# KINETICS OF PHOTOREDUCTION OF ACETOPHENONE AND $\alpha,\alpha,\alpha$-TRIFLUOROACETOPHENONE

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# Abstract

## Kinetics of Photoreduction of Acetophenone and $\alpha,\alpha,\alpha$-Trifluoroacetophenone

by

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The kinetics of photoreduction of acetophenone and $\alpha,\alpha,\alpha$-trifluoroacetophenone by p-xylene in benzene have been examined in this work. Products of the photoreductions are the expected coupling products derived from p-xylyl and semipinacol radicals. The effects of p-xylene concentration on quantum yields and of triplet state quencher on relative quantum yields of 1,2-di-p-tolylethane formation were examined. The various rate constants were determined by the steady state analysis of these data.

Emission spectra indicate that trifluoroacetophenone possesses a $\pi,\pi^*$ (unreactive) lowest triplet and yet, with p-xylene trifluoroacetophenone triplets react ($k_h = 9.7 \times 10^7$ sec) two orders of magnitude faster than the $n,\pi^*$ (reactive) acetophenone triplets ($k_h = 7.0 \times 10^5$ sec) while undergoing radiationless decay ($k_d$) only one order of magnitude faster ($8.8 \times 10^6$ vs. $7.1 \times 10^5$ sec). Of the two ketones, trifluoroacetophenone has the lower quantum yield of 1,2-di-p-tolylethane formation with less dependence on p-xylene concentration. The quantum yields with 4.0 M p-xylene are 0.08 and 0.04 for acetophenone and trifluoroacetophenone respectively.

If the commonly accepted mechanism for photoreduction is assumed, then the radicals generated disproportionate more than ten times faster than they couple. The unlikelyness of this occurrence and the high reactivity of trifluoroacetophenone triplets suggests that the major source of inefficiency in product formation arises from an intermediate charge-transfer state.

Experiments for further elucidation of the unusual reactivity of trifluoroacetophenone are presented.

# KINETICS OF PHOTOREDUCTION OF ACETOPHENONE AND α,α,α-TRIFLUOROACETOPHENONE

By

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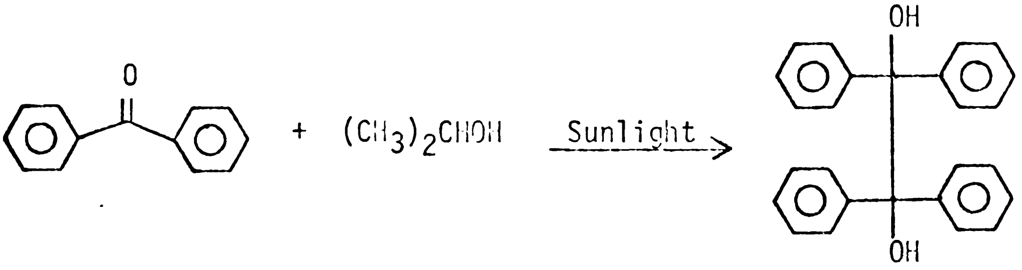
# I. Introduction

Photoreduction is an old reaction in chemistry dating from the early 1900's when Ciamician and Silber (1) first discovered that action of sunlight on a solution of benzophenone in alcohol gave a good yield of benzopinacol.



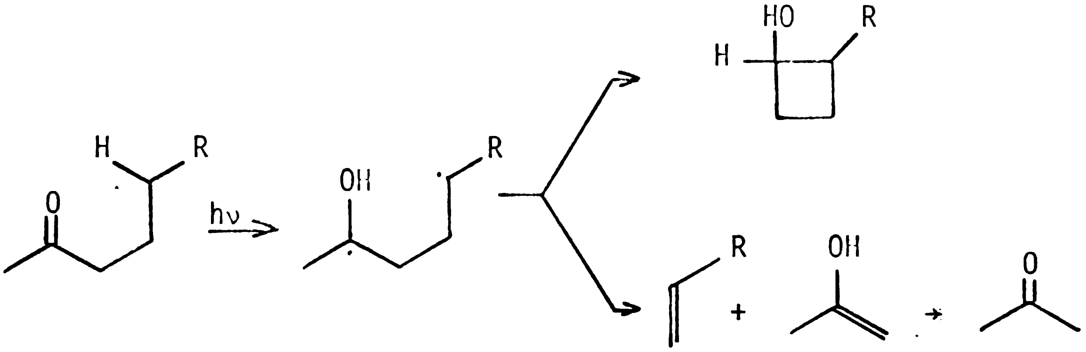
(1)

Until the 50's most photoreductive work was directed toward synthetic applications, since the yields are generally good and the products more easily prepared than by non-photochemical methods. Schonberg and Mustafa (2) have written a comprehensive review on this early pioneering work in synthetic photochemistry.

It has only been in the past decade, however, that large numbers of groups have become interested in the mechanisms of such reactions and admittedly their successes have been due in part to the vast improvement in modern instrumentation which enables us to routinely measure exceedingly small concentrations of photoproducts.

In this work we have examined the kinetics of photoreduction of acetophenone and $\alpha,\alpha,\alpha$-trifluoroacetophenone by p-xylene with the intent of determining what effect the strongly electron withdrawing trifluoromethyl group, $\alpha$ to the carbonyl, has on the photoreduction.

The photoreduction of ketones, whether intra- or intermolecular, is simple the transfer of a hydrogen atom to the carbonyl oxygen, although the competing physical processes involved have not been easy to elucidate. Intramolecular photoreduction, often referred to as the Norrish type II process, involves the abstraction of a γ-hydrogen by an excited state of the ketone and subsequent reactions of the 1,4-biradicals produced (3).



(2)

However, the work described in this thesis is concerned exclusively with intermolecular photoreduction. Ketones can be photoreduced intermolecularly by abstraction of a hydrogen atom from a suitable substrate yielding semipinacol radicals and hydrogen donor radicals. These radicals may then proceed on to their characteristic reactions depending on the conditions employed, as shown for example, in equations (3-6).

$$>C=O^{*} + DH \longrightarrow >\dot{C}OH + D\cdot \qquad (3)$$

$$>\dot{C}OH + >\dot{C}OH \longrightarrow -\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}- \qquad (4)$$

$$D\cdot + D\cdot \longrightarrow DD \qquad (5)$$

$$D\cdot + >\dot{C}OH \longrightarrow D\overset{|}{\underset{|}{C}}OH \qquad (6)$$

The hydrogen source is usually an alcohol, but other sources with abstractable hydrogen have been employed; for example: alkanes (4), amines (5), toluene (6), and tributylstannane (7).

Most of the work in this area of photoreduction has been with aryl ketones. Aliphatic ketones tend to undergo type I cleavages more readily than aryl ketones (for example, diethyl ketone is not photoreduced in isopropylbenzene but produces only products initiated by ethyl radicals (8)) and those ketones possessing $\gamma$-hydrogen atoms preferentially undergo type II photoelimination (9), although in some cases with reactive hydrogen donors photoreduction competes favorably with photoelimination (10,11). However, simple aliphatic ketones can be photoreduced as exemplified by acetone in hexane (12), cyclohexane, (13) and with tributylstannane (14).

Much of the recent interest in intermolecular photoreduction as well as type II photoelimination concerns the controversy over $n,\pi^*$ versus $\pi,\pi^*$ triplet state reactivity. Of the two "pure" triplet states, the $n,\pi^*$ triplet is considered the most similar to <u>tert</u>-butoxy radicals. Walling and Gibian (15) and Cohen and Baumgarten (16) have shown this in the case of benzophenone triplets by measuring the relative reactivities of various hydrogen donors in competitive experiments. Although benzophenone triplets are slightly more selective and electrophilic, both selectivity and absolute rates of reaction closely parallel those of <u>tert</u>-butoxy radicals, which is in agreement with the notion that a nonbonding, n, electron is promoted to an antibonding $\pi^*$ orbital, thus creating an electron deficiency at the carbonyl oxygen relative to the ground state ketone. $\pi,\pi^*$ triplets, on the other hand, involve the promotion of an electron from a bonding orbital to an antibonding $\pi^*$ orbital forming a species more polar than the $n,\pi^*$

triplet state, and thus, should not have any close resemblance to tert-butoxy radicals.

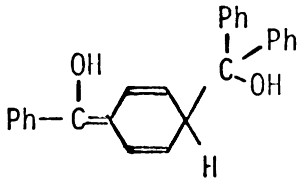
While aliphatic ketones have essentially pure $n,\pi^*$ lowest triplet states the situation is much more complex for aryl ketones since their $n,\pi^*$ and $\pi,\pi^*$ triplet levels are energetically close together. The wide variance in triplet state reactivities associated with aromatic ketones has been attributed to the relatively unreactive nature of $\pi,\pi^*$ triplet states (7,17). Unsubstituted benzophenone has an energy spacing of about 2400 $cm^{-1}$ between the lower $n,\pi^*$ triplet and the $\pi,\pi^*$ triplet states while the spacing for acetophenone is only about 440 $cm^{-1}$ (18,19). Methyl substitution on the aromatic nucleus lowers the $\pi,\pi^*$ relative to the $n,\pi^*$ triplet state and in the case of methyl substituted acetophenone the levels are inverted with the $\pi,\pi^*$ state becoming the lower triplet state. The electron withdrawing trifluoromethyl group, however, has the opposite effect in that it increases the energy of the $\pi,\pi^*$ relative to the $n,\pi^*$ triplet state (19,20).

Aliphatic ketones undergo the type II photoelimination several times faster than the corresponding phenyl ketones. For example 2-pentanone and 2-hexanone have rate constants of $6.4 \times 10^7$ and $9.8 \times 10^8$ $sec^{-1}$, respectively, assuming $k_q = 2.45 \times 10^{10}$ l $mole^{-1}$ $sec^{-1}$ in heptane (21), while those of butyrophenone (22) and valerophenone (23) are $6.6 \times 10^6$ and $1.4 \times 10^8$ $sec^{-1}$, in benzene. These results, together with the fact that certain ketones, such as $\alpha$- valeronaphthone (24) and p-phenylbutyrophenone (9), possessing $\pi,\pi^*$ lowest triplet states do not undergo photoelimination has led to the general conclusion that reactive ketones possess nearly pure $n,\pi^*$ lowest triplets while unreactive ketones possess $\pi,\pi^*$ lowest triplets. Those with intermediate reactivities are ones whose $\pi,\pi^*$ and $n,\pi^*$ levels, lying close in energy, are vibronicly coupled.

The effect of methyl substitution on photoreactivity in the benzophenone series is considerably smaller than in the acetophenone series. Yang (19) argues that methyl substitution lowers the $\pi,\pi^*$ triplet relative to the $n,\pi^*$ triplet in both cases. However, since the energy gap is much larger in the benzophenone series, the methyl substituted benzophenones still have reactive low-lying $n,\pi^*$ triplets although somewhat more coupled to the $\pi,\pi^*$ triplets. Acetophenone, on the other hand, having a smaller energy separation between $n,\pi^*$ and $\pi,\pi^*$ triplets and thus more $\pi,\pi^*$ character in the lowest triplet state, is less reactive than benzophenone. Methyl substituted acetophenones have $\pi,\pi^*$ lowest triplets coupled to $n,\pi^*$ upper triplets and it is this large enhancement of $\pi,\pi^*$ character in the lowest triplet state which gives rise to the considerable reduction in their photoreactivities. Trifluoromethyl substitution in either case increases the energy of the $\pi,\pi^*$ relative to the $n,\pi^*$ triplet, thereby increasing the $n,\pi^*$ character of the lowest triplet state and therefore, the photoreactivity of both ketones.

Porter prefers to attribute a lack of triplet state reactivity to charge transfer (CT) triplets (25) and puts $\pi,\pi^*$ triplet state reactivity at about 10% that of $n,\pi^*$ triplet states (26). The question of whether CT states are discrete entities or merely manifestations of substituent effects on the $\pi,\pi^*$ state is one of degree since in essence a CT triplet is a $\pi,\pi^*$ triplet in which electron density is strongly directed by heteroatoms.

A related current area of interest concerns the actual fate of the excited ketone triplet state in solution. It has been apparent for some time that those processes depicted in equations (3-6) must be an over simplification of the situation. Pitts (27) first reported that a colored, oxygen sensitive intermediate, characterized by a strong long wave length absorption band ($\lambda_{max}$ ca. 325 mu), was produced in the photoreduction of benzophenone by isopropanol. Backstrom (28) ascribed this intermediate to a charge transfer complex between an isopropanol radical and a semipinacol radical. Schenck (29) and Filipescu (30) proposed I and II, respectively, as non-radical intermediates in dilute benzophenone solutions.



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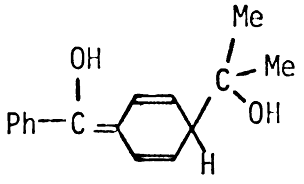


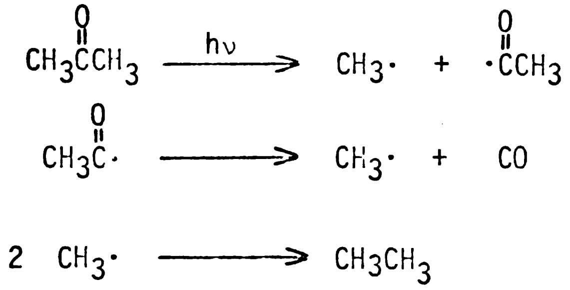
II

The question seems to be not whether intermediates exist but how much they effect the kinetics of the reaction. Filpescu has proposed that all products proceed through intermediate II while Wagner (31) has estimated that for the photoreduction of benzophenone by benzhydrol, no more than 10% of the radicals produced form intermediates such as I. These intermediates once formed, however, may be responsible for inefficiencies of product formation as well as quenching of excited states.

The literature abounds with reports of substituent effects on the quantum yields of both photoreduction and photoelimination. Unfortunately, it is difficult to glean any significant information about triplet state reactivities from quantum yields alone. Quantum yields do not give accurate measures of relative rates at which two excited species undergo a particular reaction if the competing reactions of the two species occur at different rates of if the particular reactions occurs so much faster than the competing reactions that $\Phi = 1$. For example, a comparison of butyrophenone with γ-methyl valerophenone shows that the quantum yield for type II photoelimination decreases a factor of two in going from a primary γ-hydrogen to a tertiary γ-hydrogen (0.40 to 0.23). However, the rate constant for intramolecular hydrogen abstraction is two orders of magnitude greater in the case of γ-methyl valerophenone (6.6 versus $500\text{x}10^{6}$ $\text{sec}^{-1}$) (22).

Solvent effects have also been studied. Porter (32) found that although p-hydroxy- and p-aminobenzophenone were very unreactive in alcohol solvents, they readily underwent photoreduction in cyclohexane. Nonpolar solvents would be expected to destabilize π,π* or CT relative to n,π* triplet states. Thus, by putting the aforementioned compounds in nonpolar media the resultant increase in n,π* character of the triplet facilitates photoreduction. On the other hand, Wagner (10) has shown that polar solvents enhance the quantum yield of butyrophenone and valerophenone disappearance. Polar solvents apparently stabilize the 1,4-biradical formed and decrease the reverse γ-hydrogen transfer pathway for radiationless decay.

A comparison of the photochemistry of acetone to that of hexafluoroacetone is relevant to the discussion of acetophenone and trifluoroacetophenone. Both acetone and hexafluoroacetone have been extensively studied in the gas phase at various temperatures, pressures, and wavelengths and intensities of irradiation. Both undergo photodecomposition via complex processes to carbon monoxide and ethane (hexafluoroethane) as indicated in the simplified manner below for acetone.



$$CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{h\nu} CH_3\cdot + \cdot\overset{\overset{O}{\|}}{C}CH_3$$

$$CH_3\overset{\overset{O}{\|}}{C}\cdot \longrightarrow CH_3\cdot + CO$$

$$2\ CH_3\cdot \longrightarrow CH_3CH_3$$

These are essentially the only products under high energy conditions ($T > 100^{o}C.$, $\lambda \leq 3130$ A.) (33,34) but at lower temperatures many other radical reactions occur such as methane and biacetyl formation (33,35).

However, acetone and hexafluoroacetone differ in several respects as evidenced by the following observations. The photolysis of hexafluoroacetone in the presence of hexafluoropropene lowers the yield of carbon monoxide and forms an oxetane while acetone under the same conditions produces no oxetane with a lowering of the carbon monoxide yield. Addition of piperylene quenches all but a small amount (4-14% depending on the pressure of hexafluoroacetone) of the oxetane formation suggesting the triplet state's involvement (36).

The n,$\pi$* singlet of acetone is not quenched by olefins, benzene, or dienes in the gas phase. Although the hexafluoroacetone singlet is quenched by these quenchers, it is not quenched by hexafluoropropene (37) suggesting that the electron deficient oxygen, in the case of hexafluoroacetone, is interacting with the $\pi$-system of the quencher except for hexafluoropropene, where the electron density of the double bond is reduced by the inductive effects of the fluorine. Charge transfer could account for the quenching by benzene.

Finally, there are differences in the absorptions and emissions of these compounds. The absorption spectra for acetone, trifluoroacetone, and hexafluoroacetone are very similar, absorbing over the region 2500-3300 A but with maxima shifted toward higher wavelengths ca. 125 A per trifluoromethyl group (38). The fluorescence efficiency is an order of magnitude higher for hexafluoroacetone and the fluorescence lifetime is $7.8 \times 10^{-8}$ sec, depending somewhat on temperature (39). The phosphorescence lifetime ($3.3 \times 10^{-3}$ sec) (40) is about ten times longer than that of acetone (41).

The photolysis of trifluoroacetophenone in the gas phase produces trifluoromethyl radicals via type I processes (42,43). Although there have been no reports of trifluoroacetophenone photoreduction in solution, the literature contains numerous reports on the photoreduction of acetophenone; most dealing with the products derived thereof. Two studies (20,44) have determined the rates of hydrogen abstraction ($k_h$) and radiationless decay ($k_d$). These results together with the results of our investigation of the photoreduction of acetophenone and trifluoroacetophenone will be presented and discussed in the next section of this thesis.

# II. Results and Discussion

In terms of mechanism, we can visualize the photoreduction of a ketone in solution as follows. Light is absorbed by the ketone, A, which is excited vertically according to the Frank-Condon principal to one of the excited singlet electronic states. In solution the first excited singlet state, $^1A^*$, is rapidly ($< 10^{-12}$ sec) attained through internal conversions. The excited singlet can decay with rate $k_i$ back to the ground state or intersystem cross with rate $k_{isc}$ to the excited triplet state, $^3A^*$. The excited triplet can undergo three processes: Decay to the ground state with rate $k_d$, transfer its energy to a quencher molecule, Q, with rate $k_q$, or react with the hydrogen donor, DH, with rate $k_h$. The radicals so produced may couple to form products with rate $k_c$ or disproportionate back to the ground state with rate $k_{dis}$.

Scheme I

$$A + h\nu \xrightarrow{I_a} {}^1A^*$$

$$^1A^* \xrightarrow{k_i} A$$

$$^1A^* \xrightarrow{k_{isc}} {}^3A^*$$

$$^3A^* \xrightarrow{k_d} A$$

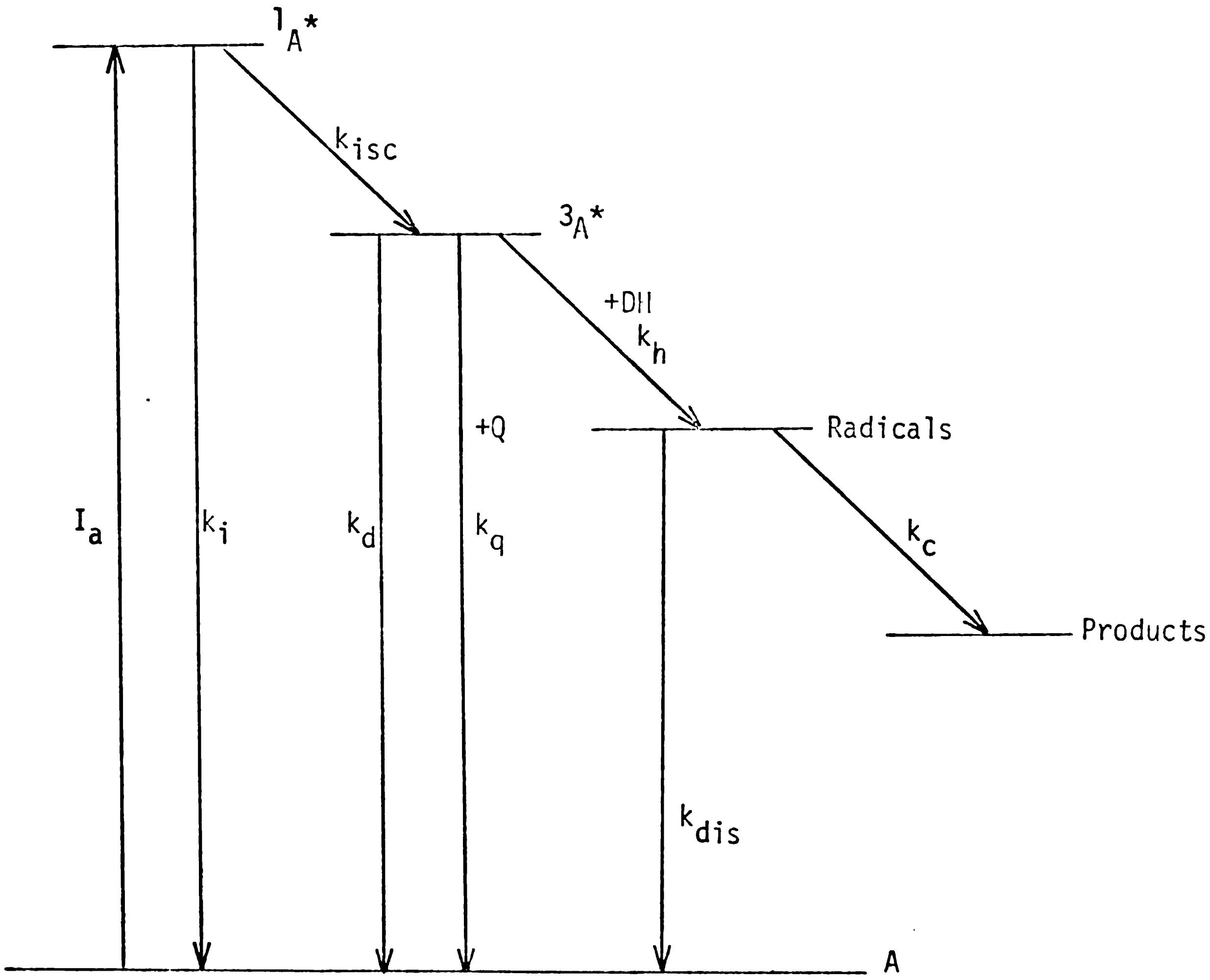
$$^3A^* + Q \xrightarrow{k_q} A + {}^3Q^*$$

$$^3A^* + DH \xrightarrow{k_h} \text{Radicals} \quad (AH\cdot + D\cdot)$$

$$\text{Radicals} \xrightarrow{k_c} \text{Products} \quad (DD + AHD + AHAH)$$

$$\text{Radicals} \xrightarrow{k_{dis}} A + DH$$

These processes may also be represented schematically by the following energy level diagram.



In order to evaluate the rate constants involved we must first define what is meant by the term quantum yield and derive expressions relating quantum yields to rate constants. The primary quantum yield, $\phi_X$, is a measure of the efficiency or probability of the one step process giving reaction products immediately from the excited state and may be defined as (45):

$$\phi_x = \frac{d[x]/dt}{I_a} = \frac{\text{number of molecules, radicals, or ions of x formed/cm}^3\text{ sec}}{\text{number of quanta absorbed by reactant/cm}^3\text{ sec}} \quad (7)$$

Products arising from subsequent excited states (eg., the triplet state) must be considered in terms of their probability of formation from that state. Thus, we define $P_x$ as the probability that those molecules in a subsequent excited state will form products by process x.

Finally, we define the total quantum yield, $\Phi_x$, a measure of the efficiency or probability of a multiple step process, as (46).

$$\Phi_x = \frac{\text{number of molecules finally formed}}{\text{number of quanta absorbed}} \quad (8)$$

Thus, from the energy diagram (vide supra) the total quantum yield for product formation would be given as :

$$\Phi_{Prod} = \phi_{isc} \; P_h P_c \quad (9)$$

If we make use of the steady state approximation theory, which asserts that highly reactive species which do not appear as final products, rapidly build up in concentration to some constant, low value at which time the reaction of these species equals the rate of their formation, then from Scheme I, the rate of formation of $^1A^*$ is given by:

$$\frac{d[^1A^*]}{dt} = I_a - k_i[^1A^*] - k_{isc}[^1A^*] \simeq 0 \quad (10)$$

Therefore,

$$[^1A^*] = I_a/(k_i + k_{isc}) \quad (11)$$

but,

$$\phi_{isc} \equiv \frac{d[{}^3A^*]}{dt} / I_a = \frac{k_{isc}[{}^1A^*]}{I_a} \qquad (12)$$

combining (11) and (12),

$$\phi_{isc} = k_{isc}/(k_{isc} + k_i) \qquad (13)$$

Similarly,

$$\Phi_{Prod} = \phi_{isc}\, P_c \left( \frac{k_h[DH]}{k_d + k_h[DH] + k_q[Q]} \right) \qquad (14)$$

when no quencher molecules are present [Q] = 0 and,

$$\Phi^o_{Prod} = \phi_{isc}\, P_c \left( \frac{k_h[DH]}{k_d + k_h[DH]} \right) \qquad (15)$$

Taking the ratio of (15) to (14) we obtain the useful Stern-Volmer expression.

$$\frac{\Phi^o_{Prod}}{\Phi_{Prod}} = 1 + \frac{k_q[Q]}{k_d + k_h[DH]} \qquad (16)$$

The lifetime of the triplet state, $\tau$ is given by the following expression:

$$\tau = 1/(k_d + k_h[DH]) \qquad (17)$$

thus,

$$\frac{\Phi^o_{Prod}}{\Phi_{Prod}} = 1 + k_q[Q]\tau \qquad (18)$$

A plot of $\Phi^{o}_{Prod}/\Phi_{Prod}$ versus [Q] will have a slop of $k_q$ and intercept at 1.

By taking the reciprocal of equation (14), another useful expression is obtained, the reciprocal quantum yield.

$$\frac{1}{\Phi_{Prod}} = \frac{1}{\phi_{isc}P_c}\left(1 + \frac{k_d}{k_h[DH]}\right) \qquad (19)$$

A plot of $1/\phi_{Prod}$ versus 1/[DH] gives an intercept of $1/\phi_{isc}P_c$ and a slope of $(1/\phi_{isc}P_c)(k_d/k_h)$.

From equation (17), a plot of $1/\tau$ versus [DH] will have a slope of $k_h$ with an intercept of $k_d$.

In summary, Stern-Volmer plots determine $\tau$, reciprocal quantum yield plots determine $\phi_{isc}P_c$ and $k_d/k_h$, and reciprocal lifetime plots determine $k_h$ and $k_d$.

Quenching Studies:

Degassed benzene solutions containing 0.1 or 0.2 M ketone, 0.1-2.5 M p-xylene (a particular value for each run), and various concentrations of naphthalene quencher were irradiated at 3660 A and analyzed for 1,2-di-p-tolylethane (DTE) formation by vapor phase chromatography (VPC). The Stern-Volmer plots were linear out to large percentages of quenching (Figures 1 and 2) although points obtained at low naphthalene concentrations tended to lie below the line, particularily in the case of acetophenone, perhaps indicating that some naphthalene molecules react with the excited triplet state of the ketone. Nevertheless, the Stern-Volmer plots are sufficiently valid to indicate a striking difference between the $k_q\tau$ values of trifluoroacetophenone and those of acetophenone as set forth in Table 1.

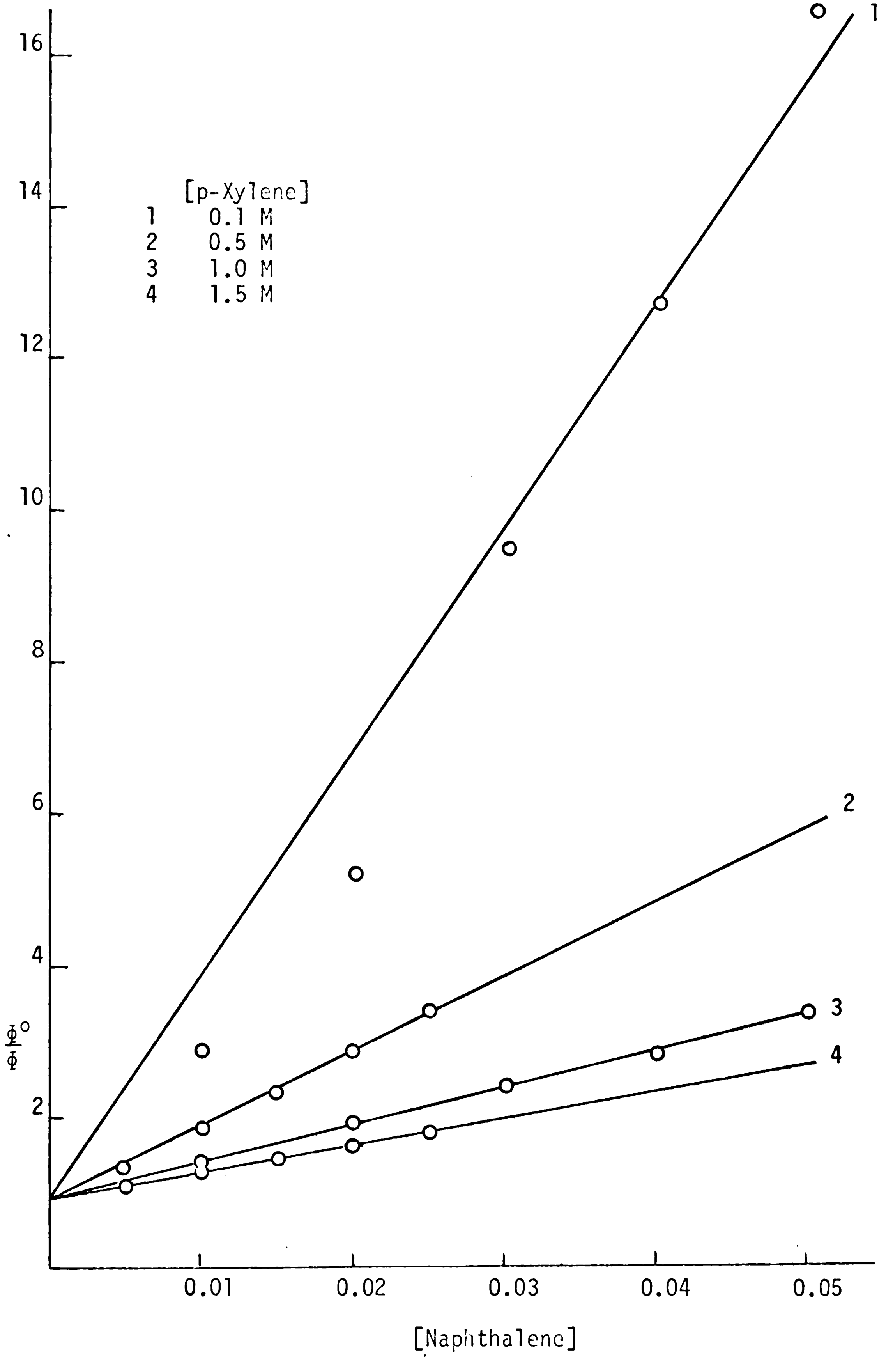


Figure 1. Stern-Volmer plots for varying concentrations of p-xylene with trifluoroacetophenone.

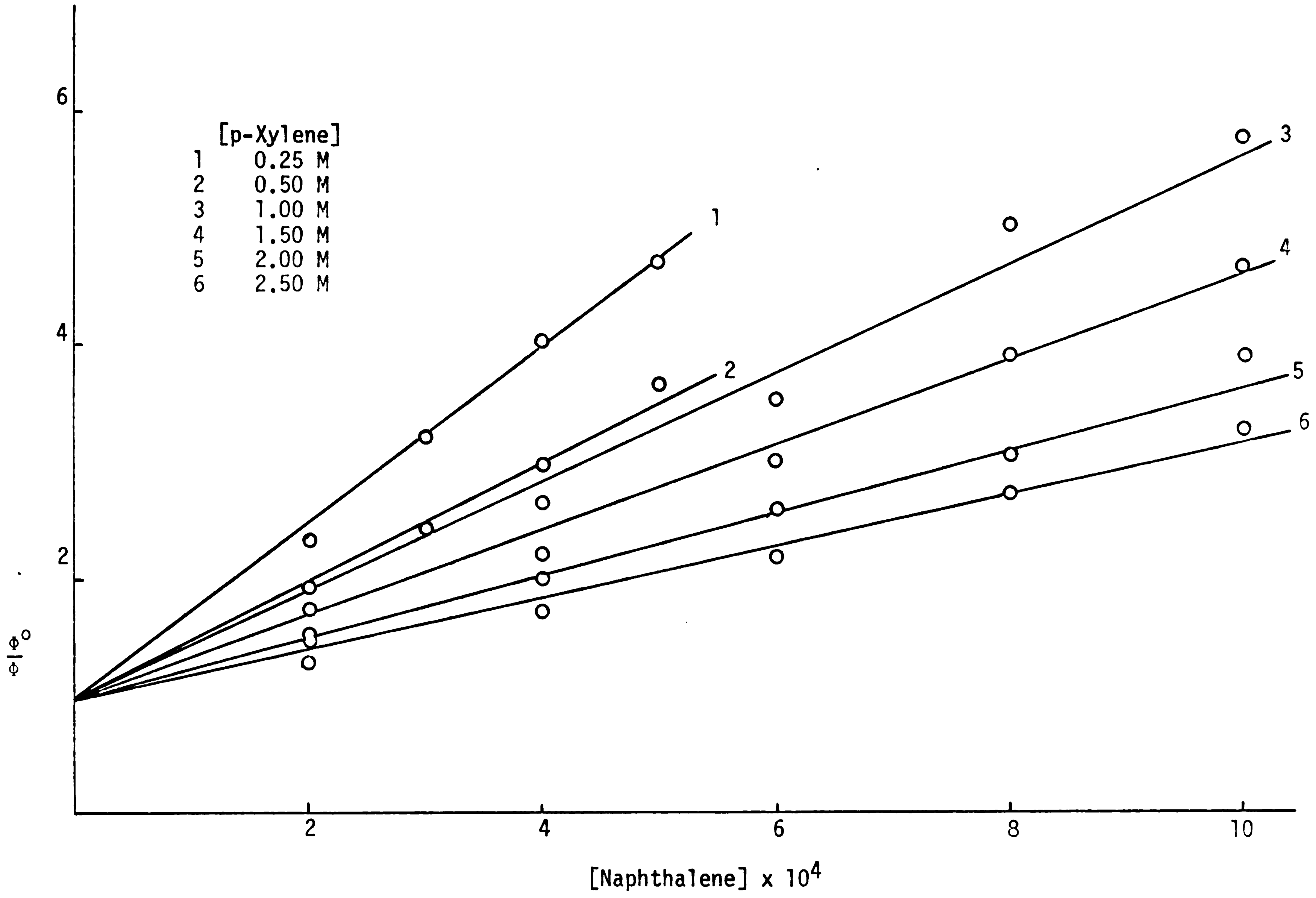


Figure 2. Stern-Volmer plots for varying concentrations of p-xylene with acetophenone.

Table 1. Quenching of Acetophenone and Trifluoroacetophenone by Naphthalene in Benzene.

| [p-xylene], M | $k_q\tau$, $M^{-1}$ | $1/\tau X10^{-5}$, $sec^{-1}$ |
|---|---|---|
| | Acetophenone | |
| 0.25 | 7560 | 6.6 |
| 0.50 | 5050 | 9.9 |
| 1.00 | 4600 | 10.9 |
| 1.50 | 3570 | 14.0 |
| 2.00 | 2610 | 19.2 |
| 2.50 | 2158 | 23.2 |
| | Trifluoroacetophenone | |
| 0.10 | 298 | 168 |
| 0.50 | 94.4 | 530 |
| 1.00 | 48.3 | 1040 |
| 1.50 | 33.8 | 1480 |

The rate constant for energy transfer to naphthalene, $k_q$, is dependent on the viscosity of the solvent and has a value of $5.0x10^9$ $M^{-1}$ $sec^{-1}$ in benzene (47). This value was used to calculate the $1/\tau$ values in Table 1.

Reciprocal lifetime plots from equation (17) shown in Figures 3 and 4 give good values for $k_h$ (slope) and approximate values for $k_d$ (intercept) as indicated in Table 3.

Quantum Yield Determinations.

Degassed benzene solutions containing 0.1 M ketone and various concentrations of p-xylene were irradiated at 3130 A and analyzed for DTE formation by VPC. Actinometery was performed by parallel irradiation of 0.1 M valerophenone in benzene, and then measuring the amount of acetophenone formed by VPC. The quantum yield for this reaction was taken as 0.33 (48). Reciprocal quantum yield plots (equation (19)), shown in Figure 5 give values

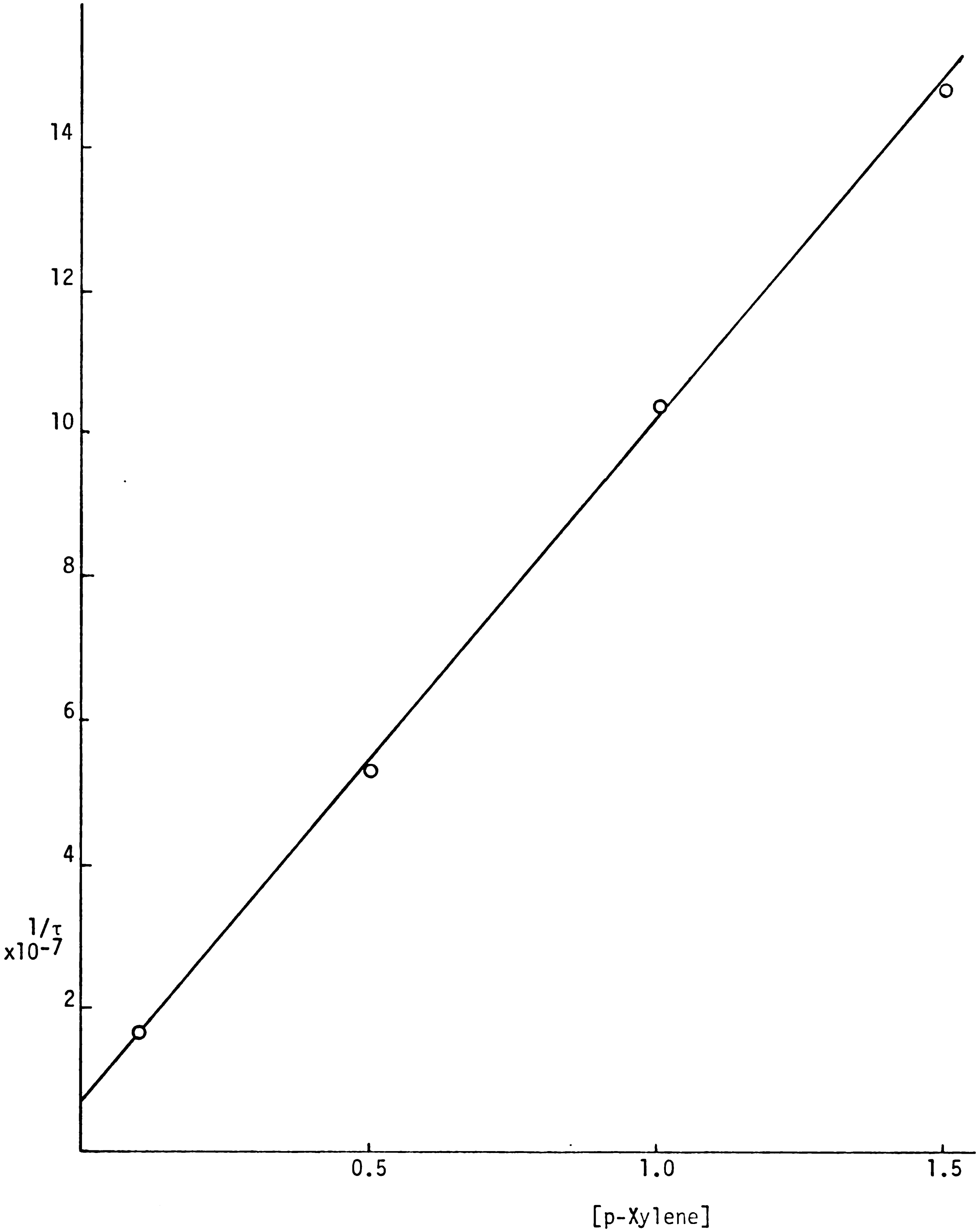


Figure 3. Reciprocal lifetime plot for trifluoroacetophenone.

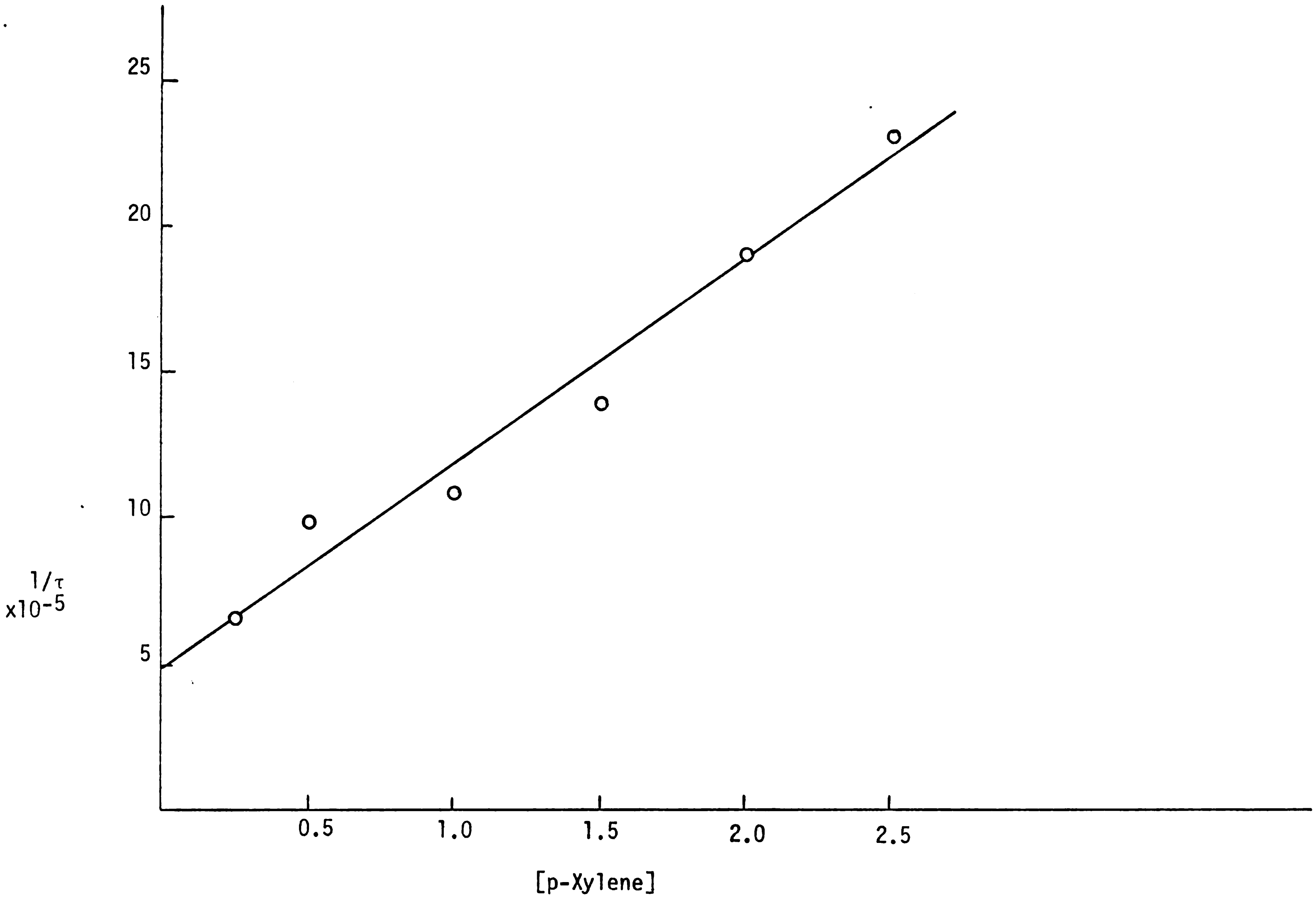


Figure 4. Reciprocal lifetime plot for acetophenone.

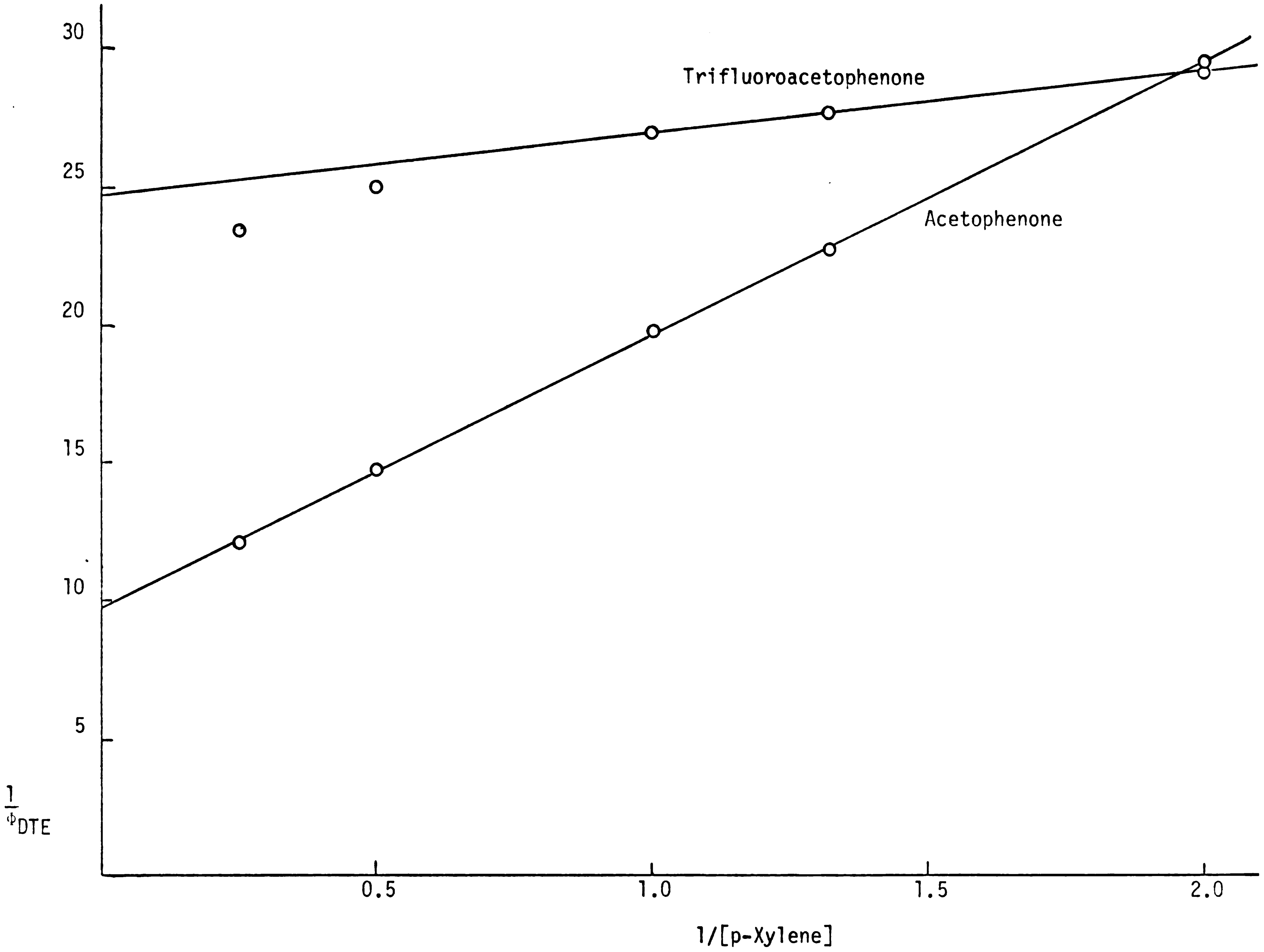


Figure 5. Reciprocal quantum yield plots for acetophenone and trifluoroacetophenone.

Table 2. Quantum Yields of 1,2-Di-p-tolylethane Formation with Various Concentrations of p-Xylene and 0.1 M Ketone.

| p-Xylene, M | $\Phi_{DTE}$ | |
|---|---|---|
| | Acetophenone | Trifluoroacetophenone |
| 4.00 | 0.082 | 0.042 |
| 2.00 | 0.068 | 0.040 |
| 1.00 | 0.051 | 0.037 |
| 0.75 | 0.044 | 0.036 |
| 0.50 | 0.034 | 0.034 |

for $k_d/k_h$ of 1.01 and 0.091 for acetophenone and trifluoroacetophenone respectively*. Thus, while just over half the acetophenone triplets decay back to the ground state, only one tenth of the trifluoroacetophenone triplets are lost through radiationless decay. Using the values of $k_h$ obtained from the reciprocal lifetime data, the $k_d$ values are easily calculated (shown in Table 3) and are reasonably close to those obtained from intercepts of reciprocal lifetime plots.

The reciprocal quantum yield plots shown in Figure 5 have intercepts of 9.8 and 24.8 for acetophenone and trifluoroacetophenone respectively. Equation (19) predicts an intercept of $(1/\phi_{isc})(1/P_c)$. However, $\phi_{isc}$ for acetophenone has been shown to equal 1 (49). Thus, the intercepts give values for $P_c$ as shown in Table 3.

It is of interest to note that these intercepts are much greater than 1 and would indicate that the p-xylyl radicals couple to produce DTE only 10 and

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* In the case of trifluoroacetophenone, the two values at high p-xylene concentrations were not included in the determination of slope and intercept since relative quantum yields were not determined at these concentrations.

Table 3. Kinetic Data for Photoreduction of Acetophenone and Trifluoroacetophenone.[a]

| Quantity | Acetophenone | Trifluoroacetophenone |
|---|---|---|
| $k_h$[b] | $7.0\times10^{5}$ sec$^{-1}$ | $9.7\times10^{7}$ sec$^{-1}$ |
| $k_d$[c] | 4.9 | 0.7 |
| $k_d$[d] | 7.1 | 0.9 |
| $P_c$ | $10.2\times10^{-2}$ | $4.0\times10^{-2}$ |

[a] All slopes and intercepts analyzed by least squares. [b] Slope of reciprocal lifetime plot. [c] Intercept of reciprocal lifetime plot. [d] Calculated from the slope of the reciprocal quantum yield plot and the value of $k_h$ from the reciprocal lifetime plot.

4% of the time for acetophenone and trifluoroacetophenone respectively. Since the photoproduct distribution, as displayed in Tables 4 and 5, for both ketones is similar and the p-xylyl radicals produced by either system should behave the same, then either the intercepts must contain some probability factor in addition to $P_c$ or $(k_{dis})_{ACP} << (k_{dis})_{TFA}$. It seems quite unlikely that radical disproportionation could account for all the observed inefficiency of product formation especially in view of the fact that similar systems, benzophenone-benzhydrol (31) and benzophenone-isopropanol (50), have intercepts which indicate > 90% coupling of radicals. Thus the inefficiency could lie in the formation of an intermediate charge-transfer state which can proceed on to radicals or decay back to the ground state. If this is indeed the case, then the results demand that from the charge-transfer state the rate of decay divided by the rate of radical formation for trifluoroacetophenone be much greater than for acetophenone.

Mass Balance Experiments.

As shown by equations (3-6), every mole of ketone which disappears should produce one mole of p-xylyl radicals which in turn should be manifest in either DTE of the alcohol. If DTE were the only photoproduct, then the maximum quantum yield for the formation of DTE would be 0.5 since two p-xylyl radicals are necessary for the formation of DTE. However, as shown in Table 4, three photoproducts are observed for each ketone.

Table 4. VPC Area Percentages of Photoproducts.[a]

| Ketone | DTE | Alcohol | Pinacol |
|---|---|---|---|
| Acetophenone | 35.9 | 45.7 | 18.4 |
| Trifluoroacetophenone | 30.6 | 56.1 | 13.4 |

[a] Averages of two separate determinations for each ketone.

Table 5 attempts to correlate disappearance of ketone (K-) with appearance of p-xylyl radicals in DTE and the respective alcohols. The percent of total p-xylyl radicals present in DTE is calculated directly by the following formula.

$$\frac{\text{\% of total p-xylyl}}{\text{radicals in DTE}} = \frac{[\text{DTE}]}{[\text{k-}]} \times \frac{\text{2 moles p-xylyl radicals}}{\text{mole DTE}} \times 100\% \qquad (20)$$

The percent of total p-xylyl radicals present in the alcohols is calculated by using the area percentages from Table 4 and the following formula.

$$\frac{\text{\% of total p-xylyl}}{\text{radicals in alcohol}} = \frac{\text{area \% alcohol}}{\text{area \% DTE}} \times \frac{[\text{DTE}]}{[\text{k-}]} \times 100\% \qquad (21)$$

Table 5. Distribution of p-Xylyl Radicals in Photoproducts Based on Ketone Disappearance. [a]

| Ketone | [K-] | [DTE] | $\frac{[DTE]}{[K-]}$ | $\frac{\text{alcohol}}{\text{DTE}}$ [b] | % p-Xylyl Radicals Accounted for by DTE | % p-Xylyl Radicals Accounted for by Alcohol [c] |
|---|---|---|---|---|---|---|
| ACP | 0.0191 | 0.00613 | 0.322 | 1.27 | 64.4 | 41.0 |
| TFA | 0.0331 | 0.00741 | 0.224 | 1.84 | 44.8 | 41.4 |

[a] All concentrations in moles/liter. [b] VPC peak area ratio. [c] Assuming VPC sensitivities the same for all photoproducts.

Thus, from Table 5 the maximum quantum yields of DTE formation may be calculated and are 0.32 and 0.22 for acetophenone and trifluoroacetophenone respectively. The observed quantum yields, however, were much lower (see Table 2) which indicates significant inefficiencies along the path to product formation.

Absorbance and Emission Spectra.

The UV spectra for acetophenone and trifluoroacetophenone displayed in Figures 6 show the $^1B_{2u} \leftarrow {}^1A_{1g}$ ($^1L_b \leftarrow {}^1A$) ca. 2850 A and $^1B_{1u} \leftarrow {}^1A_{1g}$ ($^1L_a \leftarrow {}^1A$) ca. 2500A bands shifted to longer wavelengths for trifluoroacetophenone, while the $n,\pi^*$ absorptions above 3200 A are very similar. The shift of the $\pi,\pi^*$ band is ca. 10 kcal/mole.

Trifluoroacetophenone emission spectra (51) closely resemble those obtained by Griffin (52), although exponential decay was linear and lifetimes somewhat lower. The triplet emissions were quite long (0.057 sec in methylcyclohexane and isopentane, and 0.20 sec in ethanol) suggesting a $\pi,\pi^*$ lowest triplet with possibly some $n,\pi^*$ character, in contrast to the known $n,\pi^*$ lowest triplet state in acetophenone (20). The vibrational spacing of

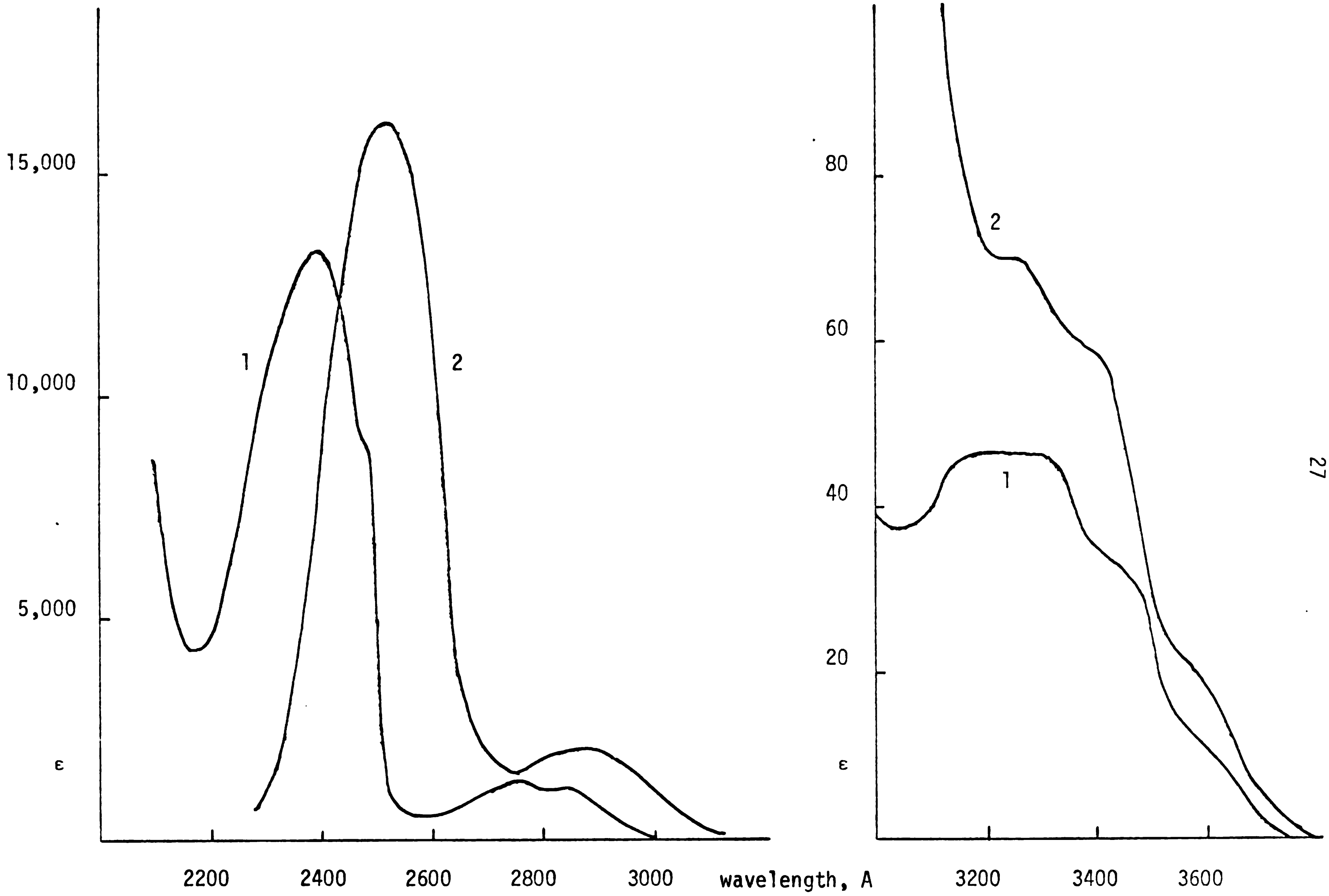


Figure 6. UV spectra of acetophenone (1) in cyclohexane (from reference (45), p. 378) and trifluoroacetophenone (2) in hexane.

of the emission spectra was ca. 1700 $cm^{-1}$ for trifluoroacetophenone in methylcyclohexane which compares well with the 1730 $cm^{-1}$ absorption observed in the IR spectra.

In conclusion, the evidence we have examined in this work has clearly shown trifluoroacetophenone to have unusual reactivity in photochemical reduction with p-xylene when compared to acetophenone. The results presented show that hydrogen abstraction from p-xylene by the triplet state of acetophenone is about $7\times10^{5}$ $sec^{-1}$. Yang (20) found a value of $9\times10^{5}$ $sec^{-1}$ in 2.0 M 2-propanol and Cohen (44) observed a rate of $2.5\times10^{6}$ $sec^{-1}$ with α-methylbenzyl alcohol assuming that $k_q$ for naphthalene in benzene equals $5\times10^{9}$ $sec^{-1}$. Walling and Gibian (15) reported that p-xylene has a relative reactivity of about half that of 2-propanol towards hydrogen abstraction by the triplet state of benzophenone. Thus, our value for hydrogen abstraction by the triplet state of acetophenone from p-xylene is reasonable.

The results further present a paradoxical situation in that emission spectra indicate that trifluoroacetophenone possesses a $\pi,\pi^*$ (unreactive) lowest triplet and yet, with p-xylene trifluoroacetophenone triplets react two orders of magnitude faster than the $n,\pi^*$ (reactive) acetophenone triplets while undergoing radiationless decay only one order of magnitude faster. Furthermore, the low quantum yield of product formation and the high intercepts of the reciprocal quantum yield plots indicate that a major source of inefficiency occurs after the triplet state reaction.

A priori, several explanations exist for these observations. The rate enhancement for trifluoroacetophenone triplets may be solely due to increased electron affinity of the oxygen arising from the electron withdrawing nature of the trifluoromethyl group, thus increasing the propensity for hydrogen abstraction, with inefficiency of product formation occurring by radical disproportionation. On the other hand, it may be that the rate observed is that of the trifluoroacetophenone triplets rapidly forming a strong charge-transfer complex with p-xylene with a large probability of subsequent decay from this state to the ground state accounting for the inefficiency of product formation. It is also possible that whatever species is produced from the triplet state is also responsible for quenching of excited triplets.

As pointed out in the introduction, indications of intermediates have been previously noted (27-31). In this work it was originally planned to follow ketone disappearance by UV analysis. However, irradiated samples absorbed more strongly in the 325-350 mu region than unphotolyzed samples although the spurious absorption decayed slowly when samples were not analyzed immediately or rapidly when exposed to air. This intermediate, whether similar to I or II or a charge-transfer species, would surely be an efficient quencher.

The following is a delineation of experiments that should help clarify the questions posed by this research.

1. If the rate measured is that of triplet ketone reacting with p-xylene to form a charge-transfer species, then changing to a nonaromatic hydrogen donor should eliminate any charge-transfer contribution to the rate of triplet reaction. Thus the photoreduction of trifluoroacetophenone should be studied in cyclohexane or 2-propanol.

2. If the observed inefficiency of product formation arises from disproportionation of radicals, then p-substitution of toluene with electron withdrawing or electron donating groups should increase or decrease, respectively, the efficiency of product formation. Thus, the reaction could

be studied with p-methoxy- or p-trifluoromethyltoluene acting as the hydrogen donor.

3. If the rate enhancement of intermolecular photoreduction is real, then the same effect should be obserable for type II photoelimination. Thus, the rates of photoelimination for compounds such as 1,1,1-trifluoro-2-pentanone or α,α-difluorobutyrophenone should be determined.

# III. Experimental

### A. *General Procedures*.

1. *Photolyses*. After solutions of the proper concentration were prepared, 2.8 mm of each was placed in a Kimex 13x100 mm culture tube and degassed four times to $1 \times 10^{-3}$ torr in freeze-thaw cycles and sealed *in vacuo*. The samples were irradiated in parallel on a rotating "merry-go-round" apparatus (53) immersed in a water bath to insure that each sample absorbed the same intensity of light. The quantum yield determinations were made with the 3130 A line of a 450 W Hanovia medium pressure mercury arc isolated with a 1 cm path of 0.002 M potassium chromate in a 1% aqueous solution of potassium carbonate. The 3660 A line of a 450 W Hanovia medium pressure mercury arc was isolated with a set of Corning No. 7083 filter combinations and was used for the Stern-Volmer quenching experiments.

2. *Vapor Phase Chromatography (VPC)*. Analyses were conducted on an Areograph Hy-Fi, model 600-D, with flame ionization detector, and equipped with a 6'x1/8" column containing 4% QF-1 and 1% Carbowax 20 M on Chromsorb G. Peak areas were measured by disk integration.

3. *Spectra*. UV spectra were taken on a Unicam SP 800 recording spectrophotometer with matched 10 mm quartz cells. A Beckman DUR spectrophotometer equipped with a Gilford model 220 linear absorbance converter was used for routine UV work. IR were taken on a Perkin-Elmer 237B infrared spectrophotometer using sodium chloride sandwich cells. NMR were obtained from a Varian A-60.

### B. *Solvent Purification and Compound Preparations*.

1. *Benzene*. Reagent grade benzene was washed with concentrated

sulfuric acid until the acid layer no longer turned yellow. It was then washed with dilute sodium hydroxide, water, and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and distilled from phosphorous pentoxide.

2. p-Xylene. p-Xylene was purified in the same manner as benzene.

3. Acetophenone (ACP). Acetophenone from Matheson Coleman and Bell was distilled under reduced pressure and the center cut taken. VPC analysis revealed no significant impurities.

4. $\alpha,\alpha,\alpha$-Trifluoroacetophenone (TFA). Trifluoroacetophenone purchased from Columbia Organic Chemicals was distilled under reduced pressure and the center fraction retained. VPC analysis revealed no significant impurities.

5. Naphthalene. Naphthalene from Matheson Coleman and Bell was recrystallized from ethanol.

6. Tridecane ($C_{13}$) and Hexadecane ($C_{16}$). Both alkanes were purified in the same way as benzene except distillation was under reduced pressure.

7. Octadecane ($C_{18}$). Octadecane was purified in the same fashion as benzene and recrystallized from ethanol.

8. Nonadecane ($C_{18}$). Nonadecane from Chemical Samples Company was used without further purification.

9. 1,2-Di-p-tolylethane (DTE). p-Methyl benzylbromide was first synthesized by refluxing a mixture of p-Xylene, N-bromosuccinimide, and benzoyl peroxide in benzene. Then its Grignard was prepared and induced to couple by the addition of anhydrous cobalt (II) chloride. The yellow solid formed was sublimed and then recrystallized from methanol (mp. 80.5-82°C.).

10. Valerophenone. Aldrich valerophenone was distilled under reduced pressure and then recrystallized twice from pentane.

### C. Kinetic Measurements.

1. Stern-Volmer Quenching Studies. The standard procedure used in preparing samples was as follows. Three types of stock solutions were prepared: p-xylene in benzene, naphthalene in benzene, and ketone with internal standard ($C_{18}$ or $C_{19}$) in benzene. Appropriate amounts of stock solutions were pipetted into 10 ml volumetric flasks and then diluted to the mark with benzene.

Tables 6 through 15 display the actual concentrations used and the measurements taken. Two calculations were made in these tables.

$$\text{a.} \quad [\mathrm{DTE}]_{samp} = F[C_n]\,(\mathrm{DTE}/C_n)_{samp} \qquad (22)$$

where the standardization factor, F, is defined as:

$$F = \frac{[\mathrm{DTE}]_{std}}{[C_n]_{std}} \times (C_n/\mathrm{DTE})_{std} \qquad (23)$$

with ($C_n$/DTE) being the VPC peak area ratio of internal standard to 1,2-di p-tolylethane.

$$\text{b.} \quad \Phi^{o}/\Phi = [\mathrm{DTE}]^{o}/[\mathrm{DTE}], \qquad (24)$$

where $[\mathrm{DTE}]^{o}$ is the concentration of 1,2-di-p-tolylethane in the absence of the quencher, naphthalene.

Table 6. Stern-Volmer Quenching Study with 0.2 M Trifluoroacetophenone and 0.1 M p-Xylene.[a]

| Sample | [Naphthalene] | $\mathrm{DTE}/C_{18}$[b] | $[\mathrm{DTE}]\times10^5$ | $\Phi^{o}/\Phi$ |
|---|---|---|---|---|
| 0 A[f] | 0 | 0.329 | 345[c] | |
| 0 B[f] | 0 | 0.247 | 259[d] | |
| 1 | 0.01 | 0.112 | 117.7[c] | 2.93 |
| 2 | 0.02 | 0.0629 | 66.2[c] | 5.22 |
| 3 | 0.03 | 0.0598 | 63.0[e] | 9.58 |
| 4 | 0.04 | 0.0451 | 47.2[e] | 12.80 |
| 5 | 0.05 | 0.0346 | 36.3[e] | 16.63 |

[a] Plotted in Figure 1. All concentrations in moles/liter. 0.01 M $C_{18}$ internal standard, F = 1.05. [b] VPC peak area ratio; column temperature 175°C. [c] Sample irradiated 65 hours. [d] Sample irradiated 54 hours. [e] Sample irradiated 119 hours. [f] Average of three samples.

Table 7. Stern-Volmer Quenching Study with 0.1 M Trifluoroacetophenone and 0.5 M p-Xylene.[a]

| Sample | [Naphthalene] | $DTE/C_{19}$[b] | $[DTE]x10^5$ | $\Phi^o/\Phi$ |
|---|---|---|---|---|
| 0[c] | 0 | 1.369 | 317 | |
| 1 | 0.005 | 1.005 | 233 | 1.36 |
| 2 | 0.010 | 0.734 | 170 | 1.87 |
| 3 | 0.015 | 0.578 | 134 | 2.37 |
| 4 | 0.020 | 0.471 | 109 | 2.91 |
| 5 | 0.025 | 0.401 | 92.8 | 3.42 |

[a] Plotted in Figure 1. All concentrations in moles/liter. 0.0025 M $C_{19}$ internal standard, F = 0.928. Irradiated 91.5 hours. [b] VPC peak area ratio, column temperature 175° C. [c] Average of 3 samples.

Table 8. Stern-Volmer Quenching Study with 0.2 M Trifluoroacetophenone and 1.0 M p-Xylene.[a]

| Sample | [Naphthalene] | $DTE/C_{18}$[b] | $[DTE]x10^5$ | $\Phi^o/\Phi$ |
|---|---|---|---|---|
| 0 A[c] | 0 | 0.889 | 933[d] | |
| 0 B[c] | 0 | 0.601 | 631[e] | |
| 1 | 0.01 | 0.604 | 634[d] | 1.48 |
| 2 | 0.02 | 0.448 | 470[d] | 1.98 |
| 3 | 0.03 | 0.612 | 643[f] | 2.42 |
| 4 | 0.04 | 0.517 | 543[f] | 2.88 |
| 5 | 0.05 | 0.431 | 452[f] | 3.47 |

[a] Plotted in Figure 1. All concentrations in moles/liter. 0.01 M $C_{18}$ internal standard, F = 1.05. [b] VPC peak area ratio; column temperature, 175°C. [c] Average of three samples. [d] Sample irradiated 60 hours. [e] Sample irradiated 48 hours. [f] Sample irradiated 108 hours.

Table 9. Stern-Volmer Quenching Study with 0.1 M Trifluoroacetophenone and 1.5 M p-Xylene.[a]

| Sample | [Naphthalene] | DTE/$C_{19}$[b] | [DTE]x$10^5$ | $\Phi°/\Phi$ |
|---|---|---|---|---|
| 0[c] | 0 | 1.782 | 413 | |
| 1 | 0.005 | 1.615 | 374 | 1.10 |
| 2 | 0.010 | 1.419 | 329 | 1.25 |
| 3 | 0.015 | 1.180 | 274 | 1.51 |
| 4 | 0.020 | 1.079 | 250 | 1.65 |
| 5 | 0.025 | 0.952 | 221 | 1.87 |

[a] Plotted in Figure 1. All concentrations in moles/liter. 0.0025 M $C_{19}$ internal standard, F = 0.928. Irradiated 25 hours. [b] VPC peak area ratio; column temperature, 175°C. [c] Average of three samples.

Table 10. Stern-Volmer Quenching Study with 0.1 M Acetophenone and 0.25 M p-Xylene.[a]

| Sample | [Naphthalene] | DTE/$C_{18}$[b] | [DTE]x$10^5$ | $\Phi°/\Phi$ |
|---|---|---|---|---|
| 0[c] | 0 | 1.134 | 323 | |
| 1 | 0.0001 | 0.726 | 207 | 1.58 |
| 2 | 0.0002 | 0.484 | 137.5 | 2.35 |
| 3 | 0.0003 | 0.350 | 99.8 | 3.24 |
| 4 | 0.0004 | 0.280 | 79.8 | 4.06 |
| 5 | 0.0005 | 0.240 | 68.5 | 4.72 |

[a] Plotted in Figure 2. All concentrations in moles/liter. 0.0025 M $C_{18}$ internal standard, F = 1.14. Irradiated 48 hours. [b] VPC peak area ratio; column temperature, 175°C. [c] Average of three samples.

Table 11. Stern-Volmer Quenching Study with 0.2 M Acetophenone and 0.5 M p-Xylene.[a]

| Sample | [Naphthalene] | DTE/$C_{19}$[b] | [DTE]x$10^5$ | $\Phi^o/\Phi$ |
|---|---|---|---|---|
| 0[c] | 0 | 1.772 | 412 | |
| 1 | 0.0001 | 1.383 | 321 | 1.28 |
| 2 | 0.0002 | 0.909 | 211 | 1.95 |
| 3 | 0.0003 | 0.724 | 168 | 2.45 |
| 4 | 0.0004 | 0.595 | 138 | 2.98 |
| 5 | 0.0005 | 0.482 | 112 | 3.68 |

[a] Plotted in Figure 2. All concentrations in moles/liter. 0.0025 M $C_{19}$ internal standard, F = 0.928. Irradiated 28 hours. [b] VPC peak area ratio; column temperature, 175°C. [c] Average of two samples.

Table 12. Stern-Volmer Quenching Study with 0.2 M Acetophenone and 1.0 M p-Xylene. [a]

| Sample | [Naphthalene] | DTE/$C_{19}$[b] | [DTE]x$10^5$ | $\Phi^o/\Phi$ |
|---|---|---|---|---|
| 0[c] | 0 | 2.390 | 556 | |
| 1 | 0.0002 | 1.359 | 316 | 1.76 |
| 2 | 0.0004 | 0.903 | 210 | 2.65 |
| 3 | 0.0006 | 0.671 | 156 | 3.56 |
| 4 | 0.0008 | 0.473 | 110 | 5.05 |
| 5 | 0.0010 | 0.415 | 96.4 | 5.77 |

[a] Plotted in Figure 2. All concentrations in moles/liter. 0.0025 M $C_{19}$ internal standard, F = 0.93. Irradiated 50.5 hours. [b] VPC peak area ratio; column temperature 175°C. [c] Average of three samples.

Table 13. Stern-Volmer Quenching Study with 0.1 M Acetophenone and 1.5 M p-Xylene.[a]

| Sample | [Naphthalene] | DTE/$C_{18}$[b] | [DTE]x$10^5$ | $\Phi^o/\Phi$ |
|---|---|---|---|---|
| 0[c] | 0 | 1.911 | 540 | |
| 1 | 0.0002 | 1.229 | 347 | 1.56 |
| 2 | 0.0004 | 0.853 | 241 | 2.22 |
| 3 | 0.0006 | 0.634 | 179 | 3.02 |
| 4 | 0.0008 | 0.489 | 138 | 3.92 |
| 5 | 0.0010 | 0.394 | 111.5 | 4.69 |

[a] Plotted in Figure 2. All concentrations in moles/liter. 0.0025 M $C_{18}$ internal standard, F = 1.13. Irradiated 20 hours. [b] VPC peak area ratio; column temperature, 175°C. [c] Average of three samples.

Table 14. Stern-Volmer Quenching Study with 0.2 M Acetophenone and 2.0 M p-Xylene.[a]

| Sample | [Naphthalene] | DTE/$C_{19}$[b] | [DTE]x$10^5$ | $\Phi^o/\Phi$ |
|---|---|---|---|---|
| 0[c] | 0 | 2.520 | 586 | |
| 1 | 0.0002 | 1.649 | 383 | 1.53 |
| 2 | 0.0004 | 1.245 | 290 | 2.02 |
| 3 | 0.0006 | 0.964 | 224 | 2.61 |
| 4 | 0.0008 | 0.821 | 191 | 3.07 |
| 5 | 0.0010 | 0.645 | 150 | 3.91 |

[a] Plotted in Figure 2. All concentrations in moles/liter. 0.0025 M $C_{19}$ internal standard, F = 0.93. Irradiated 44.5 hours. [b] VPC peak area ratio; column temperature, 175°C. [c] Average of three samples.

Table 15. Stern-Volmer Quenching Study with 0.1 M Acetophenone and 2.5 M p-Xylene.[a]

| Sample | [Naphthalene] | $DTE/C_{19}$[b] | $[DTE]x10^5$ | $\Phi^o/\Phi$ |
|---|---|---|---|---|
| 0[c] | 0 | 1.980 | 570 | |
| 1 | 0.0002 | 1.498 | 431 | 1.32 |
| 2 | 0.0004 | 1.141 | 328 | 1.74 |
| 3 | 0.0006 | 0.901 | 259 | 2.20 |
| 4 | 0.0008 | 0.723 | 208 | 2.74 |
| 5 | 0.0010 | 0.603 | 173 | 3.30 |

[a] Plotted in Figure 2. All concentrations in moles/liter. 0.0025 M $C_{18}$ internal standard, F = 1.15. Irradiated 18 hours. [b] VPC peak area ratio; column temperature, 175°C. [c] Average of three samples.

2. Quantum Yield Determinations. Acetophenone and trifluoroacetophenone solutions were prepared in the same way as for the Stern-Volmer studies. 0.10 M valerophenone actinometer solutions were made by weighing 0.8122 g valerophenone into a 25 ml volumetric flask and diluting to the mark with benzene. Degassed actinometer solutions were irradiated in series and changed at half hour intervals. The ketone solutions were irradiated in parallel for periods of 1.5-3.0 hours as indicated in Table 16. Tables 16 and 17 show actual concentrations used and the measurements recorded.

Calculations of $\Phi_{DTE}$ were made from equation (25). $I_a$ was determined by

$$\Phi_{DTE} = \frac{[DTE]}{I_a} \qquad (25)$$

measuring the amount of acetophenone produced via the type II photoelimination of valerophenone and assuming $\phi_{II} = 0.33$ (48).

$$I_a = \frac{[ACP]}{\phi_{II}} \qquad (26)$$

Table 16. Reciprocal Quantum Yield Study.[a]

| Sample | Hours Irrad. | DTE/$C_{18}$ | [DTE]x$10^5$ | $I_a$ x $10^5$, Einsteins[c] | $\Phi_{DTE}$ | $1/\Phi_{DTE}$ | [p-Xylene] | 1/[p-Xylene] |
|---|---|---|---|---|---|---|---|---|
| | | | Trifluoroacetophenone | | | | | |
| 1 | 1.5 | 0.902 | 243 | 5712 | 0.0425 | 23.50 | 4.00 | 0.25 |
| 2 | 2.0 | 1.136 | 306 | 7688 | 0.0398 | 25.12 | 2.00 | 0.50 |
| 3 | 2.5 | 1.324 | 357 | 9658 | 0.0370 | 27.05 | 1.00 | 1.00 |
| 4 | 2.5 | 1.282 | 346 | 9658 | 0.0358 | 27.91 | 0.75 | 1.33 |
| 5 | 3.0 | 1.459 | 394 | 11564 | 0.0341 | 29.35 | 0.50 | 2.00 |
| | | | Acetophenone | | | | | |
| 1 | 1.0 | 1.165 | 314 | 3830 | 0.0820 | 12.20 | 4.00 | 0.25 |
| 2 | 1.5 | 1.430 | 386 | 5712 | 0.0676 | 14.80 | 2.00 | 0.50 |
| 3 | 2.0 | 1.440 | 389 | 7688 | 0.0506 | 19.76 | 1.00 | 1.00 |
| 4 | 2.5 | 1.569 | 424 | 9658 | 0.0439 | 22.78 | 0.75 | 1.33 |
| 5 | 3.0 | 1.450 | 391 | 11564 | 0.0338 | 29.57 | 0.50 | 2.00 |

[a] Plotted in Figure 5. All concentrations in moles/liter. 0.0025 M $C_{18}$ internal standard, F = 1.08.
[b] VPC peak area ratio; column temperature, 175°C. [c] From values in Table 16.

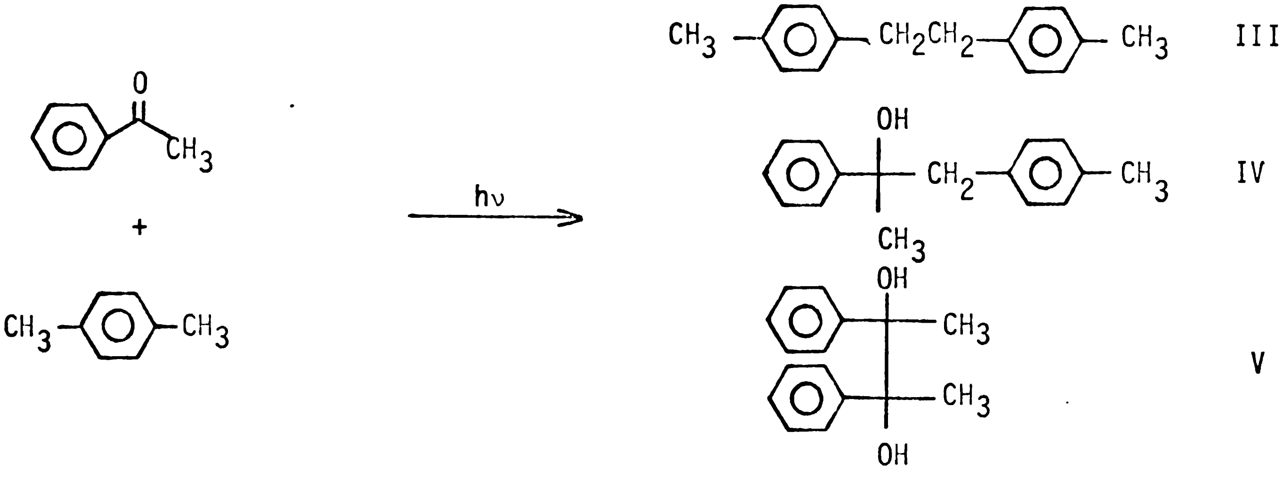
Table 17. 0.1 M Valerophenone Actinometry[a].

| Sample | Hours Irrad. | $ACP/C_{13}$[b] | $[ACP]\times10^5$ | $I_a\times10^5$, Einsteins | Cumulative $I_a\times10^5$ Einsteins |
|---|---|---|---|---|---|
| 1 | 0.5 | 2.020 | 602 | 1824 | 1824 |
| 2 | 0.5 | 2.225 | 662 | 2006 | 3830 |
| 3 | 0.5 | 2.095 | 621 | 1882 | 5712 |
| 4 | 0.5 | 2.195 | 652 | 1976 | 7688 |
| 5 | 0.5 | 2.185 | 650 | 1970 | 9658 |
| 6 | 0.5 | 2.115 | 629 | 1906 | 11564 |

[a] All concentrations in moles/liter. 0.006 M $C_{13}$ internal standard, F = 0.496.
[b] VPC peak area ratio; column temperature, 135°C.

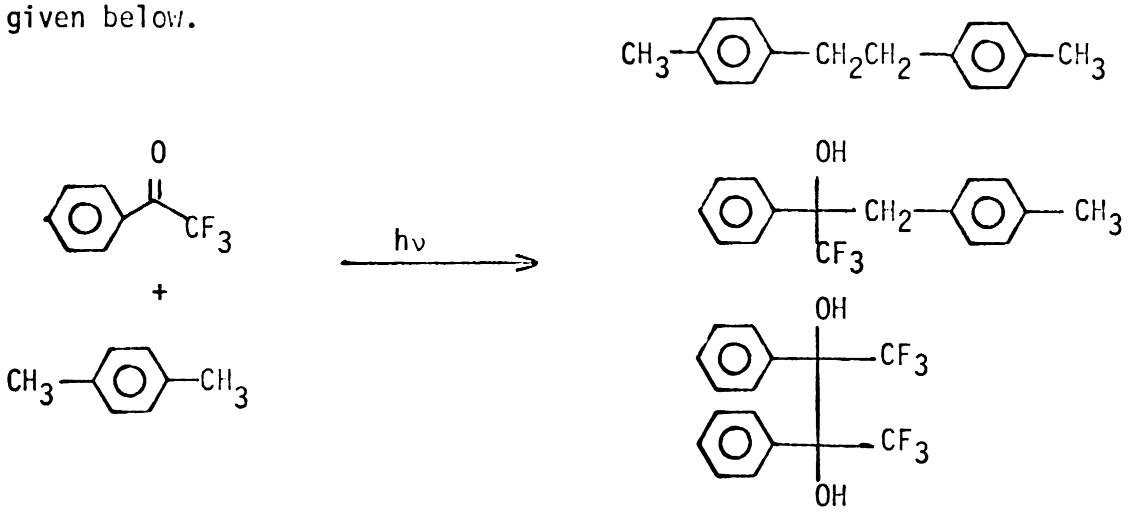
D. Product Determination.

The photoreduction of acetophenone with p-xylene in benzene yield the three expected products predicted by equations (4-6).



III was determined by comparing VPC retention times with an authentic sample of DTE. IV and V were isolated from the reaction mixture by preparative VPC (Aerograph A-350B with 5' x1/4" 10% QF-1, 60/80 Firebrick, Chromsorb W). The IR of IV showed an alcohol peak at 3470 $cm^{-1}$ (see figure 7). The NMR revealed 9 aromatic protons centered at 3.05τ, 2 methylene protons at 7.10τ, 1 alcohol proton at 8.13τ and two methyl groups at 7.77 and 8.58τ. The low field signal being attributable to the methyl group on the aromatic ring (see figure 9). The NMR spectra of V showed 10 aromatic protons at 2.80τ, 2 alcohol protons at 7.38 and 7.67τ and two methyl groups at 8.42 and 8.50τ. Compound V having two asymmetric centers should be composed of a meso form and a d,l pair.

Products from the photoreduction of trifluoroacetophenone had VPC retention times similar to those of acetophenone and were assumed to be as given below.



III

VI

VII

E. <u>Mass Balance Experiments</u>. Samples were prepared exactly as described previously with actual concentrations given in Tables 18 and 19. After irradiation 1 ml of the TFA solution was pipetted into a small vial containing exactly 1 ml of a 0.10 M $C_{13}$ standard solution. The concentration of unphotoreduced TFA was then determined by VPC analysis. 1 ml of the photolyzed ACP solution was pipetted into a small vial containing exactly 1 ml of a 0.1 M $C_{16}$ standard solution. The concentration of unphotoreduced ACP was determined by VPC analysis. The remaining TFA and ACP solutions were analyzed for all photoproducts and the $C_{18}$ internal standard.

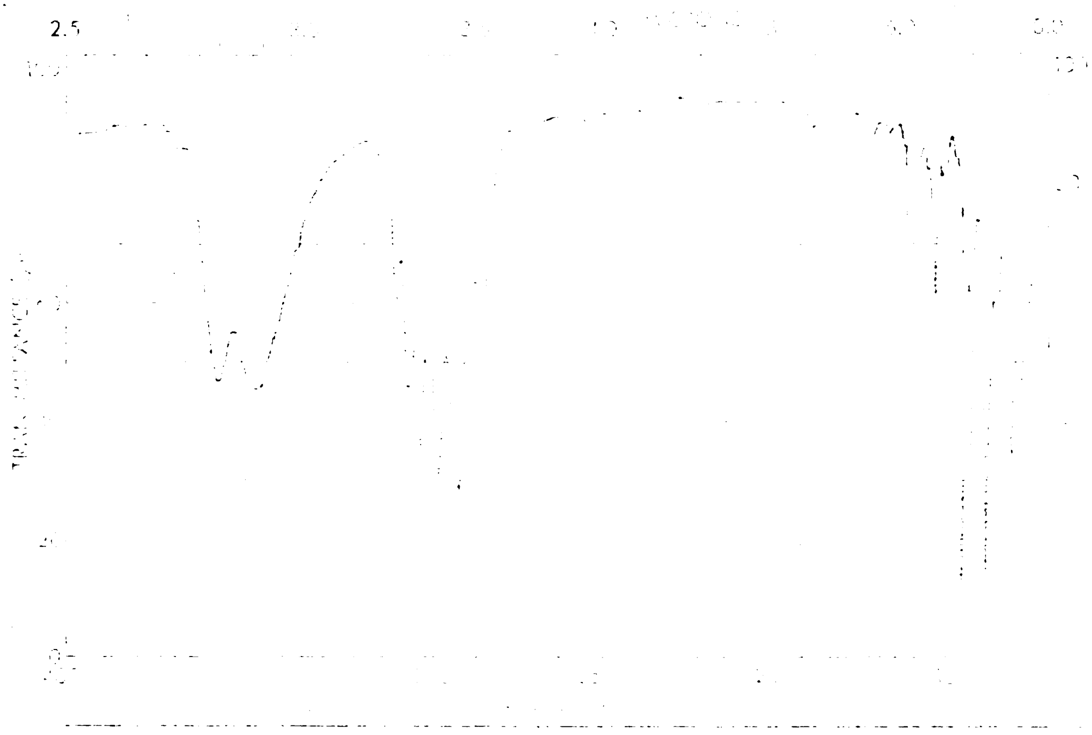


Figure 7. IR spectra of 1-p-tolyl-2-phenyl-2-propanol(IV).

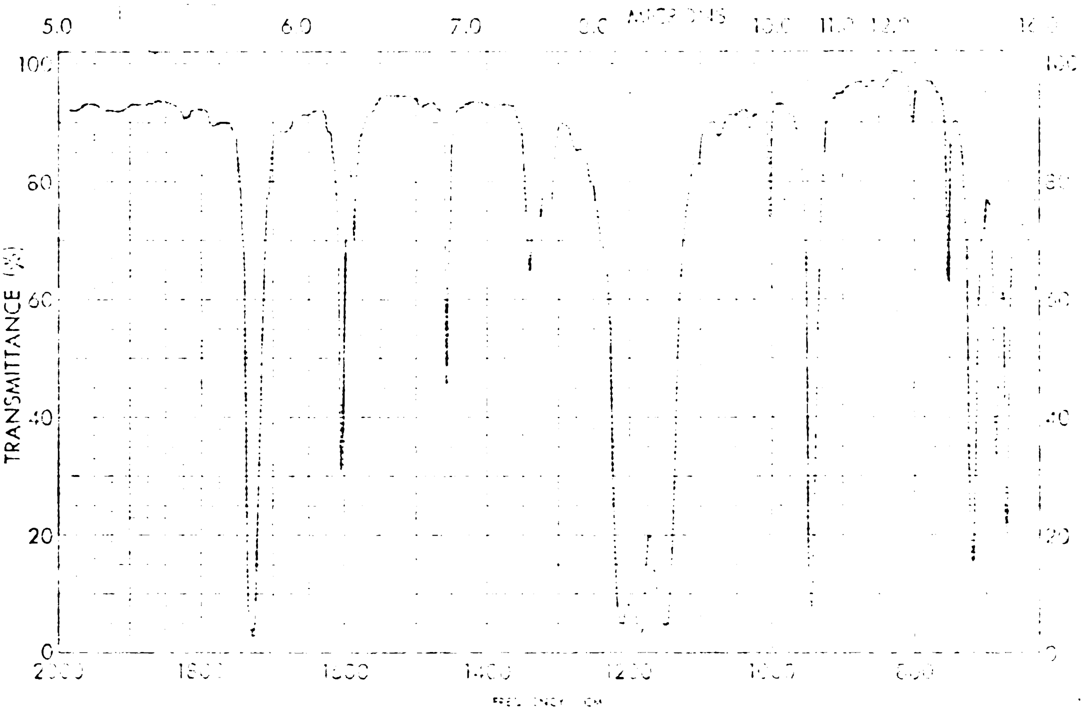


Figure 8. IR spectra of trifluoroacetophenone.

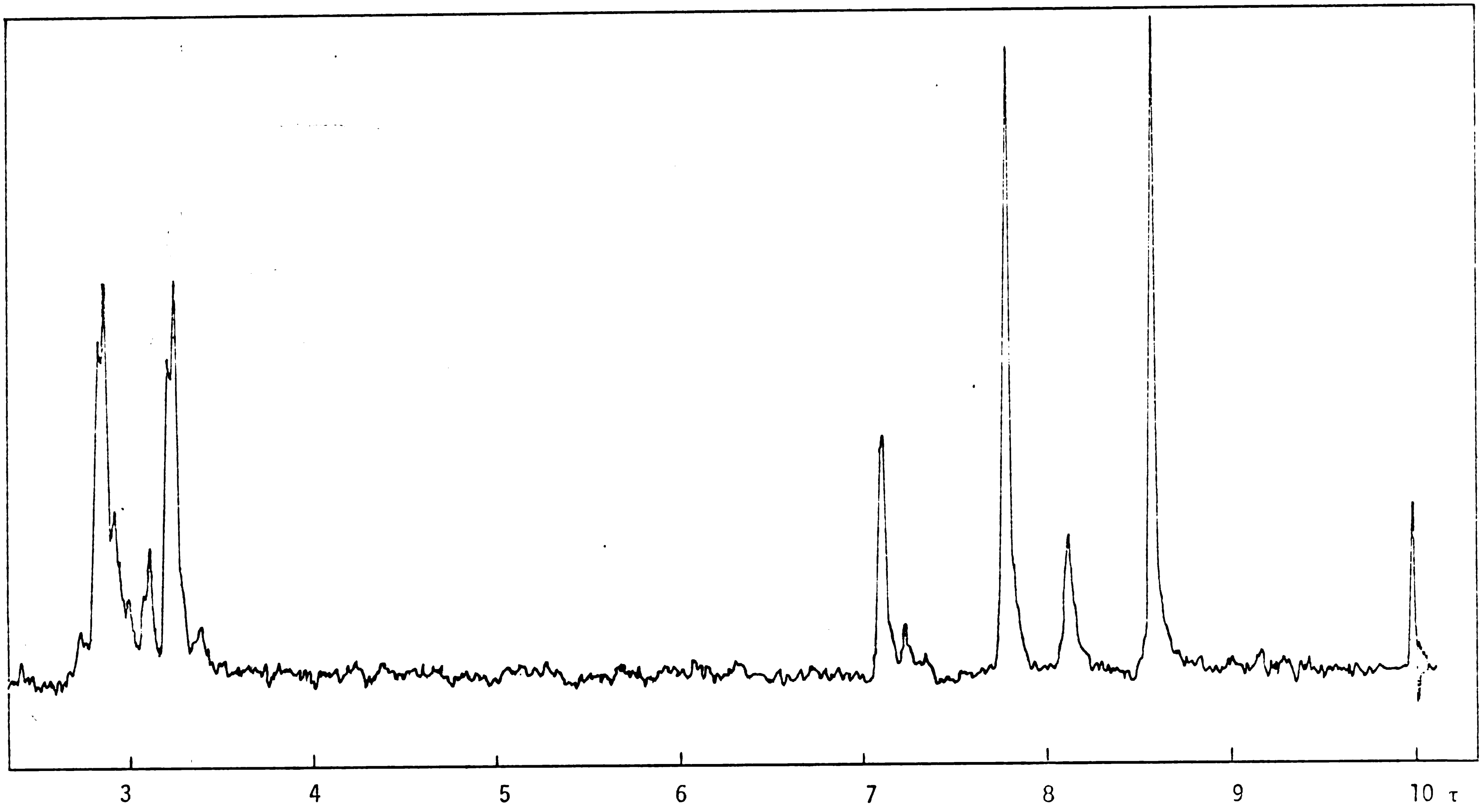


Figure 9. NMR spectra of 1-p-tolyl-2-phenyl-2-propanol(IV).

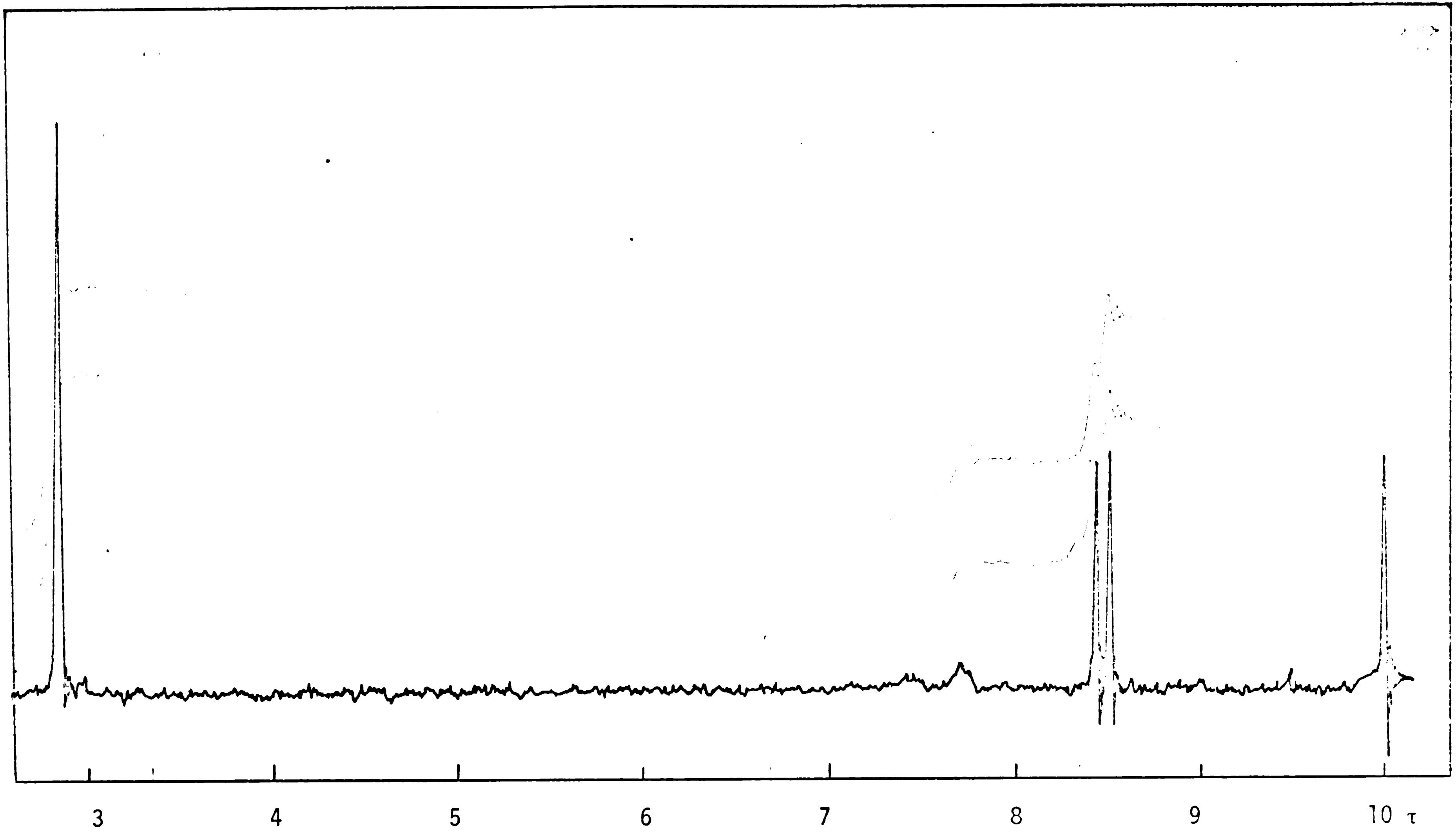


Figure 10. NMR spectra of 2,3-diphenyl-2,3-butadiol(V).

Table 18. Mass Balance Experiment for 0.10 M Acetophenone and 1.00 M p-Xylene[a].

| Sample | DTE[b] | IV[b] | V[b] | DTE/$C_{18}$[c] | [DTE] x10$^5$ | ACP/$C_{16}$[d] | [ACP+] | 2x[ACP+][e] | [ACP-] | $\frac{[DTE]}{[ACP-]}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 36.2 | 45.2 | 18.6 | 2.19 | 627 | 0.379 | 0.0409 | 0.0818 | 0.0182 | 0.344 |
| 2 | 35.6 | 46.2 | 18.2 | 2.09 | 599 | 0.371 | 0.0400 | 0.0800 | 0.0200 | 0.300 |
| Ave. | 35.9 | 45.7 | 18.4 | | | | | | | 0.322 |

[a] All concentrations in moles/liter. 0.0025 M $C_{18}$ internal standard, F = 1.146. F = 2.16 for 0.05 M $C_{16}$ standard. [b] Product percentage from VPC peak area ratio. [c] VPC peak area ratio; column temperature 175$^o$C. [d] VPC peak area ratio; column temperature 135$^o$C. [e] Photolyzed solutions were diluted a factor of 2 in analysis for acetophenone.

Table 19. Mass Balance Experiment for 0.10 M Trifluoroacetophenone and 1.00 M p-Xylene[a].

| Sample | DTE[b] | VI[b] | VII[b] | DTE/$C_{18}$[c] | [DTE] x10$^5$ | TFA/$C_{13}$[d] | [TFA+] | 2x[TFA+][e] | [TFA-] | $\frac{[DTE]}{[TFA-]}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 30.8 | 57.2 | 12.0 | 2.66 | 761 | 0.319 | 0.0334 | 0.0668 | 0.0332 | 0.229 |
| 2 | 30.4 | 55.0 | 14.7 | 2.52 | 721 | 0.320 | 0.0335 | 0.0670 | 0.0330 | 0.218 |
| Ave. | 30.6 | 56.1 | 13.4 | | | | | | | 0.224 |

[a] All concentrations in moles/liter. 0.0025 M $C_{18}$ internal standard, F = 1.146. F = 2.10 for 0.05 M C13 standard. [b] Product percentage from VPC peak area ratio. [c] VPC peak area ratio; column temperature 175$^o$C. [d] VPC peak area ratio; column temperature 105$^o$C. [e] Photolyzed solutions were diluted a factor of 2 in analysis for trifluoroacetophenone.

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