1974).

4. A. Schonberg and A. Mustafa, Chem. Rev., 40, 181 (1947).

5. R.S. Davidson and P.F. Lambeth, J.C.S. Chem. Comm., 1265 (1967).

6. S.G. Cohen and H.M. Chao, J. Am. Chem. Soc., 90, 165 (1968).

7. A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, ibid., 91, 1859 (1969); A. Padwa and W. Eisenhardt, ibid., 93, 1400 (1971).

8. S.G. Cohen and N.M. Stein, ibid., 93, 6542 (1971).

9. S.G. Cohen and J.B. Guttenplan, ibid., 94, 4040 (1972).

10. S.G. Cohen, A. Parola and G.H. Parsons, Chem. Rev., 73, 141 (1973).

11. S. Inbar, H. Linshitz, and S.G. Cohen, J. Am. Chem. Soc., 102, 1419 (1980).

12. P.J. Wagner, ibid., 89, 2503 (1967).

13. G. Ciamician and P. Wilber, Chem. Ber., 44, 1554 (1911).

14. S.G. Cohen and S. Aktipis, J. Am. Chem. Soc., 88, 3587 (1966).

15. J.B. Guttenplan and S.G. Cohen, *J.C.S. Chem. Comm.*, 247 (1969).

16. J.B. Guttenplan and S.G. Cohen, *J. Org. Chem.*, *38*, 2001 (1973).

17. S.G. Cohen, A.W. Rose, P.G. Stone and A. Ehret, *J. Am. Chem. Soc.*, *101*, 1827 (1979).

18. H.D. Becker, *J. Org. Chem.*, *32*, 2116 (1967); H.D. Becker, *ibid.*, *32*, 2124 (1967); H.D. Becker, *ibid.*, *32*, 2140 (1967).

19. M. Bodenstein, *Z. Physik. Chem.*, *1313*, 151 (1931).

20. C. Weizmann, E. Bergmann, and Y. Hirshberg, *J. Am. Chem. Soc.*, *60*, 1530 (1968).

21. J.N. Pitts, Jr., R.L. Letsinger, R.P. Taylor, J.M. Patterson, G. Recktenwald, and R.B. Morton, *ibid.*, *81*, 1068 (1959).

22. S.A. Weiner, *ibid.*, *93*, 425 (1971).

23. G.L. Closs and D.R. Paulson, *ibid.*, *92*, 7229 (1970).

24. D.A. Nelson and E. Hayon, *J. Phys. Chem.*, *76*, 3200 (1972).

25. H.L.J. Backstrom and K. Sandros, *J. Chem. Phys.*, *23*, 2191 (1955); H.L.J. Backstrom and K. Sandros, *Acta. Chem. Scand.*, *14*, 48 (1960).

26. J.A. Bell and H. Linshitz, *J. Am. Chem. Soc.*, *85*, 528 (1963).

27. J.N. Pitts, H.W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, *66*, 2456 (1962).

28. G.S. Hammond and W.M. Moore, *J. Am. Chem. Soc.*, *81*, 6334 (1959).

29. G. Porter and P. Suppan, *Trans. Far. Soc.*, *61* 1664 (1965); G. Porter and P. Suppan, *ibid.*, *62*, 3375 (1966).

30. N.C. Yang, D.S. McClure, S.L. Murov, J.J. Houser, and R. Dusenberg, *J. Am. Chem. Soc.*, *89*, 5466 (1967); N.C. Yang and R. Dusenberg, *ibid.*, *90*, 5899 (1968).

31. D. Bryce-Smith, *Pure Appl. Chem.*, *16*, 47 (1968).

32. P.J. Wagner, Accnts. Chem. Res., 4, 168 (1971).

33. A. Padwa, Tet. Lett., 3465 (1964).

34. C. Walling and M.J. Gibian, J. Am. Chem. Soc., 87, 3361 (1965).

35. C. Walling and M.J. Mintz, ibid., 89, 1515 (1967).

36. H. Paul, R.D. Small, Jr., and J.C. Scaiano, ibid., 100, 4520 (1978).

37. P.J. Wagner and R.A. Leavitt, ibid., 92, 5806 (1970).

38. P.J. Wagner and R.A. Leavitt, ibid., 95, 3669 (1973).

39. W.B. Mueller, unpublished results.

40. R.A. Leavitt, Ph.D. Thesis, Michigan State University, 1974.

41. D. Rehm and A. Weller, Ber. Bunsenges. Phys. Chem., 73, 834 (1969).

42. P.J. Wagner and A.E. Kemppainen, J. Am. Chem. Soc., 91, 3085 (1969).

43. A.A. Borman, C.T. Parekh, M.A.J. Rodgers and P.G. Smith, J. Photochem., 9, 11 (1978).

44. D. Rehm and A. Weller, Isr. J. Chem., 8, 259 (1970).

45. S. Arimitsu, H. Musuhara, N. Mataga, and H. Tsubomura, J. Phys. Chem., 79, 1255 (1975).

46. R.O. Loutfy, S.K. Dogra and R.W. Yip, Can. J. Chem., 57, 342 (1979).

47. I.H. Kochevar and P.J. Wagner, J. Am. Chem. Soc., 92, 5742 (1970).

48. M.W. Wolf, R.E. Brown, and L.A. Singer, ibid., 99, 526 (1977).

49. V. Balzani, F. Bolletta, F. Scandola, and R. Ballardini, Pure Appl. Chem., 51, 299 (1979); F. Scandola and V. Balzani, J. Am. Chem. Soc., 101, 6140 (1979).

50. G.B. Schuster, ibid., 101, 5851 (1979).

51. J.A. Barltrop and J.D. Coyle, "Excited States in Organic Chemistry", John Wiley and Sons, New York, 1975, p. 106-108.

52. G. Rumunni and L. Salem, Z. Phys. Chem. (Frankfurt Am. Main)., 101, 123 (1976).

53. M.J. Thomas, P.J. Wagner, M.L.M. Schilling and H.D. Roth, J. Am. Chem. Soc., 99, 3842 (1977).

54. M.J. Thomas and P.J. Wagner, ibid., 99, 3845 (1977).

55. M.L.M. Schilling, R.S. Hutton and H.D. Roth, ibid., 99, 7792 (1977).

56. V.A. Kuzmin, A.P. Darmanyan, and P.P. Levin, Chem. Phys. Lett., 63, 509 (1979).

57. M.J. Thomas, private communication.

58. K. Sandros and H.J.L. Backstrom, Acta. Chem. Scand., 16, 956 (1962).

59. W.G. Herkstroeter and G.L. Hammond, J. Am. Chem. Soc., 88, 4769 (1966).

60. P.J. Wagner and I. Kochevar, ibid., 90, 2232 (1968).

61. I.H. Leavor and G.C. Ramsay, Tet., 25, 5569 (1969).

62. A. Ledwith, P.J. Russel and L.H. Sutcliffe, J.C.S. Chem. Comm., 964 (1971).

63. S.G. Cohen and B. Green, ibid., 91, 6824 (1969).

64. M.J. Gibian and R.C. Corley, Chem. Rev., 73, 441 (1973).

65. H.H. Schuh and H. Fischer, Helv. Chim. Acta., 61, 2130 (1978).

66. P.J. Wagner, P.A. Kelso and R.G. Zepp, J. Am. Chem. Soc., 94, 7480 (1972).

67. D. Bellus and K. Schaffner, Helv. Chim. Acta., 52, 1010 (1969).

68. P.J. Wagner and G. Capen, Mol. Photochem., 1, 173 (1969).

69. P.J. Wagner and H.N. Schott, J. Am. Chem. Soc., 91, 5383 (1979).

70. P.J. Wagner, ibid., 89, 5898 (1967).

71. E.S. Huyser and C.J. Bredeweg, ibid., 86, 2401 (1964); E.S. Huyser and A.A. Kahl, J. Org. Chem., 35, 3742 (1970).

72. M. Ochi, K. Matsushita, and K. Nagao, Chem. Abst., 85, 192300x (1976).

73. H. Lam, M.S. Thesis, Michigan State University, 1975.

74. L. Geiring, M. Berder, and C. Steel, J. Am. Chem. Soc., 96, 953 (1974).

75. A. Onopchenko, J.G.D. Schulz, and R. Seekircher, J. Org. Chem., 37, 1414 (1972); A. Onopchenko and J.G.D. Schulz, ibid., 37, 2564 (1972).

76. T. Shone and Y. Matsumura, ibid., 35, 4157 (1970).

77. J.E. Barry, M. Finkelstein, E.A. Mazeda and S.D. Ross, ibid., 39, 2695 (1974).

78. K. Fukui, K. Senda, Y. Shigemitsu, and Y. Odaira, ibid., 37, 3176 (1972).

79. F.D. Lewis and T.I. Ho, J. Am. Chem. Soc., 102, 1751 (1980).

80. P.J. Wagner and D.A. Ersfeld, ibid., 98, 4515 (1976).

81. D. Bryce-Smith, G.B. Cox and A. Gilbert, J.C.S. Chem. Comm., 914 (1971).

82. J.C. Scaiano, private communication.

83. J.A. den Hollander, A.J. Hantel and P.H. Schippes, Tet., 33, 211 (1977).

84. G.L. Closs and D.R. Paulson, J. Am. Chem. Soc., 92, 7229 (1970).

85. A. Schonberg and A. Mustafa, J. Chem. Soc., 67 (1944).

86. J.F. O'Connell, J.T. Ayres, and C.K. Mann, Anal. Chem., 37, 1161 (1965).

87. M.J. Mintz and C. Walling, Organic Synthesis, Collected Vol. V, H.E. Baumgarten, Ed., John Wiley and Sons, Inc., New York, New York (1973) p. 183.

88. P.J. Wagner and A.E. Kemppainen, J. Am. Chem. Soc., 90, 5896 (1968).

APPENDIX

APPENDIX

This section contains the raw experimental data from which the results were obtained. The concentrations of reactants and standards are listed, as are the product to standard peak ratios as obtained from gas chromatographic analysis. The g.c. conditions are given in each table with the columns used designated as follows:

Column A: 8 ft. 4.6% QF-1 on chromosorb G
Column B: 5 ft. 5.0% SE-30 on chromosorb W
Column C: 6 ft. 5.0% Apiezon L on chromosorb G

All valerophenone actinometry was measured on column A at 130° C.

The product yields, given as concentrations, are calculated from the peak area ratios and the appropriate response factors, which are also listed. A sample calculation is included in the experimental section. From the product yields and the amount of light absorbed (I_a) by the samples, as determined by valerophenone actinometry, the quantum yields were determined. The quantum yields, the amount of light absorbed, and the time of irradiation are listed here. Sample calculations for quantum yields and actinometry are given in the experimental section.

Table 33. Quantum Yield Data for Acetophenone and p-Cymene (BH) in Benzene

[BH] (M)	PT/C17[a]	TT/C17[a]	TT/C17[b]	PP/C17[b]	$I_a (El^{-1})$	[PT] (10^{-3}M)	[TT] (10^{-3}M)	[PP] (10^{-3}M)
0.75	0.283[c]	0.440	0.458	0.061	0.154	1.39	2.21	0.300
1.00	0.370[d]	0.544	0.541	0.078	0.175	1.89	2.77	0.400
1.25	0.363[c]	0.544	0.566	0.071	0.154	1.78	2.73	0.347
1.50	0.435[d]	0.635	0.640	0.091	0.175	2.22	3.25	0.460
1.75	0.405[c]	0.615	0.652	0.082	0.154	1.99	3.12	0.401
2.00	0.493[d]	0.712	0.711	0.103	0.175	2.51	3.63	0.530
2.25	0.459[c]	0.691	0.717	0.091	0.154	2.26	3.46	0.446
2.50	0.545[d]	0.801	0.789	0.113	0.175	2.78	4.05	0.580

[Acetophenone] = 0.10M, 313nm, SF = 0.81

[a] Column A @150°

[b] Column B @185°

[c] [C17] = 0.0061M, 11hr.

[d] [C17] = 0.0063M, 15 hr.

Table 33. Quantum Yield Data for Acetophenone and p-Cymene (BH) in Benzene

[BH] (M)	PT/C17[a]	TT/C17[a]	TT/C17[b]	PP/C17[b]	$I_a(El^{-1})$	[PT] (10^{-3}M)	[TT] (10^{-3}M)	[PP] (10^{-3}M)
0.75	0.283[c]	0.440	0.458	0.061	0.154	1.39	2.21	0.300
1.00	0.370[d]	0.544	0.541	0.078	0.175	1.89	2.77	0.400
1.25	0.363[c]	0.544	0.566	0.071	0.154	1.78	2.73	0.347
1.50	0.435[d]	0.635	0.640	0.091	0.175	2.22	3.25	0.460
1.75	0.405[c]	0.615	0.652	0.082	0.154	1.99	3.12	0.401
2.00	0.493[d]	0.712	0.711	0.103	0.175	2.51	3.63	0.530
2.25	0.459[c]	0.691	0.717	0.091	0.154	2.26	3.46	0.446
2.50	0.545[d]	0.801	0.789	0.113	0.175	2.78	4.05	0.580

[Acetophenone] = 0.10M, 313nm, SF = 0.81

[a] Column A @150°

[b] Column B @185°

[c] [C17] = 0.0061M, 11hr.

[d] [C17] = 0.0063M, 15 hr.

Table 33 (continued)

[BH] (M)	Φ_{PT}	Φ_{TT}	Φ_{PP}
0.75	0.0090	0.0143	0.00195
1.00	0.0108	0.0158	0.00230
1.25	0.0116	0.0177	0.00226
1.50	0.0127	0.0186	0.00260
1.75	0.0129	0.0202	0.00261
2.00	0.0144	0.0207	0.00300
2.25	0.0147	0.0225	0.00290
2.50	0.0159	0.0231	0.00330

Table 34. Quantum Yield Data for α,α-Difluoroacetophenone and p-Cymene (BH) in Benzene

[BH] (M)	PT/C19	TT/C19	PP/C19	$I_a (El^{-1})$	[PT] (10^{-3})	[TT] (10^{-3})	[PP] (10^{-3})
0.75	0.691[a]	0.195	0.666	0.110	1.81	0.51	1.74
1.00	0.776[b]	0.225	0.728	0.134	2.32	0.67	2.18
1.25	0.745[a]	0.218	0.704	0.110	1.95	0.57	1.84
1.50	0.813[b]	0.240	0.756	0.134	2.43	0.72	2.26
1.75	0.786[a]	0.231	0.742	0.110	2.05	0.60	1.94
2.00	0.812[b]	0.251	0.766	0.134	2.43	0.75	2.29
2.25	0.788[a]	0.229	0.725	0.110	2.06	0.60	1.89
2.50	0.827[b]	0.259	0.779	0.134	2.47	0.77	2.33

[α,α-Difluoroacetophenone] = 0.10M, 313nm, SF = 0.99, g.c. column A @170°

[a] [C19] = 0.0026M

[b] [C19] = 0.0030M

Table 34 (continued)

[BH] (M)	Φ_{PT}	Φ_{TT}	Φ_{PP}
0.75	0.0164	0.0046	0.0158
1.00	0.0172	0.0050	0.0162
1.25	0.0177	0.0052	0.0167
1.50	0.0181	0.0054	0.0169
1.75	0.0187	0.0055	0.0176
2.00	0.0181	0.0056	0.0171
2.25	0.0187	0.0054	0.0172
2.50	0.0185	0.0058	0.0174

Table 35. Quantum Yield Data for α,α,α-Trifluoroacetophenone and p-Cymene (BH) in Benzene, Hydrocarbon Products

[BH] (M)	PT/C21	TT/C21	PP/C21	$[PT]^a$	$[TT]^a$	$[PP]^a$	I_a(E/1)	Φ_{PT}	Φ_{TT}	Φ_{PP}
$0.10^{b,e}$	0.134	0.020	0.28	0.70	0.11	1.45	0.227	0.0031	0.00047	0.0064
$0.20^{b,e}$	0.085	0.014	0.19	0.44	0.07	1.02	0.095	0.0046	0.00079	0.0107
$0.37^{c,e}$	1.840	0.382	3.52	3.68	0.76	7.01	0.508	0.0072	0.00151	0.0138
$0.60^{c,f}$	1.340	0.291	2.61	2.67	0.58	5.25	0.300	0.0089	0.00191	0.0175
$0.75^{d,g}$	0.366	0.090	0.77	1.10	0.27	2.32	0.100	0.0110	0.00270	0.0232
$1.02^{c,f}$	1.460	0.316	2.83	2.91	0.63	5.25	0.300	0.0097	0.00210	0.0175
$1.25^{d,g}$	0.439	0.106	0.92	1.32	0.32	2.76	0.100	0.0132	0.00320	0.0276
$1.75^{d,g}$	0.408	0.104	0.83	1.22	0.31	2.48	0.100	0.0123	0.00310	0.0248
$2.25^{d,g}$	0.425	0.115	0.84	1.27	0.35	2.53	0.100	0.0128	0.00340	0.0253

[α,α,α-Trifluoroacetophenone] = 0.10M, 313nm, g.c. Column B @175°, SF = 1.06

$^a10^{-3}$M; ^{b}[C21] = 0.0052M; ^{c}[C21] = 0.0021M; ^{d}[C21] = 0.0028M; ^{e}43 hr.; ^{f}24 hr.; ^{g}12 hr.

Table 36. Quantum Yield Data for α,α,α-Trifluoroacetophenone and p-Cymene (BH) in Benzene, Alcohol Products

[BH] (M)	KK/C17[a]	KT/C17[b]	KP/C17[b]	[KK][c]	[KT][c]	[KP][c]	I_a(E/l)	Φ_{KK}	Φ_{KT}	Φ_{KP}
0.10[d,f]	0.722	0.358	1.44	5.0	1.97	6.9	0.227	0.022	0.0087	0.0295
0.20[d,f]	0.315	0.211	0.74	2.2	1.17	4.1	0.095	0.023	0.0123	0.0436
0.37[e,f]	6.540	3.530	11.97	18.2	7.87	26.7	0.508	0.036	0.0155	0.0526
0.60[e,g]	3.730	2.420	7.80	10.3	5.46	17.4	0.300	0.033	0.0182	0.0579
1.02[e,g]	3.610	2.600	8.09	10.0	5.79	18.1	0.300	0.033	0.0194	0.0603

[α,α,α-Trifluoroacetophenone] = 0.10M, 313nm, g.c. Column C @210°

[a] SF = 1.32

[b] SF = 1.06

[c] 10^{-3}M

[d] [C17] = 0.0052M

[e] [C17] = 0.0021M

[f] 43 hr.

[g] 24 hr.

Table 37. Quantum Yield Data for α,α,α-Trifluoroacetophenone and p-Cymene (BH) in Acetonitrile

[BH] (M)	KK/C17[a]	KT/C17[b,c]	KP/C17[b,c]	PT/C22[d,e]	TT/C22[d,e]	PP/C22[d,e]	[KK][f,g]	[KT][f,g]
0.10	0.85	0.361	2.08	0.160	0.0132	0.268	12.9	4.41
0.20	0.78	0.443	2.31	0.254	0.0307	0.511	11.9	5.40
0.40	0.66	0.508	2.62	0.333	0.0458	0.754	10.1	6.20
1.03	0.67	0.543	2.64	0.364	0.0585	0.918	10.1	6.62

[BH] (M)	[KP][f,g]	[PT][f,g]	[TT][f,g]	[PP][f,g]	I_a(E/1)	Φ_{KK}	Φ_{KT}	Φ_{KP}	Φ_{PT}	Φ_{TT}	Φ_{PP}
0.10	25.5	1.35	0.111	2.26	0.256	0.050	0.0170	0.100	0.0053	0.00041	0.0038
0.20	28.2	2.14	0.259	4.30	0.256	0.046	0.0211	0.110	0.0082	0.00100	0.0170
0.40	32.1	2.81	0.386	6.35	0.256	0.039	0.0240	0.125	0.0111	0.00152	0.0252
1.03	32.3	3.07	0.493	7.73	0.256	0.039	0.0258	0.126	0.0123	0.00193	0.0305

[α,α,α-Trifluoroacetophenone] = 0.10M, 313nm, 19 hr.

[a] SF = 1.32; [b] g.c. Column C @210°; [c] SF = 1.06; [d] SF = 1.04; [e] g.c. Column B @205°;

[f] After irradiation a 2 ml aliquot of sample and a 1 ml aliquot of benzene containing C17 (0.0230M) and C22 (0.0163M) were mixed. The concentrations reported are calculated for the irradiated sample.

[g] 10^{-3}M

Table 38. Material Balance for the Reaction of α,α,α-Trifluoroacetophenone and p-Cymene (BH) in Benzene

[BH] (M)	TFA/C11[a] Before	TFA/C11[a] After	ΔTFA/C11[a]	Δ[TFA]	%Conversion	PT/C21[b]	TT/C21[b]	PP/C21[b]	KP/C17[c]
0.50	3.58	1.18	2.40	35.1	66	0.586	0.128	1.24	1.66
1.00	3.62	1.17	2.45	35.9	67	0.618	0.139	1.29	1.67
2.00	3.73	1.28	2.45	35.9	67	0.627	0.154	1.27	1.61

[BH] (M)	KT/C17[c]	[PT][d]	[TT][d]	[PP][d]	[KP][d]	[KT][d]	Material[e] Balance
0.50	0.497	2.01	0.44	4.26	11.6	3.47	81%
1.00	0.515	2.12	0.48	4.43	11.7	3.60	83%
2.00	0.511	2.15	0.53	4.36	11.3	3.57	81%

[α,α,α-Trifluoroacetophenone] = 0.0532M, [C11] = 0.0096M, [C17] = 0.0066M,

[C21] = 0.00324M, 313nm, 8 hr.

[a] SF = 1.53, g.c. Column B @75°; [b] SF = 1.06, g.c. Column B @205°; SF = 1.06, g.c. Column C @210°; [d] 10^{-3}M; [e] Material balance based on amount of radicals from p-cymene formed versus ketone disappearance.

Table 39. Quantum Yield Data for Acetophenone and Toluene (BH) in Benzene

[BH] (M)	BB/C14[a]	[BB] (10^{-3}M	Φ_{BB}
1.02	0.198	0.469	0.0182
1.53	0.263	0.623	0.0241
2.02	0.312	0.739	0.0286
2.50	0.363	0.860	0.0333

[Acetophenone] = .10M, [C14] = .00230M, 313nm, 7.5 hr.,

I_a = .0258E/l, g.c. column B @140°

[a] SF = 1.03

Table 40. Quantum Yield Data for α-Fluoroacetophenone and Toluene (BH) in Benzene

[BH] (M)	BB/C17[a]	BK/C17[b]	AP/C17[c]	[BB][d]	[BK][d]	[AP][d]	Φ_{BB}	Φ_{BK}	Φ_{AP}
0.52	0.252	0.194	0.165	1.35	1.11	1.83	0.033	0.0270	0.045
1.00	0.382	0.263	0.211	2.05	1.50	2.34	0.050	0.0366	0.057
1.52	0.470	0.302	0.251	2.52	1.72	2.78	0.061	0.0420	0.068
2.03	0.510	0.309	0.278	2.73	1.76	3.08	0.067	0.0430	0.075

[α-Fluoroacetophenone] = 0.1M, [C17] = 0.00429M, 313nm, 6 hr., I_a = 0.0410E/l

[a] SF = 1.25, g.c. Column B @160°

[b] SF = 1.33, g.c. Column B @160°

[c] SF = 2.58, g.c. Column A @130°

[d] 10^{-3}M

Table 41. Quantum Yield Data for α,α-Difluoroacetophenone and Toluene (BH) in Benzene

[BH] (M)	BB/C14[a]	[BB] (10^{-3}M)	Φ_{BB}
1.01	0.285	0.687	0.0269
1.49	0.334	0.805	0.0316
2.00	0.380	0.916	0.0359
2.52	0.412	0.993	0.0389

[α,α-Difluoroacetophenone] = .10M, [C14] = .00234M, 313nm, 7.5 hr., I_a = .0255E/l, g.c. Column B @140°

[a] SF = 1.03

Table 42. Quantum Yield Data for α,α,α-Trifluoroacetophenone and Toluene (BH) in Benzene

[BH] (M)	BB/C14[a]	BK/C14[b]	[BB] (10^{-3}M)	[BK] (10^{-3}M)	Φ_{BB}	Φ_{BK}
1.01	0.205	0.668	0.477	1.65	0.0128	0.0441
1.50	0.284	0.837	0.661	2.06	0.0177	0.0553
2.00	0.355	0.975	0.826	2.40	0.0222	0.0644
2.51	0.387	1.020	0.901	2.51	0.0242	0.0674

[α,α,α-Trifluoroacetophenone] = 0.1M, [C14] = 0.00226M, 313nm, 7 hr., I_a = 0.0373E/1, g.c. Column B @145°

[a] SF = 1.03

[b] SF = 1.09

Table 43. Stern-Volmer Data for Acetophenone and .5M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^\circ_{BB}/\Phi_{BB}$
0.0	0.131	1.00
0.083	0.0861	1.52
0.166	0.0629	2.08
0.414	0.0347	3.78

[Acetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0050M, 366nm, 36 hr., g.c. Column B @140°

Table 44. Stern-Volmer Data for Acetophenone and 1.0M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^\circ_{BB}/\Phi_{BB}$
0.0	0.174	1.00
0.082	0.122	1.43
0.165	0.087	2.00
0.412	0.050	3.48

[Acetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0045M, 366nm, 36 hr., g.c. Column B @140°

Table 45. Stern-Volmer Data for Acetophenone and 1.5M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^\circ_{BB}/\Phi_{BB}$
0.0	0.149	1.00
0.070	0.107	1.39
0.139	0.081	1.83
0.349	0.049	3.04

[Acetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0051M, 366nm, 36 hr., g.c. Column B @140°

Table 46. Stern-Volmer Data for Acetophenone and 2.0M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^\circ_{BB}/\Phi_{BB}$
0.0	0.186	1.00
0.068	0.137	1.36
0.136	0.108	1.72
0.340	0.0067	2.80

[Acetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0052M, 366nm, 36 hr., g.c. Column B @140°

Table 47. Stern-Volmer Data for Acetophenone and 2.5M Toluene

[Q] $(10^{-3}M)$	BB/C14	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.221	1.00
0.072	0.166	1.33
0.147	0.133	1.66
0.361	0.080	2.70

[Acetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0051, 366nm, 36 hr., g.c. Column B @140°

Table 48. Stern-Volmer Data for α-Fluoroacetophenone and 0.40M Toluene

[Q] $(10^{-3}M)$	BB/C16	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.0878	1.00
0.69	0.0323	2.72
1.39	0.0195	4.50
2.78	0.0110	7.98

[α-Fluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C16] = 0.00589M, 313nm, 10 hr., g.c. Column B @ 145°

Table 49. Stern-Volmer Data for α-Fluoroacetophenone and 0.80M Toluene

[Q] (10^{-3}M)	BB/C16	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.1480	1.00
0.69	0.0618	2.39
1.39	0.0368	4.02
2.78	0.0226	6.55

[α-Fluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C16] = 0.00589M, 313nm, 10 hr., g.c. Column B @ 145°

Table 50. Stern-Volmer Data for α-Fluoroacetophenone and 0.94M Toluene

[Q] (10^{-3}M)	BB/C16	$\Phi°_{BB}/\Phi_{BB}$
0.00	0.224	1.00
0.47	0.125	1.79
0.94	0.084	2.67
1.87	0.054	4.13

[α-Fluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C16] = 0.00300M, 313nm 11 hr., g.c. Column B @ 145°

Table 51. Stern-Volmer Data for α-Fluoroacetophenone and 1.50M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^{\circ}_{BB}/\Phi_{BB}$
0.000	0.641	1.00
0.129	0.561	1.14
0.258	0.487	1.32
0.646	0.345	1.86

[α-Fluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.00470M, 366nm, 14 hr., g.c. Column B @ 140°

Table 52. Stern-Volmer Data for α-Fluoroacetophenone and 1.87M Toluene

[Q] (10^{-3}M)	BB/C16	$\Phi^{\circ}_{BB}/\Phi_{BB}$
0.00	0.351	1.00
0.47	0.233	1.51
0.94	0.173	2.03
1.87	0.111	3.17

[α-Fluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C16] = 0.00300M, 313nm, 11 hr., g.c. Column B @ 145°

Table 53. Stern-Volmer Data for α,α-Difluoroacetophenone and .5M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.464	1.00
0.462	0.357	1.30
0.924	0.294	1.58
2.310	0.181	2.56

[α,α-Difluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0049M, 266nm, 36 hr., g.c. Column B @ 140°

Table 54. Stern-Volmer Data for α,α-Difluoroacetophenone and 1.0M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.495	1.00
0.449	0.403	1.23
0.899	0.345	1.43
2.250	0.227	2.18

[α,α-Difluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0049M, 366nm, 36 hr., g.c. Column B @ 140°

Table 55. Stern-Volmer Data for α,α-Difluoroacetophenone and 1.5M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^{\circ}_{BB}/\Phi_{BB}$
0.0	0.339	1.00
0.465	0.290	1.17
0.930	0.246	1.38
2.320	0.169	2.01

[α,α-Difluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0049M, 366nm, 36 hr., g.c. Column B @ 140°

Table 56. Stern-Volmer Data for α,α-Difluoroacetophenone and 2.0M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^{\circ}_{BB}/\Phi_{BB}$
0.0	0.350	1.00
0.465	0.298	1.17
0.930	0.264	1.33
2.320	0.187	1.87

[α,α-Difluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0048M, 366nm, 36 hr., g.c. Column B @140°

Table 57. Stern-Volmer Data for α,α-Difluoroacetophenone and 2.5M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^{\circ}_{BB}/\Phi_{BB}$
0.0	0.424	1.00
0.477	0.375	1.13
0.955	0.329	1.29
2.390	0.243	1.74

[α,α-Difluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0045M, 366nm, 36 hr., g.c. Column B @140°

Table 58. Stern-Volmer Data for α,α,α-Trifluoroacetophenone and .5M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi^{\circ}_{BB}/\Phi_{BB}$
0.0	0.0852	1.00
0.99	0.0516	1.65
1.99	0.0360	2.37
4.98	0.0184	4.63

[α,α,α-Trifluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0052M, 366nm, 38 hr., g.c. Column B @140°

Table 59. Stern-Volmer Data for α,α,α-Trifluoroacetophenone and 1.0M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.199	1.00
1.00	0.139	1.43
2.00	0.100	1.99
5.00	0.058	3.41

[α,α,α-Trifluoroacetophenone] = 0.10M, benzene solvent napthalene (Q) quencher, [C14] = 0.0049M, 366nm, 36 hr., g.c. Column B @140°

Table 60. Stern-Volmer Data for α,α,α-Trifluoroacetophenone and 1.5M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.185	1.00
1.00	0.134	1.38
2.01	0.103	1.80
5.02	0.062	2.98

[α,α,α-Trifluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0047, 366nm, 40 hr., g.c. Column B @140°

Table 61. Stern-Volmer Data for α,α,α-Trifluoroacetophenone and 2.0M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.224	1.00
0.99	0.176	1.27
1.98	0.139	1.61
4.96	0.089	2.52

[α,α,α-Trifluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0053, 366nm, 38 hr., g.c. Column B @140°

Table 62. Stern-Volmer Data for α,α,α-Trifluoroacetophenone and 2.5M Toluene

[Q] (10^{-3}M)	BB/C14	$\Phi°_{BB}/\Phi_{BB}$
0.0	0.180	1.00
1.05	0.145	1.24
5.23	0.079	2.29

[α,α,α-Trifluoroacetophenone] = 0.10M, benzene solvent, napthalene (Q) quencher, [C14] = 0.0057, 366nm, 36 hr., g.c. Column B @140°

Table 63. Product Ratios from Reaction of Indicated Ketone with p-Cymene in Benzene

Ketone	TT/PT	PP/PT	Column Used
m-CF_3-TFA[a]	-----	2.40	B
m-Me-TFA[a]	0.24	-----	A
Benzophenone[b]	1.20	-----	B
4,4'-MeO-BP[c]	1.50	-----	B
4,4'-Me-BP[b]	2.60	-----	A
m-F-AP[b]	1.10	-----	A
m-CF_3-AP[b]	1.00	-----	A
p-Me-AP[a]	1.60	-----	A
p-MeO-TFA[d]	0.53	0.68	B
p-Me-TFA[a]	0.33	0.90	A
p-Cl-TFA[a]	0.37	0.90	A
Propiophenone[e]	1.30	0.14	B
p-F-AP[a]	1.30	0.56	A
4,4'-Cl-BP[a]	1.00	0.38	A

g.c. Column A @155°, g.c. Column B @175°, 313nm,

[Ketone] = 0.10M, [p-Cymene] = 1.0M

[a] 17 hr.

[b] 23 hr.

[c] 52 hr.

[d] 59 hr.

[e] 11 hr.

Table 64. Reaction of t-Butyl Hypochlorite (ROCl) and p-Cymene in Benzene

[ROCl]	A/B[a]	[A]/[B][b]
0.015	2.26	2.40
0.030	2.28	2.42
0.060	2.05	2.17

g.c. Column B @180°, 366nm, 1.5 hr.

[a] Product A is α,p-dimethylstyrene from quantitative elimination of the tertiary chloride. Product B is 4-isopropylbenzyl chloride.

[b] Response factors for the two products were estimated by comparing cumene to α-methylstyrene and β-chloroethylbenzene to ethylbenzene.

Table 65. Reaction of di-t-Butyl Peroxide and p-Cymene in Benzene

Product	Relative Peak Area
PP	1.00
PT	5.89
TT	7.61

[di-t-butyl peroxide] = 0.10M, [p-cymene] = 0.60M,

313nm, 16 hr., g.c. Column B @180°

Table 66. Effect of Pyridine on the Photoreduction of TFA by Toluene in Benzene

[Pyridine]	BB/C16[a]	BK/C16[b]	[BB][c]	[BK][c]	$\Phi^{\circ}_{BB}/\Phi_{BB}$	$\Phi^{\circ}_{BK}/\Phi_{BK}$
0.0	0.091	0.21	0.67	1.63	1.00	1.00
0.088	0.71	0.30	0.52	2.33	1.28	0.70
0.52	0.059	0.30	0.43	2.33	1.54	0.70
2.01	0.43	0.25	0.31	1.94	2.12	0.84

[C16] = 0.0062M, g.c. Column B @140°, 313nm, 5 hr.,

[Toluene] = 0.50M, [TFA] = 0.050M

[a] SF = 1.18

[b] SF = 1.25

[c] 10^{-3}M

Table 67. Effect of Acetonitrile on Photoreduction of TFA by Toluene in Benzene

[MeCN] (M)	BB/C14[a]	BK/C14[b]	[BB] (M)	[BK] (M)
0.0	0.351	0.70	0.00145	0.00319
5.0	0.368	1.09	0.00152	0.00478
10.0	0.411	1.22	0.00170	0.00535
15.0	0.472	1.40	0.00195	0.00614

[C14] = 0.0040M, 313nm, 10 hr., g.c. Column B @140°,

[Toluene] = 0.50M, [TFA] = 0.050M

[a] SF = 1.03

[b] SF = 1.09

Table 68. Comparison of Products from Photoreduction of Acetophenone and Reaction of di-t-Butyl Peroxide

Substrate	(conc.,M)	Solvent[a]	Reaction[b]	BB/C15[c]	BK/C15[c]	KK/C15[c,d]	[BB][c]	[BK][e]	[KK][e]
p-Xylene	(0.50M)	A	K	2.09[f]	3.91[i]	2.03	2.68	5.49	3.45
p-Xylene	(0.50M)	B	K	2.62[f]	3.32[i]	2.47	3.36	4.66	4.26
Cumene	(0.50M)	A	K	1.05[g]	2.25[j]	0.82	1.28	3.10	1.39
Cumene	(0.50M)	B	K	1.27[g]	2.37[j]	1.10	1.54	3.26	1.87
Toluene	(1.00M)	C	K	0.55[h,j]	1.85[h,k]	0.95	0.83	2.77	1.62
p-Xylene	(0.39M)	A	P	3.80[f]	5.88[i]	2.17	4.87	8.26	3.69
p-Xylene	(0.39M)	B	P	3.19[f]	4.02[i]	3.09	4.09	5.64	5.26
Cumene	(0.49M)	A	P	4.54[g]	7.12[j]	2.29	5.52	9.80	3.90
Cumene	(0.51M)	B	P	4.14[g]	6.07[j]	2.88	5.03	8.36	4.90
Toluene	(1.00M)	C	P	2.68[h,j]	5.67[h,k]	1.97	4.05	8.50	3.27

313nm, 18 hr.

[a] A is acetonitrile; B is benzene; C is t-butanol.

[b] K is photoreduction of 0.050M acetophenone; P is reaction of 0.10M di-t-butyl peroxide and 0.10M 1-phenylethanol.

[c] g.c. Column B @170°; [d] SF = 1.26; [e] 10^{-3}M; [f] SF = 0.95; [g] SF = 0.90; [h] SF = 1.12;

[i] SF = 1.04; [j] SF = 1.02; [k] g.c. Column A @150°.

Table 69. Effect of Pyridine on the Photoreduction of TFA by Toluene in Acetonitrile

[Pyridine] (M)	BB/C16[a]	BK/C16[b]	[BB][c]	[BK][c]	$\Phi^{\circ}_{BB}/\Phi_{BB}$	$\Phi^{\circ}_{BB}/\Phi_{BK}$
0.0	0.313	0.98	1.51	5.02	1.00	1.00
0.065	0.230	0.76	1.11	3.90	1.36	12.9
0.50	0.076	0.30	0.37	1.54	4.12	3.27
2.05	0.024	0.09	0.12	0.46	13.00	11.00

[C16] = 0.0041M, g.c. Column B @140°, 313nm, 5 hr.,

[Toluene] = 0.50M, [TFA] = 0.050M

[a] SF = 1.18

[b] SF = 1.25

[c] 10^{-3}M

Table 70. Reaction of TFA and Toluene in Acetonitrile Quenched by DABCO

[DABCO][a]	BB/C16[b]	BK/C16[c]	KK/C16[d]	[BB][a]	[BK][a]	[KK][a]	$\Phi^\circ_{BB}/\Phi_{BB}$	$\Phi^\circ_{BK}/\Phi_{BK}$	$\Phi^\circ_{KK}/\Phi_{KK}$
0.000	0.83	2.64	0.76	5.19	17.5	5.40	1.00	1.00	1.00
0.146	1.04	2.70	1.14	6.50	17.9	8.10	0.80	0.98	0.67
0.292	1.08	2.69	1.33	6.75	17.8	9.44	0.77	0.98	0.57
0.490	1.06	2.85	1.36	6.63	18.9	9.66	0.78	0.93	0.56
0.585	0.99	2.75	1.38	6.19	18.2	9.80	0.84	0.96	0.55
0.980	0.71	2.60	1.24	4.44	17.2	8.81	1.17	1.02	0.61
1.960	0.29	1.92	0.70	1.81	12.7	4.97	2.89	1.38	1.09
2.940	0.16	1.46	0.55	1.00	9.7	3.91	5.04	1.81	1.30

[TFA] = 0.050M, [Toluene] = 1.0M, [C16] = 0.0053M, g.c. Column B @140°, 313nm, 7 hr.

[a] 10^{-3}M

[b] SF = 1.18

[c] SF = 1.25

[d] SF = 1.34

Table 71. Reaction of TFA and Toluene in Benzene Quenched by DABCO

[DABCO]^a	BB/C16^b	BK/C16^c	[BB]^a	[BK]^a	$\Phi^\circ_{BB}/\Phi_{BB}$	$\Phi^\circ_{BK}/\Phi_{BK}$
0.00	0.081	0.180	0.65	1.53	1.00	1.00
0.144	0.102	0.131	0.82	1.11	0.79	1.37
0.578	0.085	0.113	0.68	0.96	0.95	1.59
1.440	0.053	0.107	0.43	0.91	1.53	1.68

[C16] = 0.0068M, g.c. Column B @140°, 313nm, 5 hr.,

[Toluene] = 0.50M, [TFA] = 0.050M

$^a10^{-3}$M

^{b}SF = 1.18

^{c}SF = 1.25

Table 72. Reaction of TFA and p-Cymene in Benzene Quenched by DABCO

[DABCO][a]	PP/C21[b]	PT/C21[b]	TT/C21[b]	KP/C17[c]	KT/C17[c]	[PP][a]	[PT][a]	[TT][a]	[KP][a]	[KT][a]
0.00	0.76	0.36	0.049	1.11	0.30	2.30	1.07	0.149	5.20	1.38
0.34	0.80	0.38	0.059	0.97	0.24	2.40	1.14	0.177	4.53	1.12
1.70	0.63	0.32	0.053	1.01	0.23	1.90	0.97	0.161	4.73	1.06
10.70	0.17	0.10	0.021	0.74	0.18	0.52	0.31	0.064	3.48	0.85

[DABCO]	$\Phi^\circ_{BB}/\Phi_{BB}$	$\Phi^\circ_{BK}/\Phi_{BK}$	$\Phi^\circ_{P\cdot}/\Phi_{P\cdot}$[d]	$\Phi^\circ_{T\cdot}/\Phi_{T\cdot}$[d]
0.00	1.00	1.00	1.00	1.00
0.34	0.95	1.16	1.04	1.05
1.70	1.16	1.14	1.14	1.17
10.70	3.94	1.52	2.25	2.13

[TFA] = 0.050M, [p-Cymene] = 0.50M, [C17] = 0.0044M, [C21] = 0.0029, 313nm, 12 hr.

[a] 10^{-3}M; [b] $_{SF}$ = 1.06, g.c. Column B @175°; [c] $_{SF}$ = 1.06, g.c. Column C @205°;

[d] $\Phi_{P\cdot}$ and $\Phi_{T\cdot}$ are the respective sums of the primary and tertiary radicals incorporated in products.

Table 73. Reaction of TFA and Toluene in Acetonitrile Quenched by p-Dimethoxybenzene (Q)

[Q][a]	BB/C14[b]	BK/C14[c]	[BB][a]	[BK][a]	$\Phi^\circ_{BB}/\Phi_{BB}$	$\Phi^\circ_{BK}/\Phi_{BK}$
0.0	0.189	0.620	0.93	3.24	1.00	1.00
0.020	0.181	0.606	0.89	3.17	1.04	1.02
0.099	0.149	0.596	0.74	3.12	1.27	1.04
0.494	0.074	0.398	0.37	2.08	2.55	1.56

[C14] = 0.0048, g.c. Column B @140°, 313nm, 7 hr.,

[Toluene] = 0.50M, [TFA] = 0.050M

[a] 10^{-3}M; [b] SF = 1.03; [c] SF = 1.09

Table 74. Reaction of TFA and Toluene in Benzene Quenched by p-Dimethoxybenzene (Q)

[Q][a]	BB/C14[b]	BK/C14[c]	[BB][a]	[BK][a]	$\Phi^\circ_{BB}/\Phi_{BB}$	$\Phi^\circ_{BK}/\Phi_{BK}$
0.0	0.0516	0.167	0.260	0.89	1.00	1.00
0.058	0.0517	0.166	0.261	0.89	1.00	1.01
0.289	0.423	0.140	0.213	0.75	1.22	1.19
1.450	0.0253	0.095	0.128	0.51	2.04	1.76

[C14] = 0.0049M, g.c. Column B @140°, 313nm, 7 hr.,

[Toluene] = 0.50M, [TFA] = 0.050M

[a] 10^{-3}M; [b] SF = 1.03; [c] SF = 1.09

Table 73. Reaction of TFA and Toluene in Acetonitrile Quenched by p-Dimethoxybenzene (Q)

$[Q]^{a}$	$BB/C14^{b}$	$BK/C14^{c}$	$[BB]^{a}$	$[BK]^{a}$	$\Phi^{\circ}_{BB}/\Phi_{BB}$	$\Phi^{\circ}_{BK}/\Phi_{BK}$
0.0	0.189	0.620	0.93	3.24	1.00	1.00
0.020	0.181	0.606	0.89	3.17	1.04	1.02
0.099	0.149	0.596	0.74	3.12	1.27	1.04
0.494	0.074	0.398	0.37	2.08	2.55	1.56

[C14] = 0.0048, g.c. Column B @140°, 313nm, 7 hr.,

[Toluene] = 0.50M, [TFA] = 0.050M

$^{a}10^{-3}M$; $^{b}SF = 1.03$; $^{c}SF = 1.09$

Table 74. Reaction of TFA and Toluene in Benzene Quenched by p-Dimethoxybenzene (Q)

$[Q]^{a}$	$BB/C14^{b}$	$BK/C14^{c}$	$[BB]^{a}$	$[BK]^{a}$	$\Phi^{\circ}_{BB}/\Phi_{BB}$	$\Phi^{\circ}_{BK}/\Phi_{BK}$
0.0	0.0516	0.167	0.260	0.89	1.00	1.00
0.058	0.0517	0.166	0.261	0.89	1.00	1.01
0.289	0.423	0.140	0.213	0.75	1.22	1.19
1.450	0.0253	0.095	0.128	0.51	2.04	1.76

[C14] = 0.0049M, g.c. Column B @140°, 313nm, 7 hr.,

[Toluene] = 0.50M, [TFA] = 0.050M

$^{a}10^{-3}M$; $^{b}SF = 1.03$; $^{c}SF = 1.09$

Table 75. Reaction of Acetophenone and Toluene in Acetonitrile Quenched by p-Dimethoxybenzene (Q)

$[Q]^a$	$BB/C14^b$	$BK/C14^c$	$[BB]^a$	$[BK]^a$	$\Phi^\circ_{BB}/\Phi_{BB}$	$\Phi^\circ_{BK}/\Phi_{BK}$
0.00	0.138	0.287	0.398	0.876	1.00	1.00
1.00	0.091	0.210	0.262	0.641	1.52	1.37
2.00	0.069	0.151	0.199	0.461	2.00	1.90
5.00	0.031	0.074	0.089	0.226	4.41	3.88
10.00	0.014	-----	0.040	-----	10.22	----

[C14] = 0.0028, g.c. Column B @140°, 313nm, 8 hr.,

[Toluene] = 0.50M, [Acetophenone] = 0.050M

[a] 10^{-3}M

[b] SF = 1.03

[c] SF = 1.09

Table 76. Effect of Trifluoroacetic Acid on the Reaction of TFA and p-Cymene in Acetonitrile, Run 1

[Acid] (M)	PT/C21[a]	TT/C21[a]	PP/C21[a]	KP/C21[b]	KT/C21[b]	[PT][c]	[TT][c]	[PP][c]	[KP][c]	[KT][c]
0.000	0.645	0.086	1.60	4.79	0.92	1.93	0.26	4.78	16.7	3.21
0.067	0.582	0.056	1.30	5.22	1.04	1.74	0.17	3.89	18.1	3.64

[TFA] = 0.050M, [p-Cymene] = 0.50M, [C17] = 0.0033M, [C21] = 0.0028M, 313nm, 20 hr.

[a] SF = 1.06, g.c. Column B @175°

[b] SF = 1.06, g.c. Column C @205°

[c] 10^{-3}M

Table 77. Effect of Trifluoroacetic Acid on the Reaction of TFA and p-Cymene in Acetonitrile, Run 2

[Acid] (M)	PT/C21[a]	PP/C21[a]	KP/C17[b]	KP/C17[b]	[PT][c]	[PP][c]	[KP][c]	[KT][c]
0.00	0.103	0.269	0.622	0.107	0.297	0.776	2.57	0.441
0.10	0.097	0.223	0.700	0.129	0.281	0.643	2.87	0.532
0.50	0.056	0.112	0.480	0.089	0.162	0.323	1.98	0.367
1.04	0.024	0.050	0.321	0.050	0.069	0.144	1.32	0.260

[TFA] = 0.050M, [p-Cymene] = 1.0M, [C17] = 0.0039, [C21] = 0.0027, 313nm, 10 hr.

[a] SF = 1.06, g.c. Column B @175°

[b] SF = 1.06, g.c. Column C @205°

[c] 10^{-3}M

Table 78. Effect of Trifluoroacetic Acid on the Reaction of TFA and p-Cymene in Benzene

[Acid] (M)	PT/C21[a]	TT/C21[a]	PP/C21[a]	KP/C17[b]	KT/C17[b]	[PT][c]	[TT][c]	[PP][c]	[KP][c]	[KT][c]
0.000	0.219	0.033	0.517	1.49	0.44	0.84	0.125	1.97	5.69	1.68
0.052	0.518	0.125	0.574	2.38	1.32	1.98	0.515	2.19	9.08	5.04
0.112	0.518	0.074	0.476	2.11	1.33	1.98	0.282	1.82	8.05	5.08

[TFA] = 0.050M, [p-Cymene] = 0.50M, [C17] = 0.0036, [C21] = 0.0036, 313nm, 20 hr.

[a] SF = 1.06, g.c. Column B @175°

[b] SF = 1.06, g.c. Column C @205°

[c] 10^{-3}M

Table 79. Effect of Trifluoroacetic Acid on the Photoreduction of Acetophenone by p-Cymene in Benzene

[Acid] (M)	PT/C17[a]	TT/C17[b]	PP/C17[b]	[PT][c]	[TT][c]	[PP][c]
0.000	0.260	0.395	0.058	0.92	1.40	0.20
0.050	0.933	0.620	0.449	3.30	2.19	1.59
0.110	0.590	0.460	0.221	2.09	1.63	0.78

[C17] = 0.0044M, SF = 0.81, 313nm, 13 hr.

[Acetophenone] = 0.050M, [p-Cymene] = 0.50M

[a] g.c. Column A @150°

[b] g.c. Column B @185°

[c] 10^{-3}M

Table 80. Effect of Trifluoroacetic Acid on the Photoreduction of TFA by Toluene (BH) in Benzene

[BH] (M)	BB/C14[a]	BK/C14[b]	[BB][c]	[BK][c]	Φ_{BB}	Φ_{BK}
1.00	0.601	1.26	3.36	7.44	0.070	0.155
1.52	0.608	1.25	3.39	7.38	0.071	0.154
2.01	0.610	1.25	3.41	7.38	0.071	0.154
2.50	0.620	1.28	3.46	7.56	0.072	0.157

[C14] = 0.0054M, g.c. Column B @140°, 313nm, 9 hr.,

[TFA] = 0.10M, [Trifluoroacetic Acid] = 0.050M,

I_a = 0.0481E/1

[a] SF = 1.03

[b] SF = 1.09

[c] 10^{-3}M

Table 81. Reaction of di-t-Butyl Peroxide (ROOR) with Toluene and 1-Phenylethanol (APH_2)

[ROOR] (M)	Solvent[a]	AP/C15[b]	BB/C15[c]	BK/C15[d]	KK/C15[e]	[AP][f]	[BB][f]	[BK][f]	[KK][f]
0.020	B	0.076	0.196	0.392	0.478	0.96	1.20	2.53	3.30
0.030	B	0.175	0.248	0.437	0.459	2.21	1.52	2.82	3.17
0.051	B	0.173	0.172	0.264	0.234	2.10	1.01	1.63	1.54
0.101	B	0.374	0.310	0.430	0.335	4.35	1.81	2.65	2.21
0.152	B	0.593	0.422	0.555	0.408	7.19	2.47	3.42	2.69
0.050	A	0.076	0.173	0.279	0.146	1.00	1.09	1.86	1.04
0.100	A	0.145	0.291	0.453	0.234	1.90	1.84	3.02	1.67
0.150	A	0.204	0.361	0.610	0.322	2.67	2.28	4.07	2.29

[Toluene] = 1.0M, [1-phenylethanol] = 0.10M, 313nm

[a] B is benzene, A is acetonitrile; [b] SF = 2.30, g.c. Column A @95°; [c] SF = 1.11, g.c. Column A @140°; [d] SF = 1.17, g.c. Column A @140°; [e] SF = 1.25, g.c. Column B @170°; [f] 10^{-3}M; [g] [C15] = 0.0055M, 36 hr.; [h] [C15] = 0.0053M, 13 hr.; [i] [C15] = 0.0057M, 15 hr.

Table 82. Reaction of di-t-Butyl Peroxide with 1-Phenyl-2,2,2-Trifluoroethanol ($TFAH_2$) and Indicated Substrate (BH) in Benzene

BH	[BH] (M)	TFA/C15[a]	BB/C15	BK/C15	KK/C15[b]	[TFA][c]	[BB][c]	[BK][c]	[KK][c]
None	----	0.246	------	------	0.416	2.83	----	----	2.51
Toluene	0.38	0.050	0.334[d]	0.651[e]	0.188	0.58	1.90	3.80	1.14
Cumene	0.11	0.110	0.145[f]	0.421[g]	0.173	1.27	0.63	2.09	1.05
p-Xylene	0.11	0.021	0.399[h]	0.742[i]	0.245	0.24	1.96	4.03	1.48

[1-phenyl-2,2,2-trifluoroethanol] = 0.50M, [di-t-butyl peroxide] = 0.052M, 313nm, 19 hr., g.c. Column A programmed from 80° to 120° at 2°/minute, [C15] = 0.0051M

[a] $_{SF}$ = 2.25

[b] $_{SF}$ = 1.18

[c] 10^{-3}M

[d] $_{SF}$ = 1.11

[e] $_{SF}$ = 1.14

[f] $_{SF}$ = 0.85

[g] $_{SF}$ = 0.99

[h] $_{SF}$ = 0.96

[i] $_{SF}$ = 1.06

Table 83. Quantum Yield Data for the Reaction of Propiophenone (PP) and 1-Phenylethanol (APH_2) in Benzene

[PP] (M)	$PPH_2/C15^{a,b}$	$AP/C15^{b,c}$ Before	$AP/C15^{b,c}$ After	$\Delta AP/C15$	Pinacols[h]		
					$K_AK_A/C17^{d,e}$	$K_AK_P/C17^{e,f}$	$K_PK_P/C17^{e,g}$
0.020	-----	0.698	0.671	----	0.302	0.548	0.214
0.052	0.061	0.702	1.08	0.378	0.131	0.548	0.511
0.145	0.067	0.757	1.48	0.723	----	0.332	0.804
0.260	0.080	0.798	1.60	0.802	----	0.208	0.850

[PP] (M)	$[PPH_2]^i$	$\Delta[AP]^i$	$[K_AK_A]^i$	$[K_AK_P]^i$	$[K_PK_P]^i$	Φ_{PPH_2}	Φ_{AP}	$\Phi_{K_AK_A}$	$\Phi_{K_AK_P}$	$\Phi_{K_PK_P}$
0.020	----	----	1.77	3.08	1.14	------	-----	0.0293	0.0508	0.0189
0.052	0.51	3.57	0.77	3.08	2.72	0.0084	0.059	0.0127	0.0508	0.0450
0.145	0.56	6.83	----	1.86	4.28	0.0092	0.113	------	0.0309	0.0710
0.260	0.67	7.58	----	1.17	4.53	0.0110	0.125	------	0.0194	0.0750

[1-phenylethanol] = 0.51M, [c15] = 0.0041M, [c17] = 0.0041M, 313nm, 7 hr., I_a = 0.0605E/1

[a] SF = 2.03; [b] g.c. Column A @90°; [c] SF = 2.30; [d] SF = 1.42; [e] g.c. Column B @170°; [f] SF = 1.36; [g] SF = 1.29; [h] K_AK_A is acetophenone pinacol, K_PK_P is propiophenone pinacol, and K_AK_P is the crossed pinacol; [i] 10^{-3}M

Table 84. Quantum Yield Data for the Reaction of Acetophenone (AP) and 1-Phenylpropanol (PPH_2) in Benzene

[AP]	$APH_2/C15^a$ Before	$APH_2/C15^a$ After	$\Delta APH_2/C15$	$K_AK_A/C17^b$	$K_AK_P/C17^c$	$\Delta[APH_2]^d$	$[K_AK_A]^d$	$[K_AK_P]^d$
0.030	0.0330	0.0637	0.0307	1.97	0.420	0.378	9.18	1.87
0.060	0.0440	0.0700	0.0260	2.20	0.173	0.286	10.20	0.78
0.151	0.0627	0.0844	0.0217	1.93	0.052	0.239	9.00	0.23
0.302	0.102	0.113	0.0110	1.35	0.011	0.121	6.30	0.05

[AP]	I_a(E/1)	Φ_{APH_2}	$\Phi_{K_AK_A}$	$\Phi_{K_AK_P}$
0.030	0.0451	0.0075	0.203	0.0415
0.060	0.0451	0.0064	0.227	0.0171
0.151	0.0451	0.0053	0.199	0.0051
0.302	0.0451	0.0027	0.139	0.0011

[1-phenylpropanol] = 0.20M, [C15] = 0.0048M, [C17] = 0.0033M, 313nm, 5 hr.

[a] SF = 2.30, g.c. Column A @90°; [b] SF = 1.42, g.c. Column B @170°, K_AK_A is acetophenone pinacol; [c] SF = 1.36, g.c. Column B @170°, K_AK_P is the crossed pinacol of acetophenone and propiophenone; [d] 10^{-3}M

Table 85. Quantum Yield Data for the Reaction of Both Acetophenone (AP) and Propiophenone (PP) with 2-Propanol in Benzene

Run[a]	$APH_2/C15$[b] Before	$APH_2/C15$[b] After	$\Delta APH_2/C15$	$PPH_2/C15$[c]	$K_AK_A/C17$[d]	$K_AK_P/C17$[e]	$K_PK_P/C17$[f]	$[APH_2]$[g]
1	0.017	0.056	0.039	0.0179	1.84	1.32	0.213	0.249
2	0.018	0.035	0.017	0.0065	0.96	0.59	0.086	0.217

Run	$[PPH_2]$[g]	$[K_AK_A]$[g]	$[K_AK_P]$[g]	$[K_PK_P]$[g]	Φ_{APH_2}	Φ_{PPH_2}	$\Phi_{K_AK_A}$	$\Phi_{K_AK_P}$	$\Phi_{K_PK_P}$
1	0.101	5.59	3.84	0.589	0.0075	0.0031	0.169	0.116	0.0178
2	0.073	5.69	3.44	0.470	0.0066	0.0022	0.172	0.104	0.0142

I_a = 0.0331 E/l, 313nm, 7 hr.

[a] Run 1: [AP] = [PP] = 0.05m, [2-propanol] = 0.50M, [C15] = 0.0028M, [C17] = 0.0021M
Run 2: [AP] = [PP] = 0.10M, [2-propanol] = 1.00M, [C15] = 0.0056M, [C17] = 0.0043M

[b] SF = 2.30, g.c. Column A @90°; [c] SF = 2.03, g.c. Column A @90°; [d] SF = 1.42, g.c. Column B @170°; [e] SF = 1.36, g.c. Column B @170°; [f] SF = 1.29, g.c. Column B @170°; [g] 10^{-3}M

Table 86. Reaction of Acetophenone (AP) and Indicated Ketone (K) with 2-Propanol in Benzene

Ketone	Pinacols (%)		
	$(APH)_2$	(APH)(KH)	$(KH)_2$
p-MeO-AP[a,c]	100.0	----	---
p-Me-AP[a,c]	70.0	30.0	---
Propiophenone[a,c]	75.0	25.0	---
m-CF_3-AP[b,d]	3.5	22.5	74
TFA[b,c]	-----	----	100
m-CF_3-TFA[b,c]	-----	----	100

[Acetophenone] = 0.10M, [Ketone] = 0.10M,

[2-Propanol] = 1.0M, 313nm

[a] 5 hr.

[b] 12 hr.

[c] g.c. Column B @180°

[d] g.c. Column A @165°

Table 87. Quantum Yield Data for Acetophenone and 1-Phenylethanol (APH_2) in Benzene

$[APH_2]$ (M)	[C17] (M)	KK/C17	[KK][a]	I_a(E/l)	Φ_{KK}
0.046	0.0021	0.98	2.96	0.0386	0.077
0.104	0.0026	1.53	5.85	0.0374	0.152
0.155	0.0021	2.46	7.41	0.0386	0.192
0.209	0.0032	2.56	11.70	0.0459	0.256
0.310	0.0021	4.16	12.50	0.0386	0.324
0.400	0.0020	3.25	9.30	0.0289	0.323
0.460	0.0021	4.34	13.10	0.0386	0.338
0.490	0.0020	3.45	9.90	0.0289	0.342
0.600	0.0020	3.53	10.10	0.0289	0.350

[Acetophenone] = 0.10M, 313nm, 5 hr., SF = 1.42,

g.c. Column B @170°

[a] 10^{-3}M

Table 88. Quantum Yield Data for the Reaction of Acetophenone with 1-Phenylethanol (PhEtOH) and 1-Phenylethanol-O-d (PhEtOD) in Acetonitrile.[a] Run 1

Alcohol	[Alcohol] (M)	KK/C17	[KK][b]	Φ_{KK}
PhEtOH	0.101	1.53	4.21	0.093
PhEtOH	0.324	2.98	8.21	0.181
PhEtOH	0.419	3.71	10.20	0.226
PhEtOH	0.520	4.11	11.30	0.250
PhEtOD	0.102	1.49	4.10	0.091
PhEtOD	0.204	3.13	8.62	0.190
PhEtOD	0.322	4.34	12.00	0.264
PhEtOD	0.413	4.98	13.70	0.303
PhEtOD	0.492	5.82	16.00	0.354

[Acetophenone] = 0.10M, [C17] = 0.00194M, 313nm, 5 hr.,

SF = 1.42, g.c. Column B @185°, I_a = 0.0453E/l

[a] 10% Benzene added to dissolve standard

[b] 10^{-3}M

Table 89. Quantum Yield Data for the Reaction of Acetophenone with 1-Phenylethanol (PhEtOH) and 1-Phenylethanol-O-d (PhEtOD) in Acetonitrile.[a] Run 2

Alcohol	[Alcohol] (M)	KK/C17	[KK][b]	Φ_{KK}
PhEtOH	0.102	1.03	2.74	0.093
PhEtOH	0.204	1.71	4.54	0.154
PhEtOH	0.294	2.25	5.97	0.203
PhEtOH	0.416	2.76	7.33	0.249
PhEtOH	0.507	2.92	7.75	0.263
PhEtOD	0.099	1.08	2.87	0.097
PhEtOD	0.199	1.83	4.86	0.165
PhEtOD	0.307	2.49	6.61	0.225
PhEtOD	0.416	2.98	7.91	0.269
PhEtOD	0.499	3.23	8.58	0.291

[Acetophenone] = 0.10M, [C17] = 0.00187, 313nm, 3 hr.,

Sf = 1.42, g.c. Column B @185°, I_a = 0.0333E/l

[a] 10% Benzene added to dissolve standard

[b] 10^{-3}M

Table 90. Quantum Yield Data for TFA and 1-Phenylethanol (APH_2) in Benzene

[APH_2] (M)	KK/C16[a]	[KK][b]	Φ_{KK}
0.099	0.80	2.37	0.035
0.197	1.65	4.89	0.071
0.296	2.48	7.34	0.107
0.493	3.71	11.00	0.160
0.990	3.94	11.70	0.170
1.480	3.35	9.90	0.145

[α,α,α-Trifluoroacetophenone] = 0.10M, [C16] = 0.00235M

I_a = 0.0686E/1, SF = 1.26, g.c. Column B @165°, 313nm, 7 hr.

[a] KK is the pinacol of TFA

[b] 10^{-3}M

Table 91. Data for the Reaction of Propiophenone (PP) with Acetophenone Pinacol ($(APH)_2$) or 1-Phenylethanol (APH_2) in Benzene

Sample	Reactants			AP/C15[a]	$(APH)_2$/C17[b]	(APH)(PPH)/C17[c]	$(PPH)_2$/C17[d]
	[PP]	[APH_2]	[$(APH)_2$]				
1	0.020	0.102	-----	0.091[e]	0.490[e]	1.17[e]	0.908[e]
2	0.099	0.102	-----	1.210[e]	-----	0.85[a]	2.220[e]
3	0.020	-----	0.099	0.607[f]	-----	----	0.301[f]
4	0.049	-----	0.099	0.805[f]	-----	----	0.467[f]
5	0.099	-----	0.099	0.763[f]	-----	----	0.471[f]

313nm, 13.5 hr.

[a] SF = 2.30, g.c. Column A @85°; [b] SF = 1.42, g.c. Column B @170°; [c] SF = 1.36, g.c. Column B @170°; [d] SF = 1.29, g.c. Column B @170°; [e] [C15] = 0.00443M, [C17] = 0.00368M; [f] [C15] = 0.00348M, [C17] = 0.00383M; [g] 10^{-3}M

Sample	[AP][g]	[$(APH)_2$][g]	[(APH)(PPH)][g]	[(PPH_2)]
1	0.93	2.56	5.86	4.31
2	12.30	----	4.27	10.50
3	4.86	----	----	1.49
4	6.44	----	----	2.31
5	6.11	----	----	2.33

Table 92. Quantum Yield Data for Formation of Acetophenone (AP) from the Reaction of α-Fluoroacetophenone with 2-Propanol

[2-Propanol]	AP/C17	[AP]^a	AP
0.058	0.254	3.01	0.170
0.177	0.485	5.74	0.324
0.175	0.702	8.31	0.470

[α-Fluoroacetophenone] = 0.10M, [C17] = 0.00458M, I_a = 0.0177 E/l, g.c. Column A @125°, SF = 2.58, 2 hr., 313nm.

$^a10^{-3}$M