EVIDENCE FOR CHARGE TRANSFER IN THE PHOTOREDUCTION OF α- TRIFLUOROACETOPHENONE BY ALKYL BENZENES

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ABSTRACT

EVIDENCE FOR CHARGE TRANSFER IN THE PHOTOREDUCTION OF α-TRIFLUOROACETOPHENONE BY ALKYL BENZENES

By

Richard Alan Leavitt

A comparison of the photoreactivities of acetophenone and trifluoroacetophenone triplets toward alkyl benzenes reveals differences in the mechanisms by which they abstract hydrogen atoms. The results, detailed below, suggest that the strongly electron-withdrawing trifluoromethyl group makes the trifluoroacetophenone triplets considerably more electron-deficient than the acetophenone triplets, so that they rapidly undergo charge transfer interactions with electron-rich alkyl benzenes prior to actual hydrogen atom abstractions.

(1) Quantum yields of (substituted) bibenzyl formation were measured as a function of hydrogen donor concentration with both trifluoroacetophenone and acetophenone. The rate constants of ketone triplet-donor interaction (k_r), derived from the quantum yields, for acetophenone were consistent with previous investigations, while the k_r values for trifluoroacetophenone were 16-140 times as large as the acetophenone values (e.g.,

73 and $1.2 \times 10^5 M^{-1} sec^{-1}$ respectively, with toluene). However, the quantum yields of bibenzyl formation were much lower with trifluoroacetophenone suggesting a new source of inefficiency occurring after the initial triplet interaction.

(2) Trifluoroacetophenone's k_r values were quite sensitive to substituents on the aromatic ring of the donor. A linear Hammett correlation of log k_r versus σ_p^+ (ρ = -1.80) was found with a series of p-substituted toluenes (p-Cl-, F-, CH_3-, CH_3O-, CN-, and H-) indicating that the primary trifluoroacetophenone triplet process involves the generation of a positively charged alkyl benzene.

(3) Toluene and toluene-d_3 were found to have identical k_r values with trifluoroacetophenone which suggests that the initial triplet reaction is not hydrogen abstraction. However, the large isotope effect (3.3) observed in the maximum quantum yields indicates that the inefficiency of product formation may be due to reverse charge transfer.

A similar effect was found with cumene and cumene-α-d, although a small isotope effect (1.25) in the k_r values may indicate some direct hydrogen atom abstraction in competition with charge transfer. Actually some hydrogen abstraction must occur since cyclohexane does photoreduce trifluoroacetophenone, although with a smaller rate constant ($3.7 \times 10^6 M^{-1} sec^{-1}$) than found for alkyl benzenes in general.

(4) p-Di-*t*-butylbenzene, which cannot undergo direct hydrogen abstraction, nevertheless quenches trifluoroacetophenone triplets with a rate constant ($1.3 \times 10^{7} M^{-1} sec^{-1}$) comparable to the k_r values found for toluene and p-xylene. Therefore triplet trifluoroacetophenone must undergo similar interactions with the three substrates.

(5) Trifluoroacetophenone, unlike acetophenone, does not show selectivity toward C-H bond strength and, for example, interacts faster with toluene than with cumene.

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To Susie who came into my life at the beginning of these studies and to Kristine Marie who came to life at the conclusion.

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The author never ceased to be amazed at the way Professor Peter J. Wagner, from a distance of thirty feet, could predict rate constants from vpc peaks that hadn't even come down to the base line yet. His never ending desire to be at the front of important developments characterizes his attitude toward both research and the welfare of his students. I sincerely appreciate having had the opportunity to work with him.

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PREFACE

The work presented in this thesis represents the fruition and expansion of ideas put forward in the author's Master's thesis (Michigan State University, 1969). Necessarily some duplication of content is unavoidable in order to give an orderly account on the subject material.

Many of the results and conclusions presented in this thesis are complementary to and indeed dependent upon those appearing in the Master's thesis. Thus, a summary of this previous work is quite necessary and will be included in the introductory section.

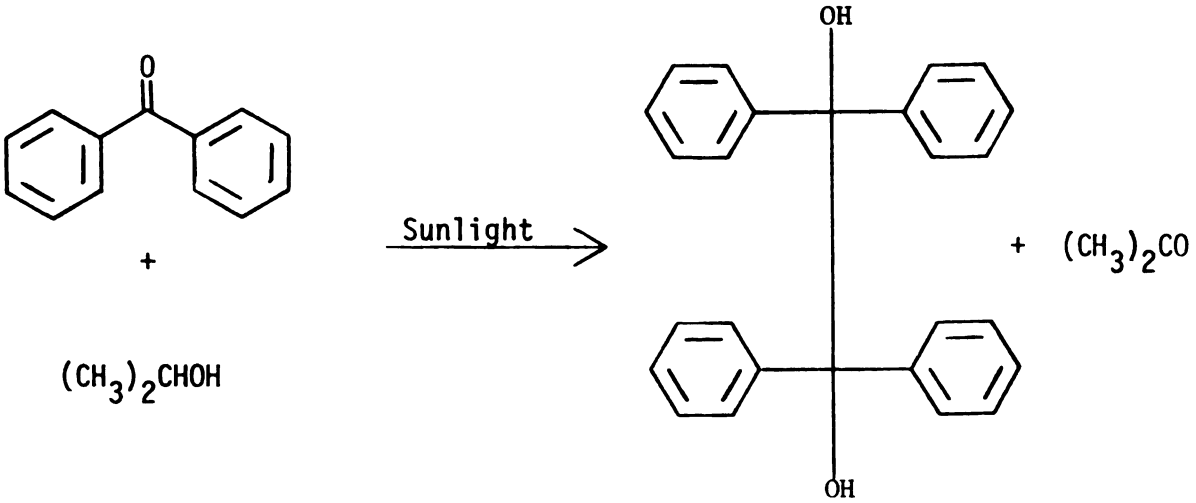
INTRODUCTION

This dissertation deals with the phenomenological events occuring after the absorption of light by alkyl aryl ketones in the presence of substrates formally capable of donating hydrogen atoms to such ketones. Specifically, the liquid phase intermolecular photoreduction of acetophenone and α-trifluoroacetophenone by various substituted alkyl benzenes has been examined in detail and new mechanistic conclusions drawn.

A. DEVELOPMENT OF MECHANISM.

1. Early Work.

Although photoreduction has always played an essential role in nature in the utilization of CO_2 by plants, products from even "simple" systems were not characterized until 1900, when Ciamician and Silber[1] first identified benzpinacol and acetone as the photoproducts from the action of sunlight on a solution of benzophenone in isopropyl alcohol. That particular system has been the subject of an enormous number of



(1)

papers and is still being actively investigated.[2]

Many other substrates have also been used as the hydrogen source, including, alkanes,[3] amines,[4] alkyl benzenes,[5] and tributylstannane,[6] in the photoreduction of aldehydes and ketones.

The current understanding of the mechanism(s) of photoreduction is based on a number of important observations and postulations. During the thirties several researchers[7-9] suggested that the photoactivated species responsible for the reaction was a biradical form of the carbonyl. Abstraction of hydrogen from the alcohol by this biradical would then yield two new radicals which subsequently could combine to give the observed products.

$$\mathrm{Ar_2CO} \xrightarrow{h\nu} \mathrm{Ar_2\dot{C}{-}\dot{O}} \xrightarrow{\mathrm{R_2CHOH}} \mathrm{Ar_2\dot{C}{-}OH} + \mathrm{R_2\dot{C}{-}OH} \qquad (2)$$

At first it was thought that products such as acetone arose from disproportionation of carbinol radicals[7,8] but Hirshberg[9] and later Pitts[10] found that optically active alcohols were not racemized when photolized in the presence of aryl ketones. Instead, carbinol radicals are apparently oxidized by reacting with ground state ketones, which in the case of the benzophenone-isopropyl alcohol system, is consistent with the observation that the quantum yield of ketone disappearance can approach 2, depending on the conditions used.[11,12]

$$\mathrm{Ar_2CO} + \mathrm{R_2\dot{C}OH} \longrightarrow \mathrm{Ar_2\dot{C}OH} + \mathrm{R_2CO} \qquad (3)$$

2. Identity of Reactive State.

Identification of the reactive excited state multiplicity responsible for photoreduction has come from both chemical and spectroscopic evidence. In 1955, Backstrom and Sandros[13] suggested that the earlier proposed biradical state could be considered equivalent to an excited triplet state and later found that the phosphorescence emission of biacetyl, which had been previously identified as occurring from the excited triplet state,[14] could be sensitized by benzophenone.[15] Terenin and Ermolaev[16] observed that in EPA glass at 77°K benzophenone sensitized the phosphorescence of naphthalene while simultaneously quenching its own phosphorescence. Also, oxygen,[10] paramagnetic metal chelates,[17] naphthalene,[18-20] conjugated dienes,[21] and various hydrogen donors[22] have all been found to quench the reactive state of benzophenone in liquid solutions. Hammond and co-workers confirmed that the reactive state was a triplet by measuring the excited state lifetimes of benzophenone in several solvent systems[5,23] and finding them much too long to correspond to excited singlet states.

Finally, although conclusive evidence for organic triplets had existed since 1945,[14b] it wasn't until 1963 that triplet states of ketones such as benzophenone[24] and 2-acetonaphthone[25] were observed directly by flash photolysis and their lifetimes measured.

3. n,π^* and π,π^* Triplets.

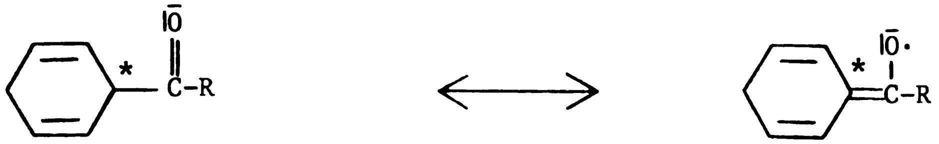
For aryl ketones the fact that two types of triplet states exist has caused considerable controversy in the interpretation of some results. The distinction between the two triplet states can be made by observation of their phosphorescence emission spectra at 77°K. n,π* triplets characteristically have much shorter emission lifetimes than π,π* triplets (on the order of several msec for n,π* and >50 msec for π,π*)[11,26] and π,π* triplet emission is much more solvent and substituent dependent.[27,28]

n,π* triplets formally arise via the promotion of a non-bonding oxygen electron to an antibonding π* orbital. The net result is a

$$\mathrm{C} = \underset{\cdot}{\dot{\mathrm{O}}}\!: \xrightarrow{n,\pi^*} \mathrm{C} \overset{*}{=} \underset{\cdot}{\dot{\mathrm{O}}}\!\cdot \qquad (4)$$

decrease in dipole moment relative to that in the ground state and a lengthened carbon-oxygen bond. Thus, with a lone non-bonding electron remaining, the oxygen becomes much more electrophilic relative to the ground state and resembles an oxy radical. In fact, Walling and Gibian,[29] Cohen and Baumgarten,[30] and Padwa[30] have found that the behavior of benzophenone, whose lowest triplet is clearly n,π* in character,[31] parallels very closely that of <u>tert</u>-butoxy radicals[32] in hydrogen abstraction from several donors.

π,π* triplets, on the other hand, involve the promotion of an electron from the π-system to an anti-bonding π* orbital. Lamola[33] has demonstrated that the π,π* triplet state of phenyl alkyl ketones corresponds to the lowest triplet state of benzene (^3L_a). Thus, unlike the n,π* triplet, the π,π* triplet has most of its excitation localized in the aromatic ring, and therefore, has an electron-rich rather than an electron-deficient carbonyl oxygen.[34]



One would expect this state to be nucleophilic and thus behave much differently toward hydrogen abstraction than the n,π^* triplet and indeed such is the case. Various naphthyl, p-phenyl and p-amino ketones, possessing lowest π,π^* triplets, show little or no tendency toward pinacolization in the presence of most hydrogen donors[6,11,27] except amines.[37-39] The significance of the latter will be presented later.

The controversy arises from situations where the n,π^* and π,π^* triplet levels are in energetic proximity. The π,π^* triplet of unsubstituted acetophenone lies only a few kcal/mole above the n,π^* triplet.[35,36] p-Methyl- or 2,3-dimethyl-substitution inverts the levels and a significant decrease in triplet reactivity is observed. Yang attributes this to a mixed state arising from vibronic coupling of π,π^* and n,π^* triplets; the more π,π^* character present the less the reactivity.

The same effect is observed for the type II reaction of phenyl alkyl ketones. Electron-donating substituents or high solvent polarity put the π,π^* triplet slightly below the n,π^* triplet and a substantial decrease in reactivity is reported.[40] Wagner and co-workers[41,42] suggest that a thermal equilibrium of the two states would still allow the upper n,π^* triplet to be the reactive state. Indeed, they have found that the reactivities of p-methoxyphenyl ketones are subject to the same inductive effects of γ and δ substituents and have the same dependence on γ C-H bond strength as unsubstituted phenyl ketones possessing n,π^* lowest triplets.

In the same context, the principal ketone studied in this thesis, α-trifluoroacetophenone, possesses a π,π^* lowest triplet,[43] and yet reacts much faster with alkyl benzenes than does acetophenone. Further aspects of this situation will be considered in the discussion section.

4. General Mechanistic Scheme and Kinetic Expressions.

One advantage liquid-phase photochemistry has over the gas-phase is that several kinetic simplifications can usually be made. Absorption of light by a ketone may produce several excited singlets with many vibrational levels. In solution, decay to the lowest excited singlet is almost instantaneous ($<10^{-12}$ sec). Thus, it may be assumed that all singlet reactions occur from the lowest singlet. For aryl ketones in general, the rate of intersystem crossing (isc) from singlet to triplet manifold is much faster (10^{11} sec^{-1})[44] than either fluorescence or radiationless decay. Thus, the excited triplet state is reached essentially with unit quantum efficiency.[45] Finally, the rate of phosphorescence is usually much slower than the rates of other triplet processes and can be ignored.

The following mechanistic scheme can be written for the photoreduction of ketone, A, by substrate, SH, in the presence of quencher, Q.

Scheme I

Process	Rate	
$A_o + h\nu \longrightarrow A^{1*} \xrightarrow{isc} A^{3*}$	Ia	(6)
$A^{3*} \longrightarrow A_o$	$k_d[A^{3*}]$	(7)
$A^{3*} + SH \longrightarrow AH\cdot + S\cdot$	$k_r[SH][A^{3*}]$	(8)
$A^{3*} + Q \longrightarrow A_o + Q^{3*}$	$k_q[Q][A^{3*}]$	(9)
$AH\cdot + AH\cdot \longrightarrow AHAH$		(10)
$AH\cdot + S\cdot \longrightarrow AHS$		(11)
$S\cdot + S\cdot \longrightarrow SS$		(12)

Under steady state conditions $d[A^{3*}]/dt = 0$ and the only directly measurable kinetic parameter is the quantum yield. Using the definition of Wagner,[46] the quantum yield for a particular photoprocess i is given by the following expression:

$$\Phi_i = \phi_{ES}\phi_R P_i \qquad (13)$$

where ϕ_{ES} represents the probabiiity that absorption of light will produce the requisite excited state; ϕ_R is the probability that the excited state will undergo the primary photoreaction necessary for process i; P_i is the probability that any metastable ground state intermediate will proceed to stable product, thus completing process i, rather than forming by-products or reverting to the ground state of the reactant.

Thus, since $\phi_{A^3*} = 1$ for aryl ketones

$$\Phi_{SS} = Y_{SS}P_{SS}\left(\frac{k_r[SH]}{k_r[SH] + k_d}\right) \tag{14}$$

Note that the factor Y_{SS}, the chemical yield of SS product, defined as [SS]/{2[SS] + [AHS]}, must be included since the measured quantum yield is based on only one of the products containing S· radicals. The term 2[SS] appears in the denominator since two ketone molecules are required for each SS molecule produced.

The ratio k_d/k_r can be determined by inverting equation (14).

$$\Phi_{SS}^{-1} = Y_{SS}^{-1}P_{SS}^{-1}\left(1 + \frac{k_d}{k_r[SH]}\right) \tag{15}$$

A plot of reciprocal quantum yield versus reciprocal substrate concentration is linear with an intercept equal to $Y_{SS}^{-1}P_{SS}^{-1}$ and a slope/intercept value equal to k_d/k_r.

When a triplet quencher is used, equation (14) becomes:

$$\Phi_{SS} = Y_{SS}P_{SS}\left(\frac{k_r[SH]}{k_r[SH] + k_d + k_q[Q]}\right) \tag{16}$$

Dividing equation (14) by equation (16) gives the familiar Stern-Volmer

$$\Phi_{SS}^{o}/\Phi_{SS} = 1 + k_q[Q]\tau \tag{17}$$

relationship where Φ^{o}_{SS} represents the quantum yield of SS formation in the absence of quencher and τ, the lifetime of the triplet state in the absence of quencher, is the reciprocal of the sum of the rates of all the reactions undergone by the triplet.

$$\tau = (k_r[SH] + k_d)^{-1} \tag{18}$$

A plot of relative quantum yield versus quencher concentration with constant substrate concentration is linear and has a slope equal to $k_q\tau$ and intercepts at 1.

The reciprocal of equation (18) is also useful since a plot of τ^{-1} versus substrate concentration is linear with an intercept equal to k_d and a slope equal to k_r.

B. PREVIOUS STUDY OF TRIFLUOROACETOPHENONE.

The substitution of fluorine for hydrogen at the α position of acetophenone results in a change in both absorption and emission spectra. The trifluoroacetophenone absorption spectrum is quite similar to but shifted ∿12 nm bathochromatically in the 230-300 nm region from that of acetophenone. The phosphorescence emission decay of trifluoroacetophenone at 77°K is exponential with a 57-msec lifetime in hydrocarbon glasses (0-0 band at 70.9 kcal) and a 200-msec lifetime in ethanol glass (0-0 band at 70.0 kcal). This implies that the L_a n,π* triplet lies slightly below the π,π* triplet, although both are undoubtedly populated at room temperature.[43]

In the author's Masters thesis the photochemical behavior of α-trifluoroacetophenone was compared to that of acetophenone using p-xylene as the hydrogen donating substrate. Basically three experiments were carried out with both ketones: 1) mass balance; 2) triplet quenching; and 3) quantum yield determination. The results of that study which have a direct bearing on the results appearing in the next section are summarized below.

With the mass balance experiment it was shown that in both cases the pinacol, bibenzyl, and cross-coupling products account for all the reacted ketone. Unambiguous identifications of the photoproducts were made with authentic samples and various spectral methods.

For each of five different p-xylene concentrations Stern-Volmer quenching of the triplet state with naphthalene at 366 nm was done to obtain values of τ according to equation (17). Plots of reciprocal lifetime versus p-xylene concentration according to the inverse of equation (18) then gave the values of k_d and k_r which appear in Table 1.

The absolute quantum yield of bixylyl was determined as a function of p-xylene concentration at 313 nm. Plots of inverse quantum yield versus inverse p-xylene concentration according to equation (15) gave values of k_d/k_r and Φ_{BB}^{max} which appear in Table 1.

The results of this study were quite interesting in two regards. While the reactivity of triplet acetophenone toward p-xylene agreed well with that predicted by previous investigations,[29,36,47] the rate constant, k_r, for trifluoroacetophenone triplet concentration with p-xylene was two orders of magnitude larger than that for acetophenone. Moreover, the quantum yield of bixylyl formation (Φ_{BB}^{max}) extrapolated to infinite p-xylene concentration was much lower for trifluoroacetophenone than for acetophenone.

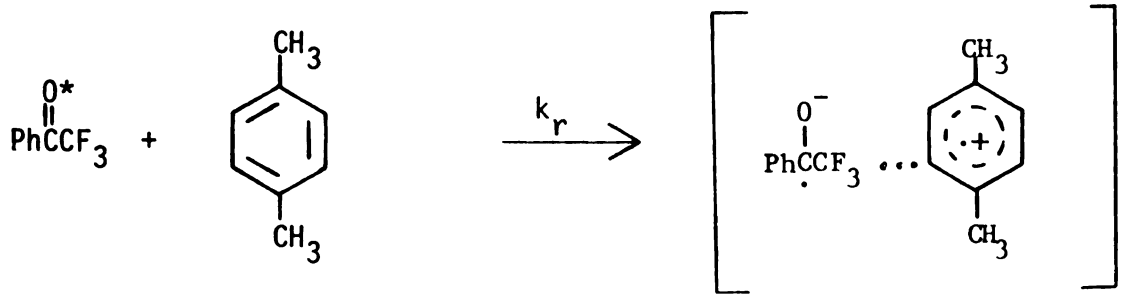
TABLE 1. Kinetic Data for the Photoreduction of Acetophenone (ACP) and Trifluoroacetophenone (TFA) by p-Xylene in Benzene.

Ketone	k_r,$M^{-1}sec^{-1}$ [a]	k_d,sec^{-1} [b]	k_d/k_r [c]	k_d,sec^{-1} [d]	Φ_{BB}^{max} [e]
TFA	9.7×10^7	7.0×10^6	0.091	8.8×10^6	0.040
ACP	7.0×10^5	4.9×10^5	1.01	7.1×10^5	0.102

[a] Slope of reciprocal lifetime plot. [b] Intercept of reciprocal lifetime plot. [c] Slope/intercept of reciprocal quantum yield plot. [d] Calculated from the slope of the reciprocal quantum yield plot and the value of k_r from the reciprocal lifetime plot. [e] Extrapolated quantum yield of bixylyl at infinite p-xylene concentration.

These results thus suggested that either the radicals produced in the trifluoroacetophenone-p-xylene system were considerably different from those of the acetophenone-p-xylene system or that in the trifluoroacetophenone-p-xylene system the photoreduction proceeded either partially or totally by another mechanism.

One of the suggestions for an alternate mechanism made at that time was for a charge transfer interaction between triplet trifluoroacetophenone and p-xylene in competition with direct radical formation. Subsequent decay of this state to give either radicals or ground state reactants could then account for the inefficiency of product formation.



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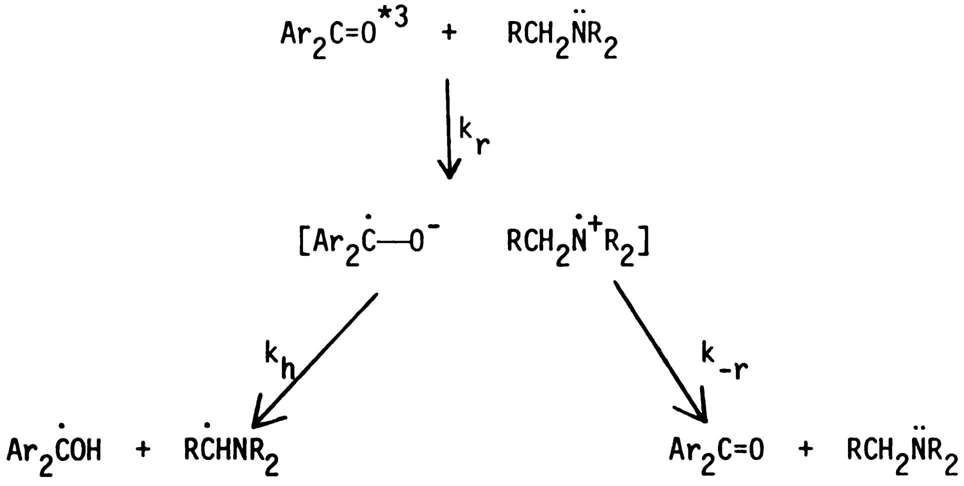
C. CHARGE TRANSFER.

The concept of charge transfer in photoreactions has previously been proposed for reductions involving amines.[27,48-50] In many cases ketones considered unreactive toward most hydrogen donors are easily reduced by amines; even normally reactive ketones have enhanced rates of interaction approaching the diffusion-controlled limit. For example, while the photoreduction of p-aminobenzophenone by 2-propanol is very inefficient, the bimolecular rate constant, k_r, for interaction with triethylamine is approximately $4 \times 10^{7} M^{-1} sec^{-1}$.[38] An extremely fast rate constant ($1.6 \times 10^{10} M^{-1} sec^{-1}$) has been reported for the photoreduction of fluorenone (π,π^* lowest triplet) by 1,4-bis(dimethylamino)benzene.[51]

Cohen has proposed that the great reactivity of amines may be associated with charge transfer or electron transfer to the ketone triplet proceeding actual proton transfer.



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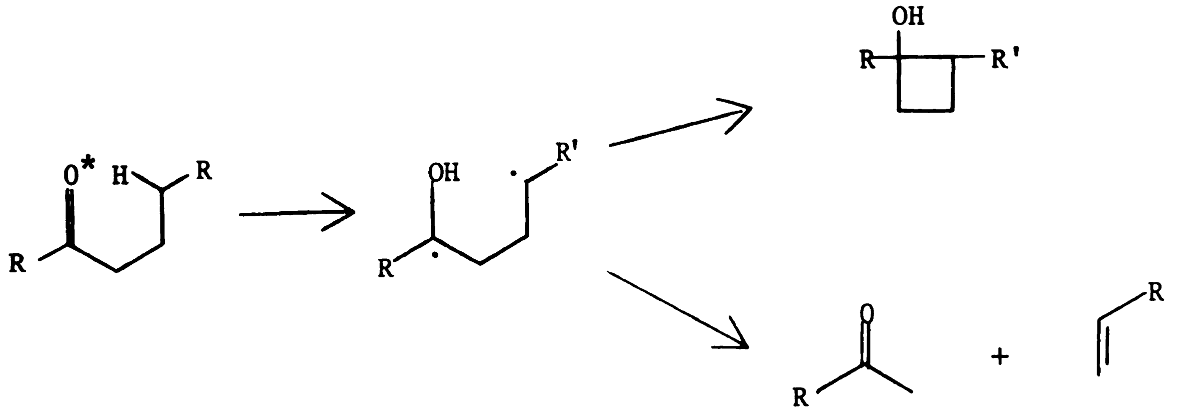
In concert with this notion Cohen has found that t-butylamine quenches the phosphorescence of benzophenone with a rate constant of $7 \times 10^{7} sec^{-1}$ which is only slightly less than amines possessing α-hydrogens and considerably larger than 2-propanol or benzhydrol.[52] In a recent study of fluorenone quenching by a series of p-substituted dimethyl anilines, Cohen and Parsons[51] found a linear relationship between log k_r and σ_p^+ values which supports the argument for development of positive charge at the nitrogen atom. In addition, reactions of similar systems show little sensitivity to C-H bond strength, no racemization of optically active amine, and no or very small deuterium isotope effects.[38,49]

The charge transfer mechanism has also been previously invoked to explain π,π^{*1} fluorescence quenching by amines.[54,56] Furthermore, plots of ϕ^{-1} versus $[\text{amine}]^{-1}$ have been found to curve sharply upward at high amine concentrations indicating singlet quenching.[38,47,56]

The type II reaction, expressed in general form below, shows close



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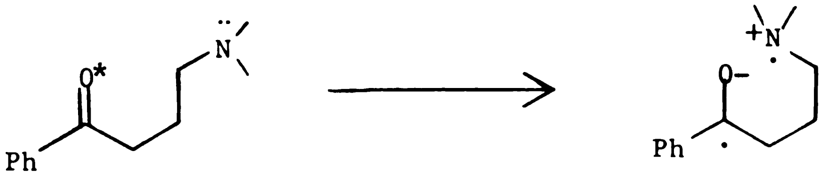
parallels with intermolecular photoreduction when amines are involved.[49,50] Again systems with low lying π,π^* triplets are found to have similar reactivities to those with n,π^* triplets.

Wagner and Kemppainen[50] in a recent study of γ-dimethylaminobutyrophenone and of amine quenching of valerophenone in various solvents have found evidence that the primary triplet ketone reaction in the presence of amines is not the normal type II γ-hydrogen abstraction process.[26] However, since they did not observe an expected rate enhancement in acetonitrile relative to that in benzene[57] they proposed the formation of a charge transfer complex between amine and ketone rather than actual electron transfer. Subsequent competitive decay of this state to the ground state and 1,4 biradicals would then account for the observed inefficiencies of product formation despite shorter triplet lifetimes.



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D. RESEARCH OBJECTIVES.

After the discovery that trifluoroacetophenone had unusual triplet state reactivity toward p-xylene a set of experiments was designed to test the validity of a charge transfer mechanism.

(1) With a charge transfer mechanism the rate constant, k_r, for triplet interaction with aromatic hydrogen donors should be sensitive to both electron donating and electron withdrawing substituents on the aromatic ring. Thus, the kinetics of photoreduction for trifluoroacetophenone with several p-substituted toluenes were examined.

(2) k_r for a charge transfer mechanism should be insensitive to deuterium substitution of the extractable hydrogens. Thus, comparisons with toluene-d_3 and cumene-α-d were made.

(3) A charge transfer mechanism would demand that even alkylbenzenes without abstractable hydrogens (α-H) be able to quench the trifluoroaceto-

phenone triplets. Thus, quenching with p-di-t-butylbenzene was examined.

(4) A comparison of trifluoroacetophenone reactivity with non-aromatic hydrogen donors was needed to set an upper limit on "normal" reduction by radical abstraction. Cyclohexane was chosen for this purpose.

(5) Actual electron transfer should be sensitive to solvent polarity. Thus, a comparison of reactivity in benzene and acetonitrile was made.

RESULTS

A. QUANTUM YIELD DETERMINATIONS.

Absolute quantum yields of (substituted) bibenzyl formation were determined for both acetophenone and trifluoroacetophenone as a function of hydrogen (deuterium) donating substrate concentration. Degassed benzene solutions containing 0.1 M ketone, internal standard (typically n-hexadecane, $\leq$ 0.004 M) and various concentrations of hydrogen donor (typically 2, 1, 0.75, and 0.5 M) were irradiated in parallel at 313 nm. After irradiation each tube was analyzed for bibenzyl product, cross-coupling product, and internal standard by vpc. Valerophenone actinometry, described in the experimental section, was used throughout to monitor the light absorption.

In all cases except for the acetophenone-toluene-d_3 system, plots of Φ_{BB}^{-1} versus $[SH(D)]^{-1}$ were linear and are depicted in Figures 1-5. Slopes drawn in these figures represent least squares fits of the data. Numerical slope and intercept values of these plots appear in Table 2. k_d/k_r and k_r values derived from these data and the k_d values from Table 1, are given in Tables 3 and 4.

B. KETONE TRIPLET QUENCHING.

1. With Naphthalene.

A comparison of trifluoroacetophenone triplet lifetimes in benzene and acetonitrile was made by using the Stern-Volmer relationship (equation

(17)) and the known k_q values for naphthalene in these solvents.[59] Degassed solutions containing 0.1 M ketone, 1.0 M p-xylene, 0.001 M C_{20} internal standard, and 0.00, 0.01, 0.02, 0.03, or 0.04 M naphthalene were irradiated in parallel at 366 nm to < 4% ketone conversion. Vpc analysis of bibenzyl and C_{20} peak areas permitted calculation of Φ^o_{BB}/Φ_{BB}. The Stern-Volmer plots were linear with $k_q\tau$ values (slopes) as indicated in Table 5.

2. With p-Di-*tert*-butylbenzene.

The quenching efficiency of p-di-*tert*-butylbenzene in the presence of trifluoroacetophenone and acetophenone was assessed using the Stern-Volmer relationship and known values of τ with toluene and p-xylene. Degassed benzene solutions containing 0.1 M ketone, internal standard ($\leq$ 0.004 M), constant concentration of hydrogen donor, and various concentrations of p-di-*tert*-butylbenzene were irradiated in parallel at 313 nm. Vpc analysis of bibenzyl or bixylyl and internal standard peaks permitted calculation of Φ^o_{BB}/Φ_{BB}. The Stern-Volmer plots were linear with $k_q\tau$ values as indicated in Table 5.

C. INTERSYSTEM CROSSING.

A comparison of the amount of *cis*-piperylene isomerized to *trans*-piperylene by trifluoroacetophenone and acetophenone will give the ϕ_{isc} for trifluoroacetophenone since ϕ_{isc} for acetophenone is unity.[45] Degassed benzene solutions containing 0.1 M ketone and 0.2 M *cis*-piperylene were irradiated in parallel at 313 nm to ∿10% formation of trans-piperylene. The data appearing in Table 14 yield a ϕ_{isc} value for trifluoroacetophenone of 0.95 which is considered to be within experimental error of 1.0, and henceforth, will be taken as unity in all calculations involving it.

TABLE 2. Least Squares Slope and Intercept Values from Φ_{BB}^{-1} versus [SH(D)] Plots for Trifluoroacetophenone (TFA) (Figures 1-4) and Acetophenone (ACP) (Figure 5).[a]

Ketone	Donor	Slope[b]	Intercept[b]
TFA	p-Methoxytoluene	0.53	10
TFA	p-Methyltoluene	2.3	25
TFA	p-Fluorotoluene	11	23
TFA	Toluene	22	19
TFA	p-Chlorotoluene	16	19
TFA	p-Cyanotoluene	2340	123
TFA	o-Methyltoluene	2.9	26
TFA	m-Methyltoluene	3.3 ± .1	33 ± 1
TFA	Toluene-d_3	80	66
TFA	Mesitylene	1.4	23
TFA	Cumene	28	14
TFA	Cumene-α-d	63	25
TFA	Cyclohexane	1060	434
ACP	p-Methyltoluene	9.9	9.8
ACP	Cumene	14	5.4
ACP	Toluene	45	7.7

[a] To check the reproducibility of these data, two completely separate determinations were made for the TFA-m-Methyltoluene system. The values given represent the averages of these two determinations.

[b] Values are estimated to be ± 3% per footnote a.

TABLE 3. Kinetic Data for Photoreduction of 0.1 M Trifluoroacetophenone by Hydrogen (Deuterium) Donating Substrates in Benzene.

Donor	Y_{BB}[a]	Φ_{BB}^{max}[b]	k_d/k_r[c]	$k_r, 10^7 M^{-1} sec^{-1}$[d]	σ_p^+[e]
p-Methoxytoluene	0.14	0.098	0.053	17	-0.78
p-Methyltoluene	0.26	0.040	0.091	9.7	-0.31
p-Fluorotoluene	0.24	0.044	0.48	1.8	-0.07
Toluene	0.24	0.053	1.2	0.73	0.00
p-Chlorotoluene	0.23	0.053	0.84	1.0	+0.11
p-Cyanotoluene	0.03	0.008	19	0.046	+0.65
o-Methyltoluene	0.24	0.038	0.11	8.0	
m-Methyltoluene	0.24	0.030	0.10 ± .005	8.8	
Toluene-d_3	0.24	0.015	1.2	0.73	
Mesitylene	0.30	0.044	0.061	14	
Cumene	0.25	0.073	2.0	0.44	
Cumene-α-d	0.25	0.039	2.5	0.35	
Cyclohexane[f]	0.08[g]	0.002	2.4	0.37	

[a] Y_{BB}, as defined in the introduction, is calculated from the $[(BB)/(CC)]_N$ values appearing in Table 8 using the following relationship: $Y_{BB} = [(BB)/(CC)]_N/\{2[(BB)/(CC)]_N + 1\}$. [b] Extrapolated quantum yield of (substituted) bibenzyl at infinite hydrogen (deuterium) donor concentration. [c] Slope/intercept values from Table 2. Values are estimated to be ± 5% based on that found for the TFA-m-Methyltoluene system. [d] Calculated from k_d/k_r values assuming $k_d = 8.8 \times 10^6 sec^{-1}$ (from Table 1). Values estimated to be reproducible ± 10%. [e] Reference (58). [f] BB is bicyclohexyl. [g] Takes into account cyclohexylbenzene.

TABLE 4. Kinetic Data for Photoreduction of 0.1 M Acetophenone by Hydrogen Donating Substrates in Benzene.

Donor	Y_{BB}[a]	Φ_{BB}^{max}[b]	k_d/k_r[c]	k_r, $10^5 M^{-1} sec^{-1}$[d]
p-Xylene	0.30	0.10	1.0	7.0
Cumene	0.28	0.18	2.5	2.8
Toluene	0.27	0.13	5.8	1.2
Toluene-d_3	0.27	e	e	e

[a,b,c] Same as Table 3. [d] Calculated from k_d/k_r values assuming $k_d = 7.1 \times 10^5 sec^{-1}$ (from Table 1). [e] Φ_{BB}^{-1} vs. $[SD]^{-1}$ was not linear.

TABLE 5. Triplet Quenching Parameters for Trifluoroacetophenone (TFA) and Acetophenone (ACP).

Ketone	Donor	Quencher	Solvent	$k_q\tau, M^{-1}$	$k_q, M^{-1}sec^{-1}$	τ,sec
TFA	p-Xylene[a]	Naphthalene	Acetonitrile	54.8	1.0×10^{10}[c]	5.5×10^{-9}
TFA	p-Xylene[a]	Naphthalene	Benzene	50.0	5.0×10^{9}[c]	1.0×10^{-8}
TFA	p-Xylene[b]	p-Di-*t*-butylbenzene	Benzene	0.25[d]	1.4×10^{7}	1.8×10^{-8}
TFA	Toluene[b]	p-Di-*t*-butylbenzene	Benzene	1.02	1.3×10^{7}	7.9×10^{-8}
ACP	Toluene[b]	p-Di-*t*-butylbenzene	Benzene	0.40[d]	3.1×10^{5}	1.3×10^{-6}

[a] 1.0000 M. [b] 0.5000 M. [c] Reference (59). [d] Stern-Volmer plots were made using only one concentration of p-di-*tert*-butylbenzene and should be regarded as estimates only.

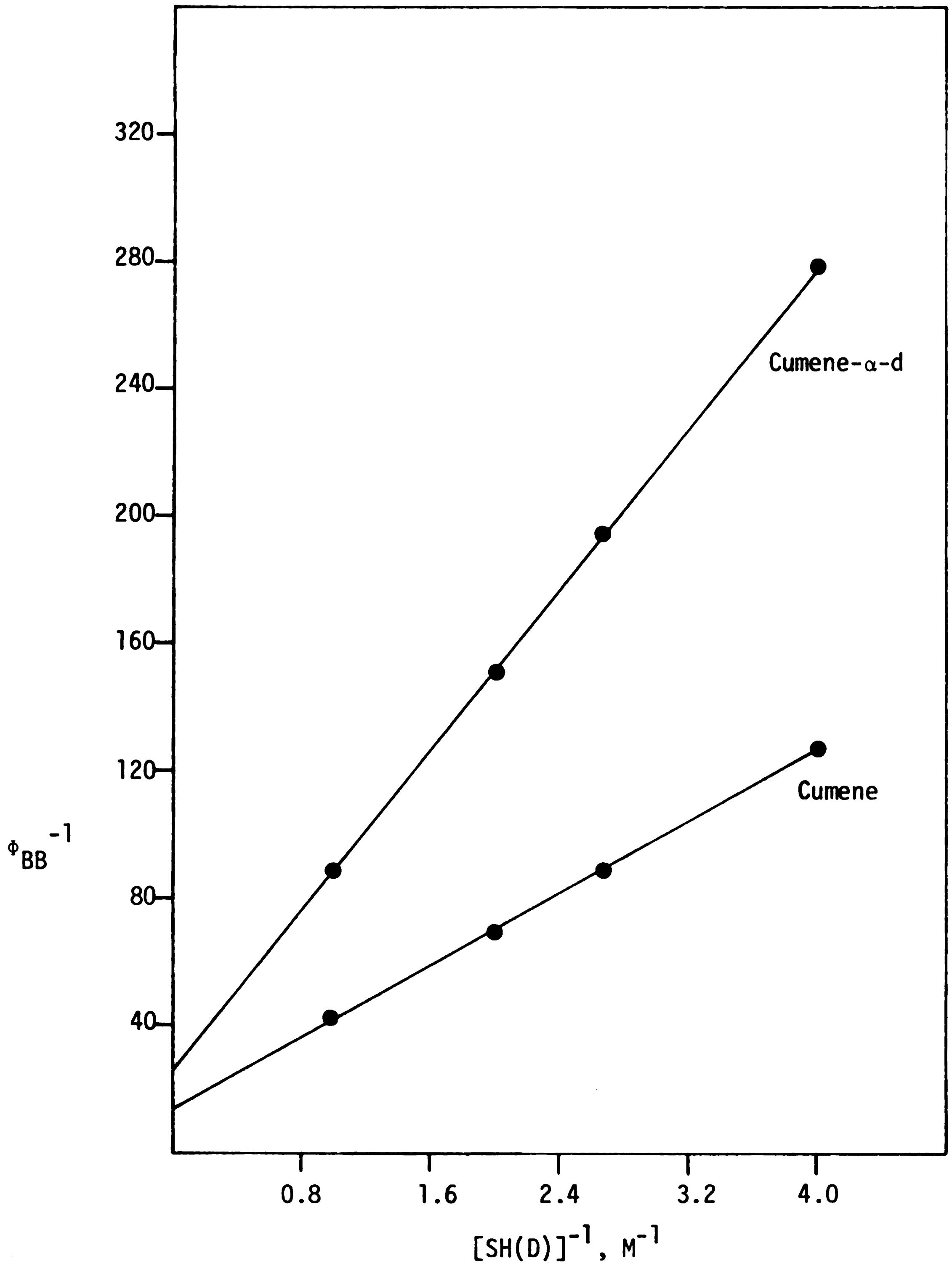


FIGURE 1. Reciprocal quantum yield plot for trifluoroacetophenone with cumene and cumene-α-d.

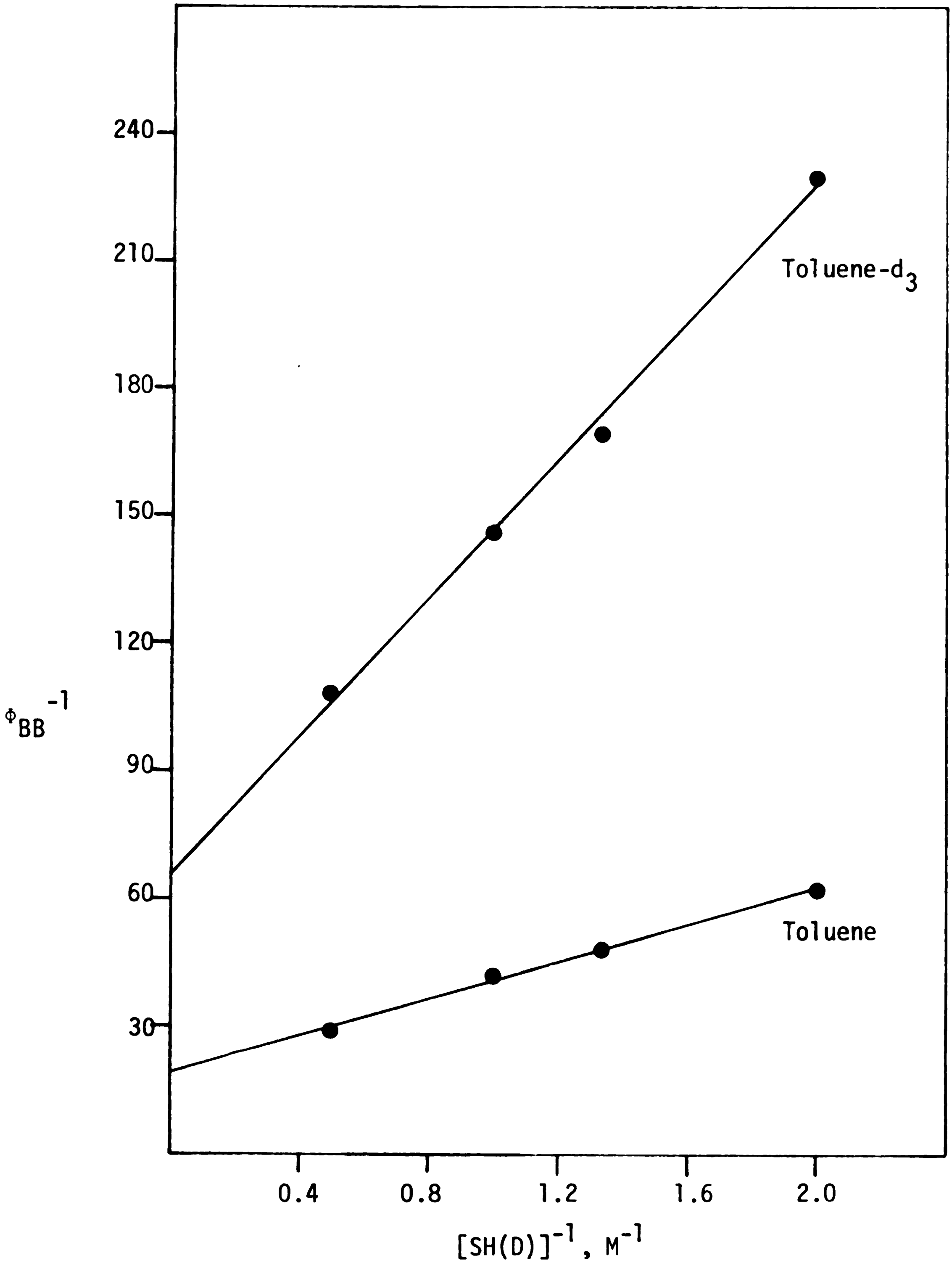


FIGURE 2. Reciprocal quantum yield plot for trifluoroacetophenone with toluene and toluene-d_3.

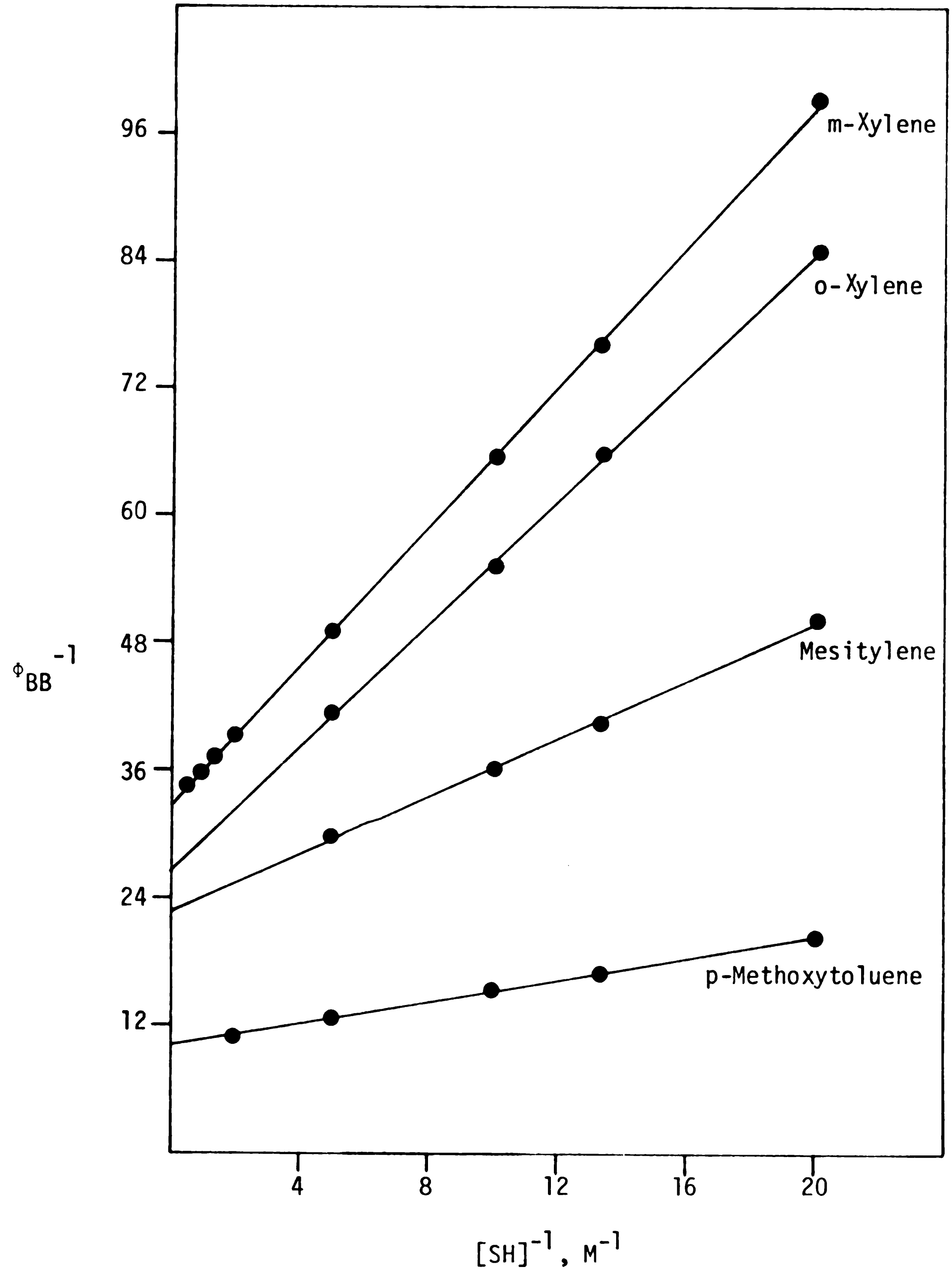


FIGURE 3. Reciprocal quantum yield plot for trifluoroacetophenone with m-xylene, o-xylene, mesitylene, and p-methoxytoluene.

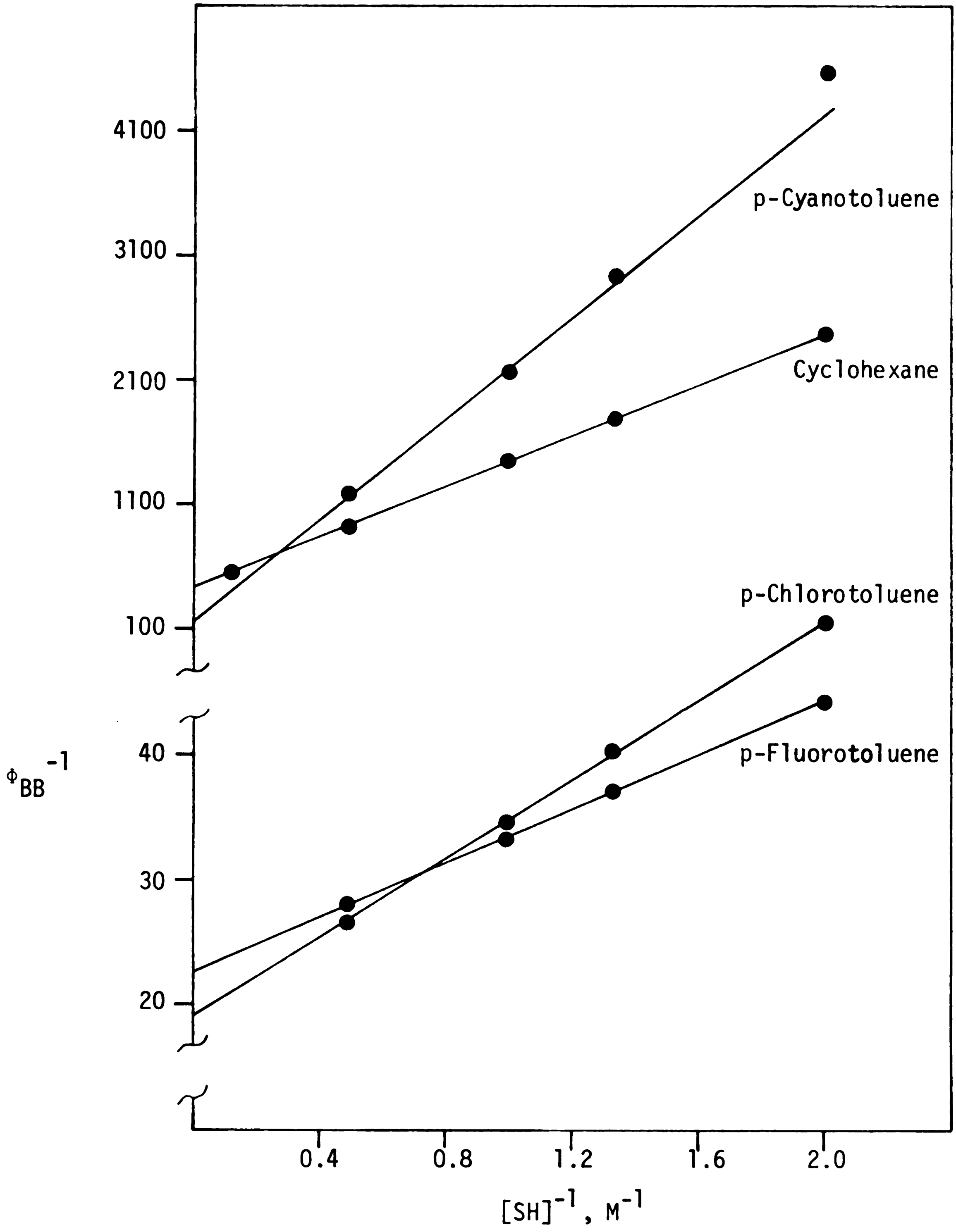


FIGURE 4. Reciprocal quantum yield plot for trifluoroacetophenone with p-cyanotoluene, cyclohexane, p-chlorotoluene, and p-fluorotoluene.

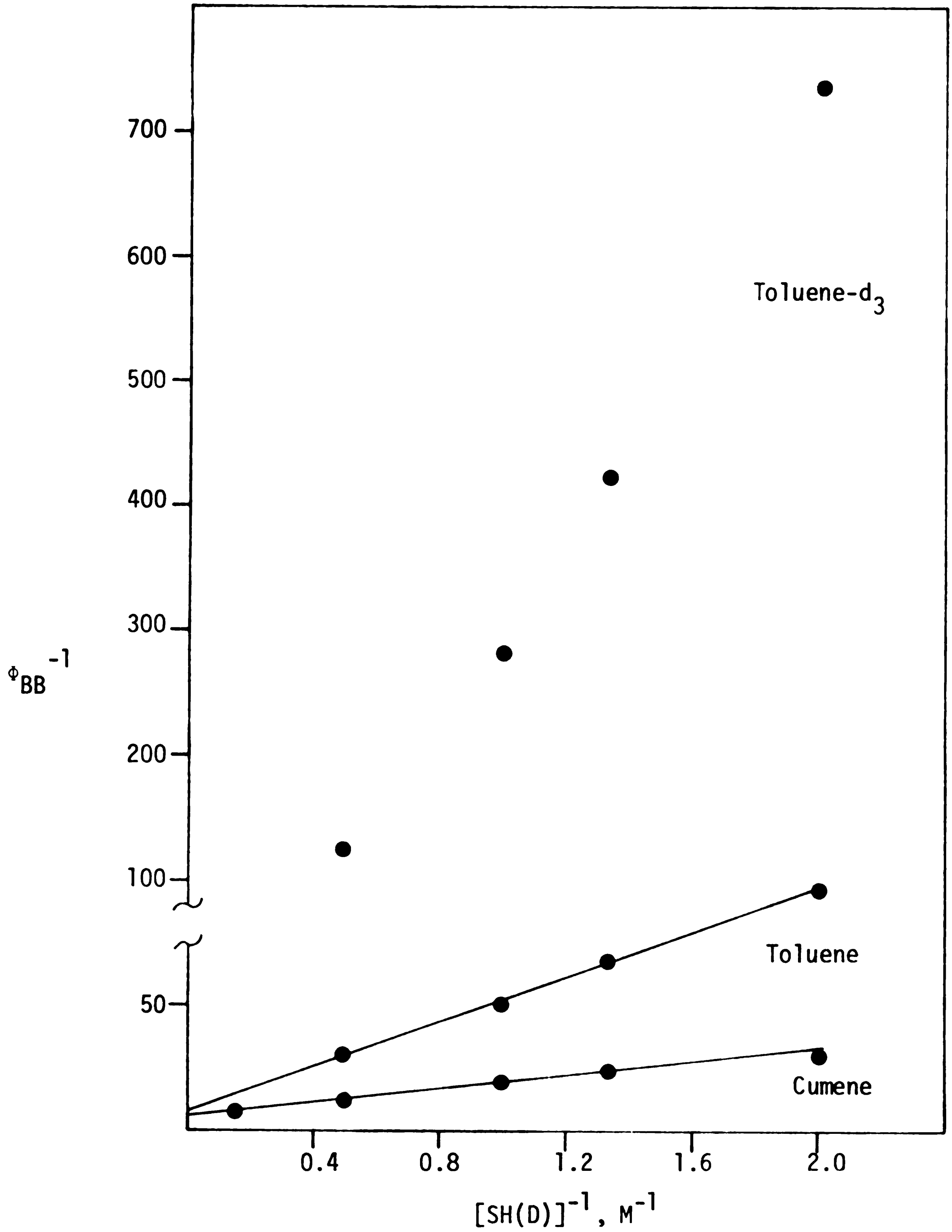


FIGURE 5. Reciprocal quantum yield plot for acetophenone with cumene, toluene, and toluene-d_3.

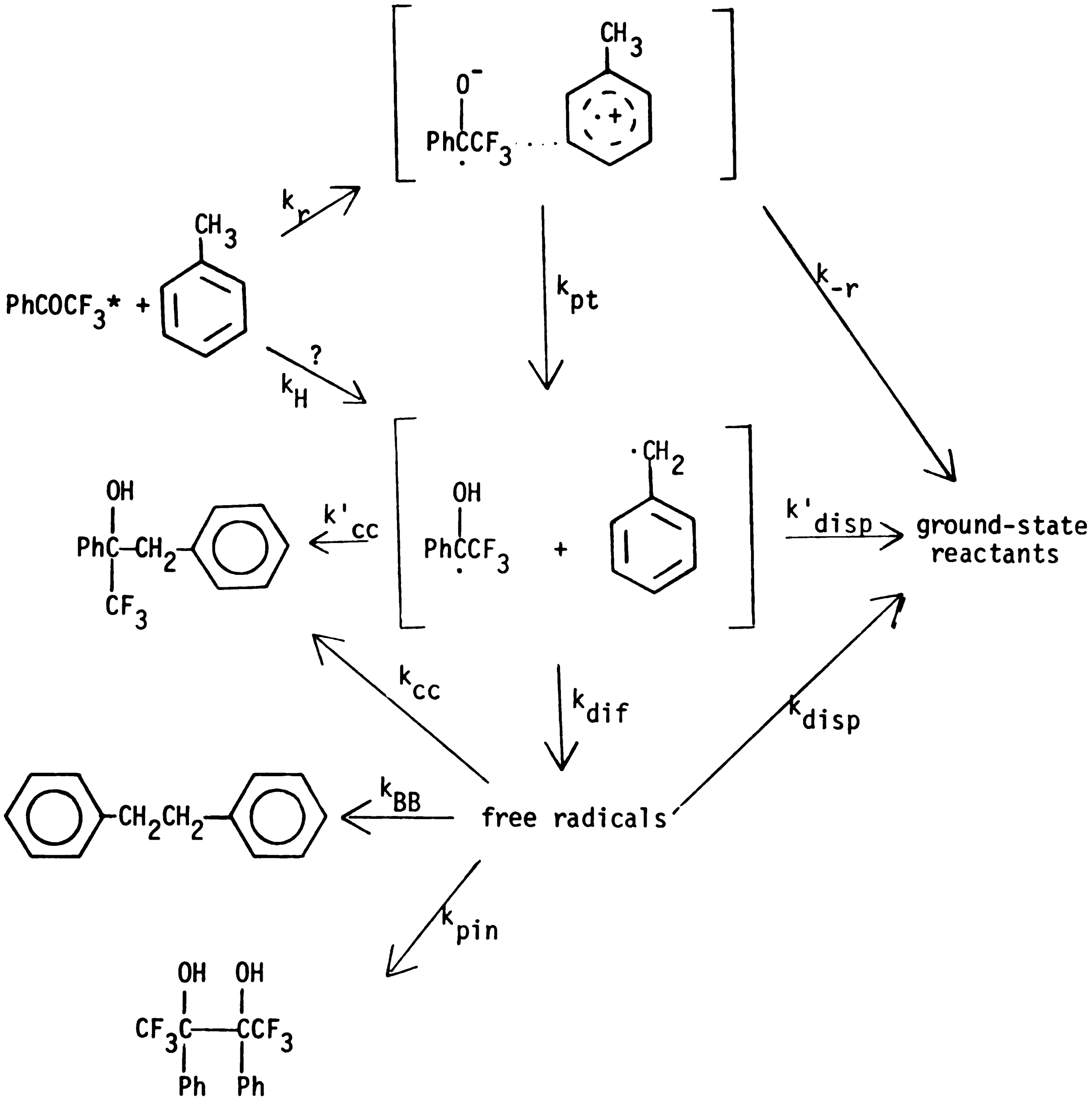
DISCUSSION

Presence of the trifluoromethyl group α to the carbonyl would be expected to have a profound influence on trifluoroacetophenone excited state reactivity. The strong electron-withdrawing group should make both the n,π^* and π,π^* trifluoroacetophenone triplets considerably more electron-deficient than those of acetophenone. For this reason one could reasonably expect trifluoroacetophenone triplets to interact with a given hydrogen donating substrate faster than do acetophenone triplets. As shown in the results section, such expectations are indeed realized (e.g., with p-xylene, k_r for trifluoroacetophenone is 140 times larger than k_r for acetophenone). However, certain relative reactivities and substituents effects are considerably different from what would be expected for a direct hydrogen abstraction process. Thus, consideration of an alternate mechanism to rationalize the differences in photochemical behavior between trifluoroacetophenone and acetophenone is warranted.

A. CHARGE TRANSFER MECHANISM

Scheme II incorporates a charge transfer mechanism into the general scheme of photoreduction presented in the introduction. Note that such a mechanistic scheme still allows for the possibility of direct hydrogen abstraction (k_H) and that a new source of inefficiency (k_{-r}) may lower quantum yields of bibenzyl formation.

SCHEME II



If charge transfer is a discrete step preceding hydrogen transfer, then certain qualitative predictions can be made concerning ketone triplet state reactivities and quantum yields. (1) Since for aromatic hydrogen donors charge transfer involves the formation of positive charge in the aromatic ring, the rate constant for that process should be enhanced with electron-donating and retarded with electron-withdrawing substituents on the ring. (2) Two effects should be observed when deuterium is substituted for hydrogen at the benzylic position of the donor: (a) One would expect k_r^H/k_r^D values very near unity since kinetics give only a measure of the initial triplet processes, which would not involve hydrogen atoms. (b) However, since hydrogen transfer (k_{pt}) must occur before product formation, a kinetic isotope effect greater than 1 should be manifest in the quantum yield of bibenzyl formation. (3) Charge transfer from aromatic donor to triplet ketone should occur even if the donor has no abstractable hydrogens. (4) In contrast to the direct hydrogen abstraction process, charge transfer interactions should be insensitive to C-H bond strength.

The results presented in the previous section do support in several ways a charge transfer mechanism for the photoreduction of trifluoroacetophenone in the presence of alkyl benzenes and are discussed individually below.

1. Hammett σ-ρ Relationship.

The first six hydrogen donors listed in Table 3, p-methoxy-, p-methyl-, p-fluoro-, p-chloro-, and p-cyanotoluene and toluene itself, show a very large spread in reactivity toward trifluoroacetophenone triplets, with p-methoxytoluene being ∿375 times more reactive than p-cyanotoluene. Such a large substituent effect would not be expected for simple alkoxy radical abstraction processes.[60,61] A Hammett plot

(Figure 6) of log k_r versus σ_p^+ values[58] is linear with slope of -1.80 as determined by least squares. This correlation with σ_p^+ thus agrees

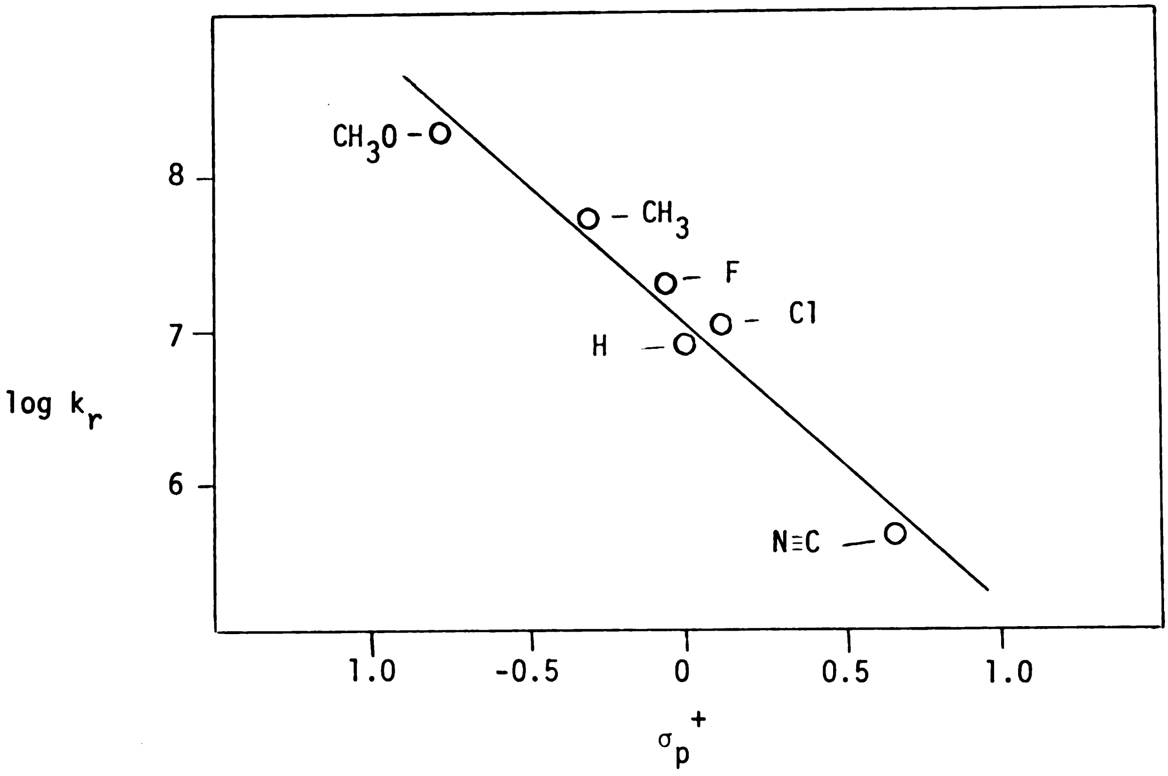


FIGURE 6. Interaction of trifluoroacetophenone triplets with p-substituted toluenes.

well with the notion of a positively charged alkyl benzene being generated in its interaction with triplet trifluoroacetophenone. The large negative ρ value is in sharp contrast with the -0.6 value found for hydrogen abstraction from alkyl benzenes by t-butoxy radicals at 40°C.[61]

This correlation also shows a striking similarity to the previously mentioned work of Cohen and Parsons.[51] They found ρ = -1.83 for a Hammett plot of fluorenone triplet interactions with p-substituted dimethylamines and concluded that electron transfer from nitrogen to ketone was the primary triplet reaction.

2. Charge Transfer Quenching.

p-Di-t-butylbenzene possesses no benzylic hydrogens and thus should be an exceedingly poor hydrogen donor compared to toluene. Such is certainly the case since no products derived from radicals of p-di-t-butylbenzene are found from photolyses with either trifluoroacetophenone or acetophenone. Yet the presence of p-di-t-butylbenzene does have a marked effect on the fate of trifluoroacetophenone triplets as shown in Table 5. The measured rate constants for the quenching of triplet ketone, k_q, are virtually the same with either p-xylene or toluene as substrate, 1.4 and 1.3 x $10^7 M^{-1} sec^{-1}$ respectively. For comparison, the respective rate constants for donor interactions with triplet trifluoroacetophenone are 9.7 and 0.76 x $10^7 M^{-1} sec^{-1}$. Thus, p-di-t-butylbenzene interacts with triplet trifluoroacetophenone almost twice as fast as does toluene but more slowly than does p-xylene. Such behavior, which cannot be hydrogen abstraction, must certainly be indicative of charge transfer interactions.

Cohen and Litt[52] found a similar phenomenon for quenching of benzophenone triplets with amines. Since product studies indicate that the abstracted hydrogen comes from C-H α to N, t-butylamine should have little effect on a strict hydrogen abstraction process. However, the similarity of k_r values for t-butylamine and 2-butylamine (7.0 and 25.0 x $10^7 M^{-1} sec^{-1}$ respectively) again suggests interception of ketone triplets before hydrogen abstraction via a charge transfer interaction.

Furthermore, the 10-fold increase in k_d for trifluoroacetophenone relative to acetophenone in benzene may itself reflect charge transfer quenching, with a rate constant of $8 \times 10^5 M^{-1} sec^{-1}$, by the aromatic solvent. Each alkyl group added to the benzene ring in effect increases the interaction by an order of magnitude. The effect apparently begins to level off with mesitylene since it is only 50% more reactive than the xylenes. The rapid decay rate in benzene[24,62,63] of triplet ketones in general has been attributed to radical-like additions[63] but could also be explained by charge-transfer. In that event a small fraction of acetophenone photoreduction by alkyl benzenes may proceed by charge transfer intermediates. p-Di-t-butylbenzene does quench acetophenone triplets with a rate constant ($3 \times 10^5 M^{-1} sec^{-1}$) ∿2% of that for trifluoroacetophenone triplets which is still ten times the possible bimolecular rate constant for benzene quenching.

3. Sensitivity to C-H Bond Strength.

Characteristic of radical processes, the rate of hydrogen abstraction from aliphatic hydrocarbons increases in the order primary < secondary < tertiary.[64] A comparison of k_r values for primary and tertiary benzylic hydrogen donors is quite revealing. Triplet acetophenone shows marked sensitivity toward C-H bond strength, being more than twice as reactive with cumene as with toluene, or seven times as reactive on a per hydrogen basis. This is in good agreement with a previous study which found a factor of 7.2.[29] Trifluoroacetophenone, on the other hand, displays no such selectivity, being almost twice as reactive with toluene as with cumene. A similar effect, in which electron transfer was proposed, has been observed for the cobaltic acetate oxidation of alkyl benzenes.[65] Such differences in selectivity clearly support a primary process other than direct hydrogen abstraction.

4. Deuterium Isotope Effects.

Hydrogen abstraction reactions generally show significant primary kinetic isotope effects since a considerable amount of bond breaking and bond making is involved in the transition state. For this reason studies of trifluoroacetophenone with toluene-d_3 and cumene-α-d were conducted.

Essentially no difference between toluene and toluene-d_3 was observed in the k_r values ($7.3 \times 10^6 M^{-1} sec^{-1}$). This would be quite unusual for a direct hydrogen abstraction process but quite compatible with charge transfer. Moore, Hammond and Foss[23b] found $k_r^H/k_r^D = 2.7$ for the photoreduction of benzophenone by benzhydrol and deuterium isotope effects >4 have been reported for the triplet type II (equation (21)) reactions of nonanophenone,[66] 5-decanone[67] and 2-hexanone.[68]

There is, however, a significant isotope effect on the quantum yields of bibenzyl formation. Table 3 shows that the maximum quantum yield with toluene-d_3 is 3.5 times smaller than that for toluene. This is an indication that after the charge-transfer complex is formed there is competition between proton transfer (k_{pt}) and back electron transfer (k_{-r}).

Unfortunately, it was not possible to make a direct kinetic comparison with the acetophenone-toluene-d_3 system since the Φ_{BB}^{-1} versus $[SD]^{-1}$ plot was not linear but curved upward, presumably because unimolecular radical scavanging reactions (by solvent or residual oxygen) begin to compete with coupling at low steady-state radical concentrations.

The individual quantum yields, however, were significantly lower than the corresponding ones with toluene.

The fact that trifluoroacetophenone triplets interact more slowly with cumene than with toluene suggests that the photoreduction with cumene may proceed in part by direct hydrogen abstraction and should thus exhibit a kinetic isotope effect. From Table 3 the k_r value for cumene-α-d is ∿20% less than the k_r value for cumene itself. The possible ± 10% experimental error in these values, however, makes the magnitude of the isotope effect difficult to assess. If one does use these k_r values and assumes an isotope effect of 5 for direct hydrogen atom abstraction, then one calculates that only 25% of the reaction with cumene involves direct hydrogen abstraction with a rate constant of $1.1 \times 10^6 M^{-1} sec^{-1}$. Again a significant isotope effect (1.9) is found in the intercepts of plots according to equation (15).

5. Solvent Effects.

Solvent effects were examined only briefly in this study but do deserve some comment. As shown in Table 5, the trifluoroacetophenone triplet lifetime in the presence of 1 M p-xylene is 10×10^{-9}sec in benzene while only 5.5×10^{-9}sec in acetonitrile. It's unlikely that k_d in acetonitrile cuuld be any larger that the $8.8 \times 10^6 sec^{-1}$ observed in benzene since in benzene k_d is already unusually large for reasons speculated on earlier. Thus k_r must increase by a factor of two in acetonitrile which, although not a large factor, is in the right direction to lend further support for the formation of charged species as the primary photochemical process of triplet trifluoroacetophenone.

6. Non-aromatic Donor.

Cyclohexane was the only non-aromatic hydrogen donating substrate utilized in this investigation and was needed to establish an upper limit for the amount of direct hydrogen abstraction by trifluoroacetophenone triplets. Its rate constant of $3.7 \times 10^{6} M^{-1} sec^{-1}$ made it second only to p-cyanotoluene as the least reactive donor measured and is significant in two regards. First, triplet trifluoroacetophenone is about an order of magnitude more reactive toward it than is triplet acetophenone.[29,69] Second, the relative smallness of this rate constant emphasizes the difference in the behavior of aromatic hydrogen donors toward trifluoroacetophenone triplets.

Benzophenone and acetophenone have been reported to be 2-3 times more reactive with cyclohexane than with toluene; and yet for trifluoroacetophenone the factor is reversed, toluene being twice as reactive as cyclohexane. Since the primary triplet reaction with cyclohexane must be hydrogen abstraction, this behavior is again a good indication that the primary trifluoroacetophenone triplet interaction with alkyl benzenes is not direct hydrogen abstraction. However, this study and results presented for cumene point out the fact that a small amount of direct hydrogen abstraction can compete with charge transfer. The amount proceeding via direct hydrogen abstraction is most important with the less reactive donors and with donors of secondary and tertiary hydrogen atoms.

7. Yields and Quantum Yields.

Quantum yields of bibenzyl formation are considerably lower for trifluoroacetophenone than for acetophenone. Theoretically, the maximum quantum yield would be 0.5 if every triplet ketone molecule produced one benzyl radical and that radical then coupled only with a like radical. However, maximum quantum yields are considerably less than 0.5 because benzyl radicals cross-couple with trifluoromethyl phenyl carbinol radicals. The maximum quantum yield of bibenzyl formation is equivalent to the Y_{BB} values appearing in Tables 3 and 4.

If one assumes little difference in rates of radical recombination, then a statistical recombination of radicals would produce two molecules of cross-coupling product for every one bibenzyl molecule, resulting in $Y_{BB} = 0.25$. Examination of the Y_{BB} values for trifluoroacetophenone in Table 3 shows the majority to be 0.25 ± 0.01 indicating close to statistical recombination of radicals. In the case of acetophenone the Y_{BB} values (0.27-0.30) from Table 4 show a somewhat higher proportion of like radical coupling. These values for both ketones would further suggest that, after their formation, the radicals have time to diffuse out of the solvent cage before recombination, since otherwise cross-coupling products would dominate.

The observed quantum yields of bibenzyl formation extrapolated to infinite donor concentration were much lower than the 0.25 predicted by Y_{BB} values for a statistical product distribution. For trifluoroacetophenone, the highest quantum yield was 0.098 with p-methoxytoluene, most of the others being in the 0.03-0.07 range. Quantum yields were substantially higher for acetophenone, being, for example, 0.18 with cumene.

The efficiency with which bibenzyl is formed after the primary triplet state process can be calculated by the following expression.

$$P_{BB} = \Phi_{BB}^{max}/Y_{BB} \tag{23}$$

For trifluoroacetophenone these values are all less than 0.30 with the exception of p-methoxytoluene ($P_{BB} = 0.70$). Each of the corresponding values for acetophenone is more than twice as large as the for trifluoroacetophenone. However, they are still significantly less than one (the largest value was 0.64 with cumene) and must indicate some disproportionation of the radicals. If one assumes similar amounts of radical disproportionation with trifluoroacetophenone, then the much smaller P_{BB} values would indicate that a large portion of the charge transfer interactions do not result in radical formation but instead in reversion to the ground state of the reactants via reverse electron transfer. This would be in agreement with the previously mentioned isotope effects on Φ_{BB}^{max}.

B. WHICH TRIPLET REACTS?

Trifluoroacetophenone is an unusual ketone in that it possesses both a π,π^* lowest triplet and enhanced triplet state reactivity. Although ketones with π,π^* lowest triplets are generally quite unreactive in photoreduction processes, two types of exceptions apparently exist. (1) Ketones that have a n,π^* triplet only a few kcal above the π,π^* triplet show moderate reactivities which can be attributed to either reactions from an equilibrium concentration of the upper triplet (n,π^*) or vibronic coupling of the two states, producing a π,π^* lowest triplet with some n,π^* character.

Regardless of how it is stated, the point is that the n,π^* state still directs the abstraction process. The high photoreactivity of trifluoroacetophenone relative to acetophenone with cyclohexane can best be attributed to the fact that the trifluoromethyl group creates a more electron-defficient, and thus more reactive, n,π^* triplet state.

(2) Ketones with π,π^* lowest triplets show enhanced reactivities in the presence of substrates capable of electron donation. Amine donors apparently have sufficiently low ionization potentials that they can give up electrons in preference to hydrogen atoms. On the other hand, trifluoroacetophenone triplets, in contrast to ketone triplets in general, apparently have a sufficiently high electron affinity that they can abstract electronic charge from such weak donors as alkyl benzenes.

To speculate on which state is responsible for this charge transfer to difficult at this point and could easily be a combination of the two states with k_r being given by the following expression,

$$k_r = X_n k_{CT}{}^{n} + X_\pi k_{CT}{}^{\pi} + X_n k_H \tag{24}$$

where X_n and X_π are the equilibrium concentrations of n,π^* and π,π^* triplets; k_{CT} are rate constants for charge transfer; and k_H is the rate constant for hydrogen atom abstraction.

C. SUMMARY.

The involvement of charge transfer in the photoreduction of trifluoroacetophenone by alkyl benzenes donors is well supported. Triplet reactivities showed marked sensitivity toward substituents on the aromatic ring of the donor, yielding a large negative ρ value from a Hammett relationship; a donor without abstractable hydrogens was found to interact with the triplets as efficiently as those donors with abstractable hydrogens; the rate constants of triplet-donor interaction were not reduced by deuterium substitution; and the reactivities did not display sensitivities to C-H bond strength, as is characteristic of hydrogen atom abstraction processes. However, direct hydrogen abstraction may be a minor competing factor since cyclohexane does photoreduce trifluoroacetophenone, although with a considerably slower rate than the aromatic donors.

D. FURTHER EXPERIMENTS.

The following experiments are just a sample of the many kinds of things that could be done with systems of a similar nature.

(1) Since the question of which triplet reacts has not been answered, future research could be directed toward elucidation of the triplet state responsible for charge transfer. The spacing of trifluoroacetophenone η,π^* and π,π^* triplets is much too close for studies of this nature. However, with appropriate substitution on the aromatic ring it should be possible to create situations where either the η,π^* or the π,π^* triptet is much lower than the other.

(2) In view of the exceedingly rapid donating capabilities of substituted amines and the rapid accepting properties of trifluoroacetophenone it should be possible to observe charge transfer interactions of the ketone singlet state.

(3) Other α-substituted acetophenones could be examined to ascertain how strongly electron-withdrawing the group need be to induce charge transfer.

EXPERIMENTAL

PART I. MATERIALS AND PROCEDURES.

A. PREPARATION AND PURIFICATION OF MATERIALS.

Purity is of critical importance in determining photochemical rate constants, since even small amounts of quencher can have large effects on slow rate constants. For example, for a hydrogen donor ($k_r = 1 \times 10^6 M^{-1} sec^{-1}$) containing 0.1% quenching ($k_q = 5 \times 10^9 M^{-1} sec^{-1}$) impurities, the intercept of the plot according to equation (15) becomes

$$\Upsilon^{-1}P^{-1}[1 + \frac{(5 \times 10^9)}{(1 \times 10^6)}(0.001)] \qquad (25)$$

or $6\Upsilon^{-1}P^{-1}$ instead of $\Upsilon^{-1}P^{-1}$ when no quencher is present. Thus, k_r (observed) would be six times the k_r (actual) with no quencher present. Therefore, all compounds used in the photolyses described in this thesis were carefully scrutinized by vpc after purification to insure against such occurrences.

1. Ketones.

a. α-Trifluoroacetophenone (Columbia Organic Chemicals) as received contained ∿10% impurities. Purification by spinning band distillation at atmospheric pressure gave a center cut that was >99.9% trifluoroacetophenone. The results of a photolysis check for quenching impurities by varying the concentration of ketone with a constant amount of hydrogen donor indicated no quenching impurities present ($k_q\tau$ = 103 and 101 for 0.1 and 0.2 M trifluoroacetophenone respectively, in the presence of 0.5 M p-xylene).

b. Valerophenone (Aldrich Chemical Company) for actinometry purposes, was distilled under reduced pressure, passed through alumina, and redistilled.

c. Acetophenone (Matheson Coleman and Bell) was distilled under reduced pressure and the center cut retained.

2. Solvents.

a. Benzene (Fisher Scientific Company, 99% thiophene free) was stirred over concentrated H_2SO_4 several times (24 hour periods) until the acid layer no longer turned yellow. The benzene was then successively washed with 1 M NaOH, distilled water, and saturated NaCl solution, followed by drying over anhydrous $MgSO_4$ and fractional distillation from P_2O_5. Only the center cut (∿80%) was retained.

b. Acetonitrile (Fisher Scientific Company) was distilled from $KMnO_4$ and Na_2CO_3 according to the procedure of O'Donnell, Ayres and Mann.[70] The center cut of a final fractional distillation was retained.

3. Hydrogen (Deuterium) Donors.

a. Toluene (Fisher Scientific Company) purification was analogous to that of benzene except that the bottle of toluene was kept in cold water while stirring with concentrated H_2SO_4 to minimize sulfonation.

b. Toluene-d_3 (Merck Sharp and Dohme of Canada Limited, 5 g, 99 mole % D) was used as received.

c. p-Chlorotoluene (Eastman Organic Chemicals) purification was analogous to that of benzene.

d. p-Fluorotoluene (Matheson Coleman and Bell) purification was analogous to that of benzene.

e. p-Methoxytoluene (Columbia Organic Chemicals) was purified by successively washing with 1 M NaOH, distilled water, and saturated NaCl solution, and dried over anhydrous $MgSO_4$. The center cut was retained from a fractional distillation over sodium.

f. p-Cyanotoluene (Eastman Organic Chemicals) was fractionally distilled from P_2O_5 and the center fraction retained.

g. p-Xylene (Aldrich Chemical Company) purification was analogous to that of toluene.

h. m-Xylene (Eastman Organic Chemicals) purification was analogous to that of toluene.

i. o-Xylene (Aldrich Chemical Company, 99+ %) purification was analogous to that of toluene.

j. Mesitylene (Matheson Coleman and Bell) purification was analogous to that of toluene except that it was fractionally distilled under reduced pressure.

k. Cyclohexane (Fisher Scientific Company) purification was analogous to that of benzene.

l. Cumene (Eastman Organic Chemicals) purification was analogous to that of toluene.

m. Cumene-α-d was prepared by reducing α-chlorocumene with a 1:1 molar ratio of $LiAlD_4$ (International Chemical and Nuclear, 99 atom % D) and $AlCl_3$. 4.66 g (0.111 mole) $LiAlD_4$ were covered with 100 ml of glyme (distilled from P_2O_5) in a 500 ml 3-necked flask equipped with a mechanical stirrer, condenser and an addition funnel containing 34 g (0.21 mole) α-chlorocumene in 75 ml of glyme. A slury of 14.82 g (0.111 mole) $AlCl_3$ in 100 ml of glyme was slowly added to the $LiAlD_4$ solution. The mixture was brought to reflux before adding the α-chlorocumene over a one hour period. After an additional hour of refluxing and subsequent cooling, 100 ml of wet ether was added to destroy any unreacted $LiAlD_4$-$AlCl_3$. The resultant solution was poured into 100 ml of 10% H_2SO_4 and the ether layer separated. The aqueous layer was extracted with three 50 ml portions of ether which were subsequently combined with the original ether layer. The ether was successively washed with saturated $NaHCO_3$ solution, cold distilled water, and saturated NaCl solution, and dried over anhydrous $MgSO_4$. The ethers were removed by distillation on a spinning band column to minimize loss of cumene-α-d. The subsequent purification procedure, analogous to that of toluene, removed the major side product, α-methylstyrene. Distillation on a spinning band column afforded a center cut that was >99.98 % cumene-α-d, with no detectable α-methylstyrene. Mass spectral analysis showed the cumene-α-d to be 96.4% d_1.

4. Quenchers.

a. Cis-piperylene (Aldrich Chemical Company) was passed through alumina followed by distillation.

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

c. p-Di-tert-butylbenzene obtained from student preparations (Friedel Crafts alkylation of benzene) was purified by three recrystallizations from methanol, mp 77-78°C.

5. Photoproducts for Identification and Standardization.

a. Bibenzyl (Aldrich Chemical Company) was recrystallized twice from methanol.

b. Bicumyl (Columbia Organic Chemicals) was recrystallized twice from methanol.

c. Bi-p-xylyl (Aldrich Chemical Company) was recrystallized twice from methanol.

d. Bicyclohexyl was prepared using the method of Wilds and McCormack,[71] which is a coupling reaction of cyclohexyl bromide induced by $CoCl_2$.

6. Internal Standards.

a. Dodecane (Aldrich Chemical Company) purification was analogous to that of benzene with a final distillation under reduced pressure.

b. Tetradecane (Columbia Organic Chemicals) purification was analogous to that of dodecane.

c. Pentadecane (Columbia Organic Chemicals) purification was analogous to that of dodecane.

d. Hexadecane (Aldrich Chemical Company) purification was analogous to that of dodecane.

e. Octadecane (Aldrich Chemical Company) purification was analogous to that of benzene with a final recrystallization from ethanol.

f. Nonadecane (Chemical Samples Company) was used without further purification.

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

7. Other Materials.

a. α-Methylstyrene (Aldrich Chemical Company) was used as received in the preparation of α-chlorocumene.

b. α-Chlorocumene was easily prepared by adding gaseous HCl to stirring α-methylstyrene cooled to 0°C. A manometer attached to the reaction flask indicated when the reaction was completed. After aspiration to remove excess HCl and drying over anhydrous $MgSO_4$, the liquid was fractionally distilled under reduced pressure. The center cut was retained for the preparation of cumene-α-d.

c. 1,2-Dimethoxyethane (Mallinckrodt Chemical Works) was fractionally distilled from P_2O_5.

C. PHOTOLYSIS PROCEDURE.

1. Preparation of Samples.

Class A volumetric flasks and pipettes were used exclusively to make up solutions for photolysis. Typically, two stock solutions, ketone-internal standard and hydrogen donor, were prepared. The appropriate amount of internal standard was weighed into a 10 ml volumetric flask and filled to the mark with solvent. 1 ml was then pipetted into a 5 ml volumetric flask containing the appropriate amount of weighed ketone and diluted to the mark with solvent. Likewise, the hydrogen donor was weighed into a 10 ml volumetric flask and diluted to the mark with solvent.

Into each of four 10 ml volumetric flasks was placed 1 ml of the ketone-internal standard stock solution, 1, 1.5, 2, or 4 ml of hydrogen donor stock solution, and solvent to fill to the mark. From each of these solutions three exactly 2.8 ml portions were withdrawn via a 5 ml syringe and injected into 13 x 100 mm pyrex culture tubes which had been drawn into small capillaries about 2 cm from the open end to facilitate sealing after degassing.

On occasions when the hydrogen donor was in limited supply (cumene-α-d and toluene-d_3) two 2.4 ml portions drawn from 5 ml volumetric flasks were injected into drawn tubes containing eleven 4 mm glass beaks. This amount of glass beads was found to keep the level of liquid high enough in the photolysis tubes to receive all the light and yet not interfere with the photolysis.

2. Degassing.

In order to remove dissolved oxygen, sample tubes were attached to a vacuum line over no. 00 one-holed rubber stoppers on individual stopcocks. The solutions were slowly frozen above liquid nitrogen and then immersed before opening to the vacuum. A minimum vacuum of 0.005 torr was attained before closing the stopcocks and allowing the tubes to thaw. After the fourth freezing and evacuation the tubes were sealed off with a torch.

3. Irradiation.

Sample tubes were irradiated in parallel on a rotating merry-go-round apparatus[72] immersed in a water bath at 25°C, to insure that the same amount of light impinged upon each sample. For quantum yield determinations a 450 watt Hanovia medium pressure mercury lamp housed in a water cooled quartz immersion well was used. The 300-320 nm region was isolated with a 1 cm path of 0.002 M potassium chromate in a 1% aqueous solution of potassium carbonate. For naphthalene quenching experiments the 366 nm region was isolated with a set of corning no. 7083 filter combinations.

D. ANALYSIS OF PHOTOLYSATE.

1. Instruments.

All analyses for photoproducts were made on the following two vpc's which used flame ionization detectors.

VPC-1: Aerograph Hy-Fi model 600D with 550 oven and 328 programmer. Leeds and Northrup Speedomax H recorder equipped with model 207 Disc integrator.

VPC-2: Varian Aerograph 1200. Leeds and Northrup Speedomax W recorder equipped with model 224 Disc integrator.

A variety of vpc columns were utilized as designated below.

COL-1: 6' x 1/8" Aluminum containing 4% QF-1, 1.2% Carbowax 20 M on 60/80 chromosorb G.

COL-2: 6' x 1/8" stainless steel containing 5% SE-30, a/w DEGS on chromosorb W.

COL-3: 25' x 1/8" aluminum containing 25% 1,2,3-Tris(2-cyanoethoxy) propane on 60/80 chromosorb P.

COL-4: 6' x 1/8" stainless steel containing 3% SE-30 on 100/120 varaport 30.

COL-5: 1.5' x 1/8" aluminum containing 15.5% diisodectylphthalate on 60/80 chromosorb P.

COL-6: 8' x 1/8" aluminum containing 4% QF-1, 1% carbowax 20 M on 60/80 chromosorb G.

2. Product Identification.

Photoproducts were identified primarily by their vpc retention times and comparisons to authentic samples.

The photolysate of trifluoroacetophenone with any of the hydrogen donors used always contained the three products shown below.

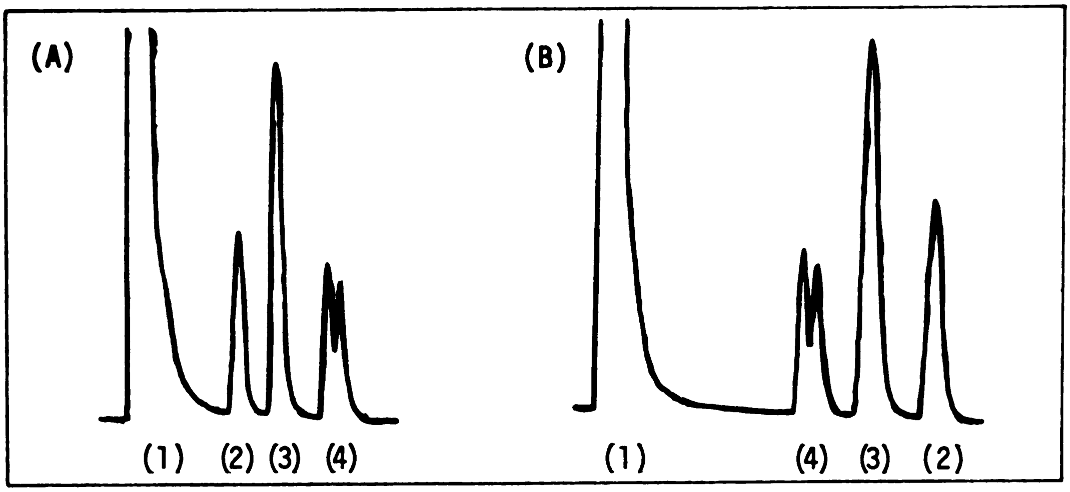


FIGURE 7. Vpc traces of photolysates of trifluoroacetophenone with (A), the lower boiling hydrogen donors, and (B), the higher boiling hydrogen donors on COL-2. (1) benzene, trifluoroacetophenone and hydrogen donor; (2) bibenzyl; (3) cross-coupling product; (4) pinacol (d,l and meso).

Since the pinacol was common to all, it was relatively easy to identify the other two products in each case. With the lower boiling hydrogen donors (p-fluorotoluene and cyclohexane) the hydrogen donor coupling product came off first followed by the cross-coupling and the double pinacol peaks. With the higher boiling hydrogen donors (p-chloro-, p-methoxy-, and p-cyanotoluene, cumene, cumene-α-d, and mesitylene) the pinacols had the shortest retention time followed by the cross-coupling and bibenzyl peaks respectively. Only the photolysates from the xylenes and unsubstituted toluene had to be analyzed on a QF-1 column (COL-1) because the three peaks overlapped on the SE-30 column (COL-2).

3. Standardization.

To determine the concentration of a photoproduct, PP, one need only compare its vpc peak area to that of an internal standard, IS.

$$[PP] = SF \ [IS]\frac{(PP)}{(IS)} \tag{26}$$

where [X] and (X) represent the concentration and vpc peak area respectively, of X. SF, the vpc standardization factor which compensates for the different molar responses for each compound, is determined by weighing out known amounts of PP and IS and measuring the relative vpc peak area ratio.

$$SF = \frac{[PP]std(IS)std}{[IS]std(PP)std} \tag{27}$$

Bicumyl, bibenzyl, bixylyl, and bicyclohexyl were standardized directly with the appropriate internal standard using the same conditions

used for the corresponding photolysate analysis. Since bimesityl, di-p-chloro-, di-p-fluoro-, and di-p-methoxybibenzyl were not readily available, they were standardized with the appropriate internal standard indirectly using the following relationship.

$$\left(\frac{(\text{toluene})}{(\text{x-toluene})}\right)\left(\frac{[\text{x-toluene}]}{[\text{toluene}]}\right) = \left(\frac{(\text{bibenzyl})}{(\text{di-x-bibenzyl})}\right)\left(\frac{[\text{di-x-bibenzyl}]}{[\text{bibenzyl}]}\right) \qquad (28)$$

thus,

$$[\text{di-x-bibenzyl}] = \text{SF}\ [\text{IS}]\frac{(\text{di-x-bibenzyl})}{(\text{IS})} \qquad (29)$$

where,

$$\text{SF} = \left(\frac{(\text{toluene std})}{(\text{x-toluene})\text{std}}\right)\left(\frac{[\text{x-toluene}]\text{std}}{[\text{toluene}]\text{std}}\right)\left(\frac{(\text{IS})\text{std}}{(\text{bibenzyl std})}\right)\left(\frac{[\text{bibenzyl}]\text{std}}{[\text{IS}]\text{std}}\right) \qquad (30)$$

Actual SF's used appear with the tables of quantum yields found in the following section.

E. ACTINOMETRY.

All sample tubes for which quantum yields were measured had ketone concentrations sufficient to absorb >99.9% of the incident light. Acetophenone formation from the type II photoelimination of valerophenone was used to monitor the light absorption. Actinometer tubes containing 0.1000 M valerophenone and 0.0050 M C_{14} internal standard in benzene were prepared as described before and irradiated in parallel with sample tubes.

Photolysate analyses were made on VPC-2, COL-6. The quantum yield of acetophenone formation under these conditions was taken to be 0.33.[40] In cases of low quantum yields, several sets of actinometer tubes had to be used in series.

cis-Piperylene-acetophenone actinometry was used to measure the quantum yield of intersystem crossing for trifluoroacetophenone. Tubes containing 0.2000 M cis-piperylene and either 0.1000 M trifluoroacetophenone or acetophenone in benzene were irradiated in parallel at 313 nm.

The triplet state of acetophenone, formed quantitatively ($\phi_{isc} = 1$) from the singlet, is completely quenched by cis-piperylene; the excited piperylene then decays to both cis- and trans-piperylene in a known ratio.[45] By use of the following relationship, the amount of excited piperylene

$$[\underline{\text{cis}}\text{-pip.}]_o \ln \frac{.555}{.555-\%\ \underline{\text{trans.}}} = [\text{pip.}^{*3}]. \qquad (31)$$

triplets produced can be calculated for both acetphenone (ACP) and trifluoroacetophenone (TFA).

Thus,

$$(\phi_{isc})\ \text{TFA} = \frac{[\text{PIP}^{*3}]\text{TFA}}{[\text{PIP}^{*3}]\text{ACP}} \qquad (32)$$

Photolysate analyses were made on VPC-1; COL-3.

EXPERIMENTAL

PART II. KINETIC DATA

A. QUANTUM YIELD OF BIBENZYL FORMATION AS A FUNCTION OF HYDROGEN DONOR CONCENTRATION.

General Comments: BB refers to the (substituted) bibenzyl formed from the indicated hydrogen donor, SH. C_n represents the internal standard. Values of $(BB)/(C_n)$ are averages of two or more tubes. I_a values were obtained from valerophenone actinometry as described previously and are averages of at least two tubes per period. Many quantum yield determinations required several sets of actinometer tubes irradiated in series.

TABLE 6. Quantum Yield of (Substituted) Bibenzyl Formation for 0.1000 M Trifluoroacetophenone in Benzene with Indicated SH, C_n, and Conditions.

Part A. p-Chlorotoluene.[a]

[SH], M	$(BB)/(C_{20})$	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
2.0000	1.694	253	0.0675	0.0375
1.0000	1.296	194	0.0675	0.0287
0.7500	1.120	167	0.0675	0.0248
0.5000	0.890	133	0.0675	0.0197

[a] 0.0010 M C_{20}, SF = 1.494. VPC-1; COL-2.

Part B. p-Fluorotoluene.[a]

[SH], M	(BB)/(C_{14})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
2.0000	1.512	152	0.0431	0.0354
1.0000	1.283	129	0.0431	0.0300
0.7500	1.449	115	0.0431	0.0268
0.5000	0.964	97	0.0431	0.0226

[a] 0.0010 M C_{14}, SF = 1.008. VPC-1; COL-2.

Part C. p-Methoxytoluene.[a]

[SH], M	(BB)/(C_{19})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
0.5000	1.164	174	0.0195	0.0891
0.2000	1.838	274	0.0346	0.0791
0.1000	1.468	219	0.0346	0.0631
0.0750	1.333	199	0.0346	0.0573
0.0500	1.131	168	0.0346	0.0487

[a] 0.0010 M C_{19}, SF = 1.49. VPC-1; COL-2.

Part D. Mesitylene.[a]

[SH], M	(BB)/(C_{19})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
0.2000	0.655	145	0.0436	0.0333
0.1000	0.540	120	0.0436	0.0275
0.0750	0.484	107	0.0436	0.0247
0.0500	0.388	86	0.0436	0.0197

[a] 0.0020 M C_{19}, SF = 1.11. VPC-1; COL-2.

Part E. *m*-Xylene.[a]

[SH], M	(BB)/(C_{19})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
2.0000	1.438	192	0.0669	0.0288
1.0000	1.376	184	0.0669	0.0275
0.7500	1.337	179	0.0669	0.0267
0.5000	1.263	169	0.0669	0.0253
0.2000	1.887	252	0.1241	0.0203
0.1000	1.415	189	0.1241	0.0152
0.0750	1.217	163	0.1241	0.0131
0.0500	0.936	125	0.1241	0.0101

[a] 0.0010 M C_{19}, SF = 1.337. VPC-1; COL-1.

Part F. *o*-Xylene.[a]

[SH], M	(BB)/(C_{19})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
0.2000	0.439	235	0.0971	0.0242
0.1000	0.329	176	0.0971	0.0181
0.0750	0.274	147	0.0971	0.0151
0.0500	0.214	114	0.0971	0.0118

[a] 0.0040 M C_{19}, SF = 1.337. VPC-1; COL-1.

Part G. *Toluene*.[a]

[SH], M	(BB)/(C_{15})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
2.0000	0.594	200	0.0579	0.0345
1.0000	0.841	275	0.1150	0.0239
0.5000	0.700	236	0.1150	0.0205
0.5000	0.548	185	0.1150	0.0161

[a] 0.0025 M C_{19}, SF = 1.35. VPC-1; COL-1.

Part H. Toluene-d_3.[a]

[SD], M	(BB)/(C_{19})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
2.0000	0.620	209	0.2265	0.00923
1.0000	0.458	155	0.2265	0.00684
0.7500	0.495	167	0.2818	0.00593
0.5000	0.436	147	0.3374	0.00436

[a] 0.0025 M C_{19}, SF = 1.35. VPC-1; COL-1.

Part I. Cumene.[a]

[SH], M	(BB)/(C_{15})	[BB], 10^{-6} M	I_a, El^{-1}	Φ_{BB}
1.0000	0.2844	972	0.0412	0.0236
0.5000	0.1693	578	0.0412	0.0143
0.5000	0.3591	1227	0.0839	
0.3750	0.2766	945	0.0839	0.0113
0.2500	0.2901	991	0.1259	0.0079

[a] 0.0040 M C_{15}, SF = 0.854. VPC-2; COL-4.

Part J. Cumene-α-d.[a]

[SD], M	(BB)/(C_{15})	[BB], 10^{-6} M	I_a, El^{-1}	Φ_{BB}
1.0000	0.2683	917	0.0830	0.01119
1.0000	0.2782	950	0.0839	
0.5000	0.2445	835	0.1259	0.00663
0.3750	0.2532	865	0.1680	0.00515
0.2500	0.2639	902	0.2507	0.00360

[a] 0.0040 M C_{15}, SF = 0.854. VPC-2; COL-4.

Part K. Cyclohexane.[a]

[SH], M	(BB)/(C_{12})[b]	[BB], 10^{-6} M	I_a, El^{-1}	Φ_{BB}
8.2482	0.192	103	0.0463	0.00222
2.0000	0.185	99	0.0917	0.00108
1.0000	0.173	93	0.1369	0.00068
0.7500	0.188	101	0.1816	0.00055
0.5000	0.172	92	0.2265	0.00041

[a] 0.0005 M C_{12}. SF = 1.07. VPC-1; COL-2. [b] BB is bicyclohexyl.

Part L. p-Cyanotoluene.[a]

[SH], M	(C_{18})/(CC)[b]
2.000	0.415
1.000	0.760
0.750	1.022
0.500	1.633

[a] 0.0020 M C_{18}. VPC-1; COL-2. [b] CC refers to the cross-coupling product, which was measured because of BB decomposition on the column.

TABLE 7. Quantum Yield of (Substituted) Bibenzyl Formation for 0.1000 M Acetophenone in Benzene with Indicated SH, C_n, and Conditions. Part A. Toluene.[a]

[SH], M	(BB)/(C_{19})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
2.0000	0.577	188	0.0574	0.0328
1.0000	0.689	225	0.1155	0.0195
0.7500	0.766	250	0.1724	0.0145
0.5000	0.543	177	0.1724	0.0103

[a] 0.0025 M C_{19}, SF = 1.305. VPC-1; COL-1.

Part B. Toluene-d_3.[a]

[SD], M	(BB)/(C_{19})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
2.0000	0.547	181	0.2262	0.00798
1.0000	0.533	176	0.4959	0.00354
0.7500	0.433	143	0.6059	0.00236
0.5000	0.250	82	0.6059	0.00136

[a] 0.0025 M C_{19}, SF = 1.32. VPC-1; COL-1.

Part C. Cumene.[a]

[SH], M	(BB)/(C_{19})	[BB], 10^{-5} M	I_a, El^{-1}	Φ_{BB}
6.4130	0.345	911	0.0686	0.1328
2.0000	0.219	578	0.0686	0.0811
2.0000	0.412	1088	0.1396	
1.0000	0.284	750	0.1396	0.0537
0.7500	0.348	919	0.2173	0.0423
0.5000	0.306	807	0.2173	0.0362
0.5000	0.387	1022	0.2890	

[a] 0.0025 M C_{19}, SF = 1.056. VPC-1; COL-1.

TABLE 8. Photolysate Hydrogen-Donor-Containing Product Distribution.

Ketone[a]	Donor	(BB)/(CC)[b]	$[(BB)/(CC)]_N$[c]
TFA	p-Fluorotoluene	0.458	0.475
TFA	p-Chlorotoluene	0.402	0.417
TFA	p-Methoxytoluene	0.189	0.196
TFA	p-Cyanotoluene	0.032[d]	0.031
TFA	Cumene	0.559	0.512
TFA	Cumene-α-d	0.524	0.480
TFA	p-Xylene	0.545	0.528
TFA	m-Xylene	0.478	0.464
TFA	o-Xylene	0.490	0.475
TFA	Mesitylene	0.824	0.756
TFA	Toluene	0.447	0.462
TFA	Toluene-α-d_3	0.429	0.444
TFA	Cyclohexane	0.111	0.085[e]
ACP	p-Xylene	0.786	0.761
ACP	Cumene	0.683	0.626
ACP	Toluene	0.588	0.609
ACP	Toluene-α-d_3	0.582	0.603

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[a] TFA = trifluoroacetophenone, ACP = acetophenone. [b] Vpc area ratios; BB = (substituted) bibenzyl, CC = cross-coupling product. Average of several determinations. [c] Normalized area ratio which takes into account number of carbon and oxygen atoms in both products. Assumes response linear with number of carbons and that a single C-O bond reduces response of that carbon by 1/2. e.g., correction factor for TFA with p-fluorotoluene would be 14.5/14. [d] Estimate. [e] Cyclohexylbenzene also produced.

B. QUENCHING STUDIES.

Relative quantum yields of (substituted) bibenzyl formation were measured as a function of quencher concentration for use in Stern-Volmer quenching plots. Studies with naphthalene and p-di-t butylbenzene used 366 nm and 313 nm light respectively. Concentrations of bibenzyl formation were kept in the 5 x 10^{-4} - 2 x 10^{-3} M region to insure linearity.

TABLE 9. 0.1000 M Trifluoroacetophenone - 0.5000 M Toluene System in Benzene. Quenching with p-Di-t-Butylbenzene.[a]

[Quencher], M	(Bibenzyl)/(C_{17})[b]	$\Phi^\circ_{BB}/\Phi_{BB}$
0.0000	0.260	1.00
0.0500	0.203	1.28
0.5000	0.174	1.49
0.7500	0.145	1.79
1.0000	0.126	2.06

[a] 0.0040 M C_{17} internal standard. VPC-2; COL-4. [b] Vpc area ratio.

TABLE 10. 0.1000 M Trifluoroacetophenone - 0.5000 M p-Xylene System in Benzene. Quenching with p-Di-t-Butylbenzene.[a]

[Quencher], M	(Bibenzyl)/(C_{18})[b]	$\Phi^\circ_{BB}/\Phi_{BB}$
0.0000	1.400	1.00
0.6000	1.215	1.15

[a] 0.00125 M C_{18} internal standard. VPC-1; COL-1. [b] Vpc area ratio.

TABLE 11. 0.1000 M Acetophenone - 0.5000 M Toluene System in Benzene. Quenching with p-Di-t-Butylbenzene.[a]

[Quencher], M	(Bibenzyl)/(C_{16})[b]	$\Phi°_{BB}/\Phi_{BB}$
0.0000	0.371	1.00
1.0000	0.266	1.40

[a]0.0040 M C_{16} internal standard. VPC-2; COL-4. [b]Vpc area ratio.

TABLE 12. 0.1000 M Trifluoroacetophenone - 1.0000 M p-Xylene System. Quenching with Naphthalene in Benzene.[a]

[Quencher], M	(Bixylyl)/(C_{20})[b]	$\Phi°_{BB}/\Phi_{BB}$
0.0000	0.714	1.00
0.0100	0.472	1.51
0.0200	0.355	2.01
0.0300	0.288	2.48

[a]0.0010 M C_{20} internal standard. VPC-1; COL-1. [b]Vpc area ratio.

TABLE 13. 0.1000 M Trifluoroacetophenone - 1.0000 M p-Xylene System. Quenching with Naphthalene in Acetonitrile.[a]

[Quencher], M	(Bixylyl)/(C_{20})[b]	$\Phi°_{BB}/\Phi_{BB}$
0.0000	0.898	1.00
0.0100	0.578	1.55
0.0200	0.430	2.09
0.0300	0.342	2.63

[a]0.0010 M C_{20} internal standard. VPC-1; COL-1. [b]Vpc area ratio.

C. DETERMINATION OF INTERSYSTEM CROSSING QUANTUM YIELD.

TABLE 14. Triplet Sensitized *cis*-*trans* Isomerization of Piperylene.[a]

Ketone[b]	Sample 1 % *trans*	Sample 2 % *trans*	Sample 3 % *trans*	Average % *trans*
Acetophenone	0.0940	0.0932	0.0949	0.0940
Trifluoroacetophenone	0.0895	0.0894	0.0912	0.0900

[a] 0.2000 M initial *cis*-piperylene. VPC-1; COL-3. [b] 0.1000 M.

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