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Hydrogen Exchange in Ketone-Semipinacol
Radical System: Kinetics and Mechanism

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HYDROGEN EXCHANGE IN KETONE-SEMIPINACOL RADICAL SYSTEM: KINETICS AND MECHANISM

BY YUANDA ZHANG

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ABSTRACT

HYDROGEN EXCHANGE IN KETONE-SEMIPINACOL RADICAL SYSTEM: KINETCS AND MECHANISM

BY

YUANDA ZHANG

Photoreduction of ketones by pinacol

The rate constants for the photoreduction of ketones by pinacol and pinacol-d_2 were measured to determine the isotope effect in the hydrogen abstraction step. No significant isotope effect was detected.

Hydrogen exchange in ketone-semipinacol radical system

After irradiation of a mixture of two ketones in the presence of 2-propanol, the ratio of steady state semipinacol radical was obtained by analysis of pinacols resulted from the radical combination. Several equilibrium constants of degenerate hydrogen exchange from semi-pinacol radical to ketone was calculated.

From the initial interaction of excited state ketone with aromatic

alcohol, the overall radical quantum yield was quantitatively measured, and the maximum quantum yield and k_d/k_r were obtained.

The rate constants of hydrogen exchange in ketone-semipinacol system were measured by a steady-state approximation method. The contribution of such rate constants to the overall competitive reactions was estimated. The substituent effect and steric effect for hydrogen exchange in ketone-semipinacol system were compared.

I would like to dedicate this thesis to my family,
for their support and patient understanding, for
their constant encouragement and love.

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TABLE OF CONTENTS

Page

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

LIST OF SCHEMES

ABBREVIATIONS

AP	Acetophenone
PP	Propiophenone
MeAP	p-Methylacetophenone
isBP	Isobutyrophenone
MeOAP	p-Methoxyacetophenone
ClAP	p-Chloroacetophenone
$(AH)_2$	2,3-Diphenyl-2,3-butanediol, acetophenone pinacol
$(PH)_2$	2,3-Diphenyl-3,4-hexadiol, propiophenone pinacol
$(ClAH)_2$	2,3-Bis(4-chlorophenyl)-2,3-butanediol p-Chloroacetophenone pinacol
$(BH)_2$	2,5-Dimethyl-3,4-diphenyl-3,4-hexadiol Isobutyrophenone pinacol
$(MeAH)_2$	2,3-Bis(4-methyl)-2,3-butanediol p-Methylacetophenone pinacol
AH_2	1-phenylethanol
PH_2	1-Phenylpropanol
$ClAH_2$	1-(4'-Chlorophenyl) ethanol
$isBH_2$	2-Methyl-1-phenylpropanol
$MeAH_2$	1-(4'-methylphenyl) ethanol

INTRODUCTION

The photoreduction of ketones by alcohols has been an important subject in photochemistry for about a century and generally considered as one of the best understood organic photochemical reactions. Since the appearance of a number of comprehensive review articles{1}, this area has undergone much expansion. A series of important and exciting research, including investigation of kinetic parameters and mechanism, has appeared. In addition, a new development in probing hydrogen exchange in ketone-semipinacol radical system has been reported.{2}

The research presented and discussed in this thesis is bimolecular hydrogen abstraction reaction focusing on the measurement of kinetic parameters by one of the important steps for hydrogen exchange in the ketone-semipinacol radical system.

<u>Bimolecular Hydrogen Abstraction Reactions in Ketone Photochemstry</u> Ketone photochemistry is one of the most intensively studied areas in organic photochemistry. The study of carbonyl compounds has helped our understanding of very fundamental questions.

Photoexcited ketones undergo characteristic hydrogen abstraction from compounds having active hydrogens. These include both bimolecular and intramolecular reactions. For the bimolecular reaction, the products are formed by the coupling and disproportionation of two radicals produced in the initial hydrogen abstraction step; hydrogen exchange from semi-pinacol radical to ground state ketone. Scheme 1. gives the mechanism for this reaction:

$$1.\ \mathrm{K} \underset{k_{d_1}}{\overset{h\nu}{\rightleftharpoons}} {}^{1}\mathrm{K}^{*} \xrightarrow{k_{isc}} {}^{3}\mathrm{K}^{*}$$

$$2.\ {}^{3}\mathrm{K}^{*} \xrightarrow{k_{d2}} \mathrm{K}$$

$$3.\ {}^{3}\mathrm{K}^{*} + \mathrm{AH_2} \xrightarrow{k_{HT}} \cdot\mathrm{KH} + \cdot\mathrm{AH}$$

$$4.\ \mathrm{K} + \cdot\mathrm{AH} \underset{k_{-ex}}{\overset{k_{ex}}{\rightleftharpoons}} \mathrm{A} + \cdot\mathrm{KH}$$

$$5.\ \cdot\mathrm{KH} + \cdot\mathrm{KH} \xrightarrow{k_{dis}} \mathrm{K} + \mathrm{KH_2}$$

$$6.\ \cdot\mathrm{AH} + \cdot\mathrm{AH} \xrightarrow{k_{dis'}} \mathrm{A} + \mathrm{AH_2}$$

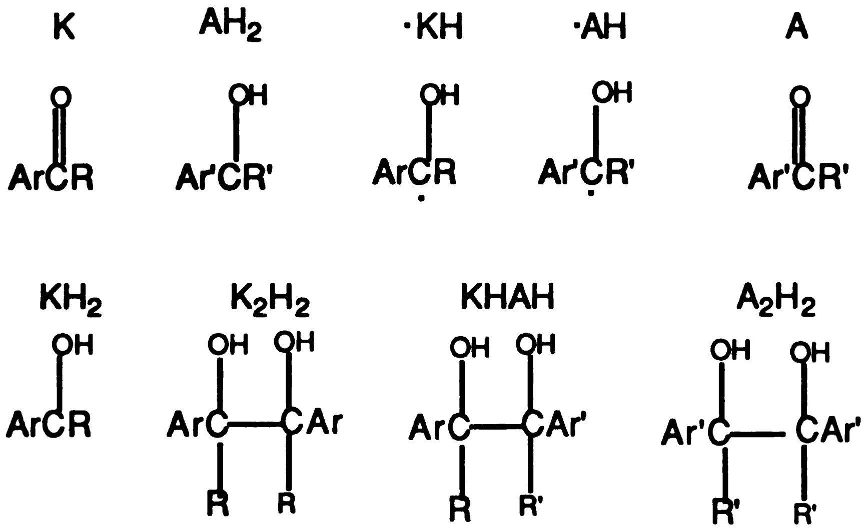
$$7.\ \cdot\mathrm{KH} + \cdot\mathrm{AH} \xrightarrow{k_{dis''}} \mathrm{KH_2} + \mathrm{A} + \mathrm{K} + \mathrm{AH_2}$$

$$8.\ \cdot\mathrm{KH} + \cdot\mathrm{KH} \xrightarrow{k_{ck}} [\mathrm{K_2H_2}]$$

$$9.\ \cdot\mathrm{AH} + \cdot\mathrm{AH} \xrightarrow{k_{ca}} [\mathrm{A_2H_2}]$$

$$10.\ \cdot\mathrm{KH} + \cdot\mathrm{AH} \xrightarrow{k_{cm}} [\mathrm{KHAH}]$$

Scheme 1: Mechanism of photoredox in ketone-semipinacol radical system



Scheme 2: The correlation between structures and abbreviations for Scheme 1.

The experiments presented in this thesis attempted to measure the rate constants of hydrogen exchange reactions occurred during the irradiation of ketone with alcohol in degassed benzene. The comparison of these rate constants with other competitive rate constants would give us a better understanding of the actual processes occurring in the old photoredox reaction.

There are five factors expected to influence the reaction: the strength of the bond being broken, the strength of the bond being formed; polar or charge-transfer effects on the energy of the transition state relative to the energy of the reagents; steric effects on the approach of the substrate; solvent effects on the reagent, substrate, and transition state.

Each of these effects has an influence on the rate constant for the abstraction of a hydrogen atom by an excited state of a carbonyl compound. During the course of research involving the photoreduction of ketones, a wide variety of reactions have been reported. The reactions closely related to the research presented in this thesis are summarized below.

The rate constants of hydrogen abstraction are strongly affected by C-H bond strength. The triplet carbonyl reactions are corresponding to the following step:

$$^{3}R_2'CO^{*} + H\text{-}R \longrightarrow R_2'\dot{C}\text{-}OH + \cdot R \qquad (1)$$

$$\Delta H = D(R\text{-}H) - \{ E_T - E_\pi + E(O\text{-}H)\}$$

where $E_\pi = E(C{=}O) - E(C\text{-}O)$ is the carbonyl "π-bond energy". The term $\{E_T - E_\pi + E(O\text{-}H)\}$ represents the strength of the forming bond.[3] Previtali and Scaiano[4] carried out a bond-energy-bond-order calculation for hydrogen abstraction by triplet benzophenone and acetcphenone. They took E_π and $E(O\text{-}H)$ to be the same for both carbonyl groups. They also indicated that the best available interpretation of equation (1) was that of considering the $^3n, \pi^*$ state of carbonyl compounds as a biradical, where the oxygen atom behaved as a true free radical center. A resonance stabilization of the carbonyl with a benzene ring lowers the C-O π-bond energy because the semi-pinacol radical is resonance stabilized.

The $^3n, \pi^*$ state of carbonyl compound is radical- like and has a reactivity very similar to that observed with t-butoxy radicals.[5] The energy of hydrogen abstraction by triplet benzophenone can be obtained from the following thermochemical cycle:

$$
\begin{array}{rclll}
(C_6H_5)_2C{=}O & \longrightarrow & (C_6H_5)_2\dot{C}{-}\dot{O} & +\ 69\ \text{kcal/mol} & (2) \\
(C_6H_5)_2CHOH & \longrightarrow & (C_6H_5)_2C{=}O + H_2 & +\ 9\ \text{kcal/mol} & (3) \\
H_2 & \longrightarrow & 2H\cdot & +\ 104\ \text{kcal/mol} & (4) \\
H\cdot + (C_6H_5)_2\dot{C}{-}OH & \longrightarrow & (C_6H_5)_2CHOH & -\ 78\ \text{kcal/mol} & (5) \\
\hline
(C_6H_5)_2\dot{C}{-}OH & \longrightarrow & (C_6H_5)_2\dot{C}{-}\dot{O} + H\cdot & +\ 104\ \text{kcal/mol} & (6)
\end{array}
$$

Where equation (2) is the triplet excitation energy of bezophenone known from spectroscopic data,[6] equation (3) and (4) are available from standard thermochemical tables. The energy of equation (5) has been estimated by Gibian according to several results[7]. The accepted value of energetics for t-butoxy radicals is 104 kcal/mol[8] which gives the same value for bezophenone triplet, uncertain by at least 5-10 kcal/mol.

The activation energy for abstraction of an unactivated secondary hydrogen is 3-3.5 kcal/mole; the activation entropy dependents on the system.{3,9} This activation energy is also comparable to the t-butoxy radicals.

Most phenyl ketones have two low-lying triplets, an n, π* and a π,π* triplet, whose energy levels are affected by the ring substituents.{10} The n, π* triplet comes from excitation of a nonbonding electron of the carbonyl group to a π-antibonding orbital, creating an electron deficient oxygen. The chemical behavior of the n, π* triplet state is similar to an alkoxyl radical, and hydrogen abstraction is the predominant reaction for the n, π* triplet state.{11} In a π, π* triplet, excitation of a π electron to a π-antibonding orbital makes the oxygen atom slightly electron rich (Figure 1.), slowing down the hydrogen abstraction and making the π, π* triplet much less reactive than the n, π* triplet. In general, electron withdrawing substituents stabilize the n, π* triplets relative to the π,π* triplets and electron donating groups lower the π,π* triplet energy levels.{12}

Figure 1. n, π* and π, π* excited state

Ring substituents have significant effect for the observed rate in the reactions. 4-Methylbenzophenone shows a 1.5 fold decrease in the rate constant of hydrogen abstraction, while 4-trifluoromethylbenzophenone, which n, π^* lowest triplets are easily photoreduced by 2-propanol,{13} shows 1.8 fold increase in the rate of hydrogen abstraction, as compared to benzophenone. The photoreduction of 4-trifluoromethylacetophenone (n, π^* lowest triplet state) shows a 6 fold increase in the rate of hydrogen abstraction, but 4-methylacetophenone (π, π^* lowest triplet state) has a 10 fold decrease in reactivity, with reference to acetophenone.{14}

Lewis{15} et al. have examined the steric effects in the bimolecular hydrogen abstraction from 2-propanol by aryl-alkyl-ketone triplet from 2-propanol and found that the rate constant for acetophenone photoreduction decreased with increasing α-methyl substitution. The results are given in Table 1:

Table 1: Quantum yields and rate constants for photolysis of acetophenone 1, propiophenone 2 and isobutyrophenone 3 in 2-propanol-benzene solvent.

Ketone	$\Phi_{pinacol}$	$\Phi_{benzhydrol}$	$K_r\ M^{-1}S^{-1} X 10^5$	$K_d\ X\ 10^5\ S^{-1}$
1	0.37	0.007	6.8	3.4
2	0.19	0.033	4.4	3.2
3	0.071	0.049	0.9	3.4

From Table 1, the quantum yields of pinacol formation and the rate constant for hydrogen abstraction (K_r) decrease with increasing α-substitution. There is no corresponding increase in rate constant for triplet decay (K_d), therefore the authors concluded that the decrease in reactivity is due to the structural effect: increased steric hindrance at α position makes abstraction of a hydrogen from 2-propanol more difficult, and the steric effects can play an important role in determining the rate of hydrogen abstraction reaction.

Lewis[16] also reported further evidence for a steric requirement for hydrogen abstraction by employing 2,4-dimethyl-3-heptanol as a hydrogen donor given in Table 2.

Table 2: Quantum yields for 2,4-dimethyl-3-heptanone formation and kinetic data for acetophenone **1**, propiophenone **2**, and isobutyrophenone **3** with 2M 2,4-dimethyl-3-heptanol in benzene:

Ketone	Φ	$K_r M^{-1} S^{-1} X 10^5$
1	0.185	2.8
2	0.130	2.5
3	0.055	0.6

Table 2 reflect a substantial decrease in reactivity when compared with the 2-propanol results in Table 1.

M. Y. Moss, et al.{17} have reported that relative reactivity of bimolecular hydrogen abstraction by triplet benzophenone depends on the size of the secondary alcohols. They mixed benzophenone (0.5-3.0 moles) with two pure alcohols (6-26 moles each), after irradiation for 12-30 hours, mole ratios of the two generated ketones were followed by GLC analysis using predetermined calibration curves. The results of the competition for hydrogen abstraction are shown in Table 3:

Table 3: Competitive Hydrogen Abstraction

Substrate	Relative Reactivity
2-Propanol	1.00
Methyl-t-butylcarbinol	0.9 ± 0.02
3-Heptanol	0.67 ± 0.02
Methylisobutylcarbinol	0.39 ± 0.01
Methylneopentylcarbinol	0.18 ± 0.01
Diisobutylcarbinol	0.074 ± 0.001

The results indicated that the reactivity of hydrogen abstraction decreases as steric hindrance and chain-branching increases.

Neckers and Huyser[18] reported the relative reactivities for peroxide-induced reductions of substituted acetophenone given in Table 4:

Table 4: Reactivities of substituted acetophenone with 2-butanol (Di-t-butyl peroxide induced at 125° C)

Substituent	k/k_0
p-Cl	3.01
H	1.00
p-Me	0.59

$$k/k_0 = \log(A_0/A) / \log(B_0/B)$$

where k/k_0 is the relative reactivity ratio, A_0 and B_0 are quantities of the substituted acetophenone and acetophenone before reaction, A and B are the quantities of the two ketones after reaction. From Table 4, an electron releasing group, para methyl substituent, decreases the reactivity of the carbonyl of acetophenone toward reaction with the 1-hydroxyalkyl radical, whereas electron withdrawing para chloro substituent increases the reactivity.

The different rate constants for hydrogen abstraction reaction in solvents of different polarity suggest a change in reactivity with the polarity of media. Gramain et al.[19] reported that the rate constant for hydrogen abstraction by acetophenone from 2-propanol was 4.8 X 10^6 $M^{-1}s^{-1}$ in carbon tetrachloride as solvent. In the case of the acetophenone-2-propanol system, the second order rate constants were 19 X 10^5 $M^{-1}s^{-1}$ in benzene and 7 X 10^5 $M^{-1}s^{-1}$ in neat 2-propanol. {20, 10(a)} In the xanthone-2-propanol system, the rate constants for hydrogen abstraction were 1.1X10^8 $M^{-1}S^{-1}$ in CCl_4, 4.1X10^5 $M^{-1}S^{-1}$ in 1:1 CCl_4-2-propanol, 2.1X10^5 $M^{-1}S^{-1}$ in neat 2-propanol.{21} Wagner {22} has indicated that the carbonyl oxygen became electron deficient in n, π^* triplet, the polar solvents generally make the hydrogen bonding unstable, even though the solvent effects can be observed, there must be reverse hydrogen transfer by polar solvents and reduced the rate constants for the bimolecular hydrogen abstraction reaction.

Early Mechanistic Studies Hydrogen abstraction by an n, π^* triplet ketone was first reported by Ciamician and Silber.{23} They reported that the action of sunlight on a mixture of benzophenone and ethanol formed a precipitate identified as benzpinacol. This initial report led to interests in the mechanistic aspects and the measurement of relative rate constants.

G. S. Hammond et al.{24} studied the photoreduction of bezophenone and deduced the analysis method to calculate the ratio of rate constants for triplet decay over hydrogen abstraction. They accounted for the mechanism shown in scheme 3:

$$K \underset{K_{d_1}}{\overset{h\nu}{\rightleftarrows}} {}^{1}K^{*} \xrightarrow{K_{isc}} {}^{3}K^{*}$$

$${}^{3}K^{*} \xrightarrow{K_{d_2}} K$$

$${}^{3}K^{*} + BH_2 \xrightarrow{K_r} KH\cdot + BH\cdot$$

$$KH\cdot + BH\cdot \xrightarrow{\alpha} (KH)_2 + (KHBH) + (BH)_2 + KH_2 + B$$

$$KH\cdot + BH\cdot \xrightarrow{1-\alpha} K + BH_2$$

Scheme 3: Hammond's mechanism of photoreduction

1. The efficiency of triplet formation is:

$$\Phi_{isc} = \frac{k_{isc}}{k_{isc} + k_{d1}}$$

2. The efficiency of intermediate formation is :

$$\frac{k_r[BH_2]}{k_r[BH_2] + k_{d2}}$$

3. The efficiency of the intermediate going to product is α

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

$$\Phi = \alpha\Phi_{isc}\left(\frac{k_r[BH_2]}{k_r[BH_2] + k_{d2}}\right)$$

By inverting the equation for Φ , a linear plot of $1/\Phi$ versus $1/[BH_2]$ can be obtained.

$$\Phi^{-1} = (\alpha\Phi_{isc})^{-1}\left(1 + \frac{k_{d2}}{k_r[BH_2]}\right) \qquad (7)$$

The slope of the plot is $k_d/(\alpha\Phi_{isc}k_r)$, and the intercept is $1/\alpha\Phi_{isc}$. In Hammond's equation, the intercept equals one.

$$\frac{K_d}{k_r} = \frac{\text{slope}}{\text{intercept}} \qquad (8)$$

The value of maximum quantum yield was obtained from infinite concentration of substrate which is reciprocal of the intercept.

$$\Phi_{mex} = \alpha\Phi_{isc} \qquad (9)$$

Flash photolysis and ESR techniques are excellent methods for the study of hydrogen abstraction reaction, but the kinetics of the hydrogen exchange between ketone-semipinacol radical can not be detected directly by the flash technique, because the degeneracy of the reaction prevents measurement by absorption or ESR spectroscopy. M. F. Quinn et al.{25} reported the results of a flash photolysis study of benzophenone in ethanol. They suggested the mechanism including combination and disproportionation products. They can not detect if some of the disproportionation products should come from ketone-semipinacol radical interaction.

There are some early research{26} reported when bezophenone irradiated with 2-propanol, cyclohexanol and benzyl alcohol yielding acetone, cyclohexanone and benzaldehyde.

Weizman{27} reported an investigation of the photoreductions of acetophenone with butanol, acetophenone with cyclohexanol, cyclohexanone with cyclohexanol, and acetone with butanol. The products were pinacols from the starting ketone and another ketone or aldehyde corresponding to the starting alcohol. They concluded that the first step of irradiation is the activation of the carbonyl compound, leading to a diradical form. This form react with the carbinol, splitting the C-H* bond and giving two radicals (Figure 2). They indicated that the two radicals were subsequently

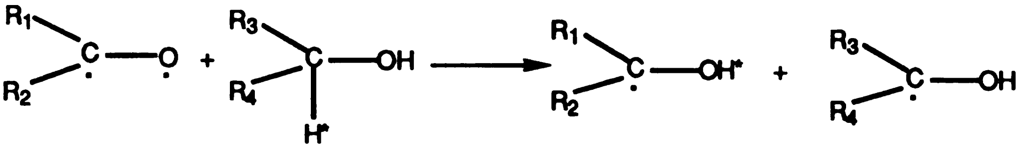


Figure 2: Primary products of photoreduction

stabilized by symmetrical or unsymmetrical dimerization or by a second oxidation-reduction process.

Franzen(28) first reported that hydrogen exchange with starting ketone removes most of semi-pinacol radical produced from the starting alcohol before it can react with another radical (Figure 3).

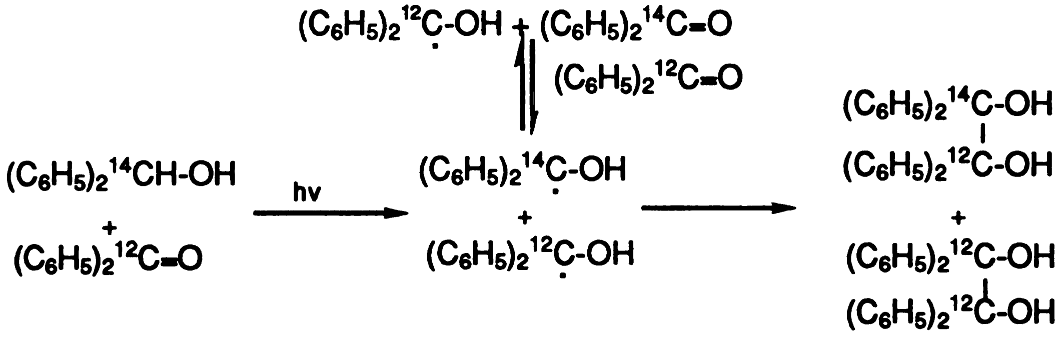


Figure 3: Hydrogen exchange with starting ketone.

Schuster[29] demonstrated that the primary photochemistry gives a triplet radical pair which do not couple directly, but escape from solvent cage followed by a series of hydrogen transfer reaction with ground state ketone or labeled benzhydrol (Figure 4).

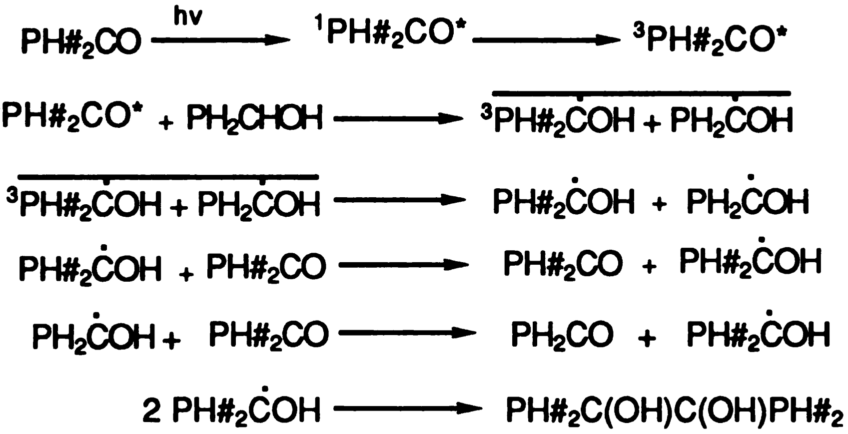


Figure 4: Schuster's mechanism. (# represents some positional or isotopic label)

Warashina et al.[30] observed the kinetic behaviors of electron spin resonance spectra during photolysis of benzophenone in ethanol, with and without sodium methoxide. The diphenylhydroxymethyl radicals and hydroxyethyl radicals revealed by ESR gave a firm evidence of hydrogen abstraction of excited bezophenone from ethanol, in the presence of sodium methoxide, and the diphenylhydroxymethyl radicals being transformed into bezophenone ketyl anions. The observed concentration of diphenylhydroxymethyl radical and bezophenone ketyl anion formed during the photolysis of benzophenone in ethanol was plotted as a function of sodium methoxide concentration, giving the rate constant of benzpinacol formation at the value of 3 X10^7 mol^{-1}·L·S^{-1}.

G. O. Schenck et al.{31} studied the mechanism of the ketone-semipinacol interaction by electron spin resonance spectra. They irradiated benzene solution of benzhydrol with high concentration of benzophenone and found that the ketone-semipinacol radical interaction was due to hydrogen-bonded complexes of type II. (Figure 5.) They excluded the mechanism of ketyl anion formation by Warashina.

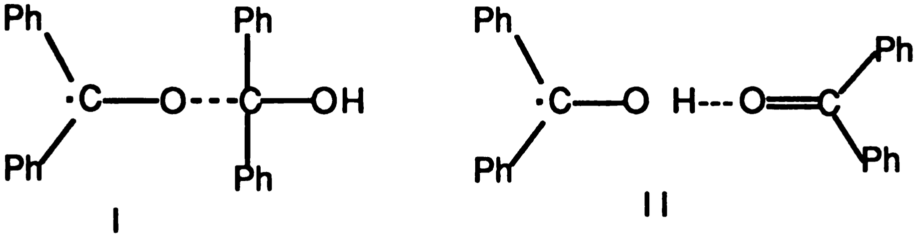


Figure 5: Hydrogen bonded complexes of ketone-ketyl interaction

J. N. Pitts{32} et al. studied the photoreduction of benzophenone in isopropyl alcohol. They observed quantum yields close to unity for benzopinacol and acetone, but no cross pinacol was formed. They assumed that the dimethylketyl radical of acetone transfered hydrogen to benzophenone to form the more stable free radical of benzhydrol. This step was much faster relative to the combination reaction because of the strong reducing nature of the dimethylketyl radical of acetone.

Neckers and Huyser{18} demonstrated the mechanism reported by J. N. Pitts. They studied the decomposition of di-t-butyl peroxide in a solution of acetophenone in 2-butanol, reducing acetophenone to acetophenone pinacol and oxidizing 2-butanol to 2-butanone. They examined the products stoichiometrically and found the amount of 2-butanone formed is in excess of the expected amount of peroxide used. From this result, they assumed that the excess of 2-butanone came from the interaction of 1-hydroxyalkyl radicals with the aromatic ketone producing benzhydrol radicals which proceed to disproportionation and combination reactions.

Closs{33} et al. have studied the benzaldehyde proton signals by CIDNP spectra and suggested that bezoin is formed by cage collapse and the escaping free radicals are polarized oppositely to cage product, in which the hydrobenzyl radical transfers a hydrogen atom to benzaldehyde to give polarized benzaldehyde and unpolarized hydroxybenzyl radicals. The later step is similar to the hydrogen transfer as suggested by J. N. Pitts.

C. Steel et al.{2} studied the photoreduction of bezophenone by 2-propanol in acetonitrile, focusing on the rate constant for hydrogen transfer from semi-pinacol radical of acetone to benzophenone (K) by measuring the quantum yields of benzopinacol (K_2H_2), using numerical methods and some literature data. They used the approximate equation (10) at steady state:

$$\frac{2\Phi_{K_2H_2} - 1}{(1 - \Phi_{K_2H_2})^{1/2}} = \frac{k_{ex}[K]}{k_{dis}^{1/2}\ I^{1/2}} \qquad (10)$$

They neglected the self and crossing disproportionation reaction of steps 5 and 7 in Scheme 1. In equation (10), I is the rate of light absorption (Einstein/Ls) by benzophenone and they used literature value $k_{dis} = 2 \times 10^9\ M^{-1}S^{-1}$[34], and found $k_{ex} = 2 \times 10^4\ M^{-1}S^{-1}$. They used the Newton-Raphson method[35] to get the semi-benzopinacol radical value X. Using

$$\Phi_{K2H2} = (1 - \alpha)\ k_{ck}\ [x]^2/I$$

they set α at the value of 0.01, the k_{ck}, in acetonitrile, was $1.05 \times 10^8\ M^{-1}S^{-1}$[36], and obtained model curves. By comparing the model curves with the experimental data, they reported the rate constant for the hydrogen transfer from semi-acetopinacol radical to bezophenone is $(3.5 \pm 1.5) \times 10^4\ M^{-1}\ S^{-1}$ at 298 K.

RESULTS

Quantum yield

Quantum yield was determined by parallel irradiation at 313 nm of degassed sample solutions and an actinometer in a merry-go-round apparatus at 25° C. The sample contained ketone and the hydrogen donor. The solvent was degassed benzene. The actinometer was a 0.1 M solution of valerophenone in benzene.[37] Percentage of conversion was kept as low as possible, usually around 10%, linear plots were obtained in the $1/\Phi$ region of 1-6 or larger for all ketones and alcohols. The ratios of product to standard were obtained by HPLC or GC analysis.

Photoreduction of ketones by pinacols

The quantum yields of the photoreduction for ketones by pinacol and pinacol-d_2 (70% deuterated) have been measured to see the isotope effect. The solution was prepared in various concentrations of pinacol and 0.1M ketone in degassed benzene. All samples were irradiated in parallel at 313 nm for the same amount of time which assured that each sample absorbed the same intensity of light. Analyses were performed on HPLC. The reaction shows no isotope effect in the hydrogen abstraction step. Table-5 gives the slope and intercept of plotting. The measurements were shown in Table 16, 17 and plotted in Figure 6,7.

Table 5: Results for photoreduction of various ketones by acetophenone pinacol and acetophenone pinacol-d_2:

Reactants	Slope	Intercept
$PP/[AH]_2$	0.76 ±0.041	19 ± 2.7
$PP/[AD]_2$	0.96 ±0.033	22 ± 2.0
$MeOAP/[AH]_2$	0.86 ±0.048	10 ± 2.9

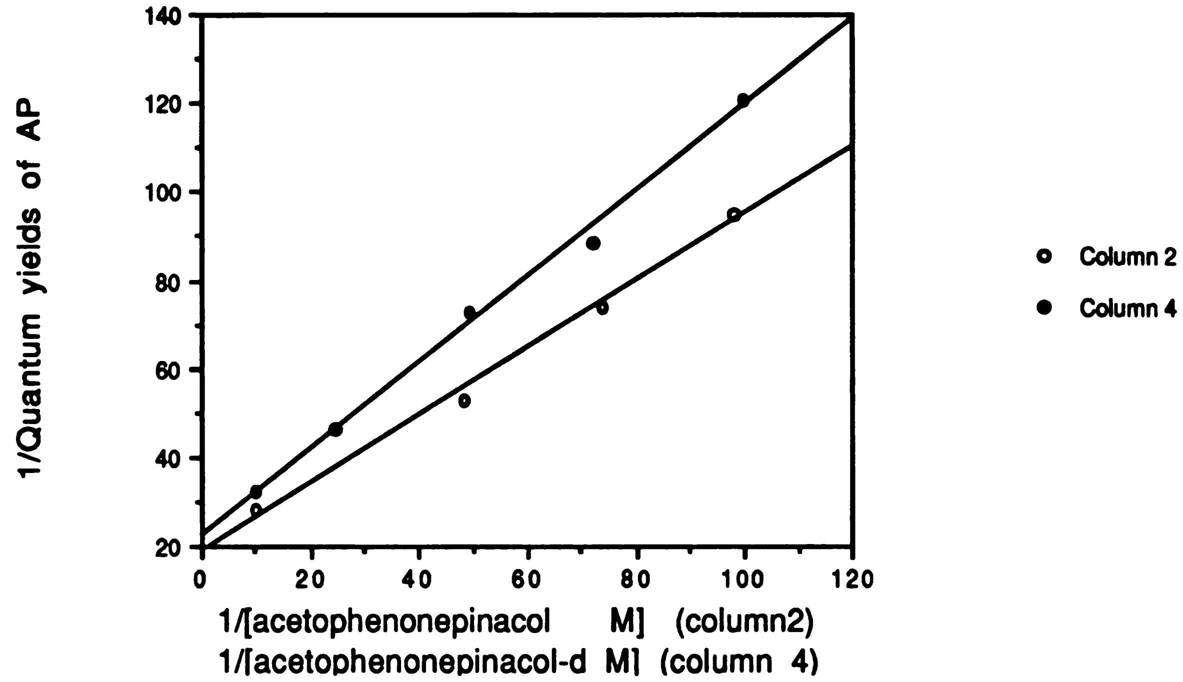


Figure 6: Reaction of 0.1M propiophenone with acetophenone pinacol (column 2) and acetophenone pinacol-d_2 (column 4) in benzene:

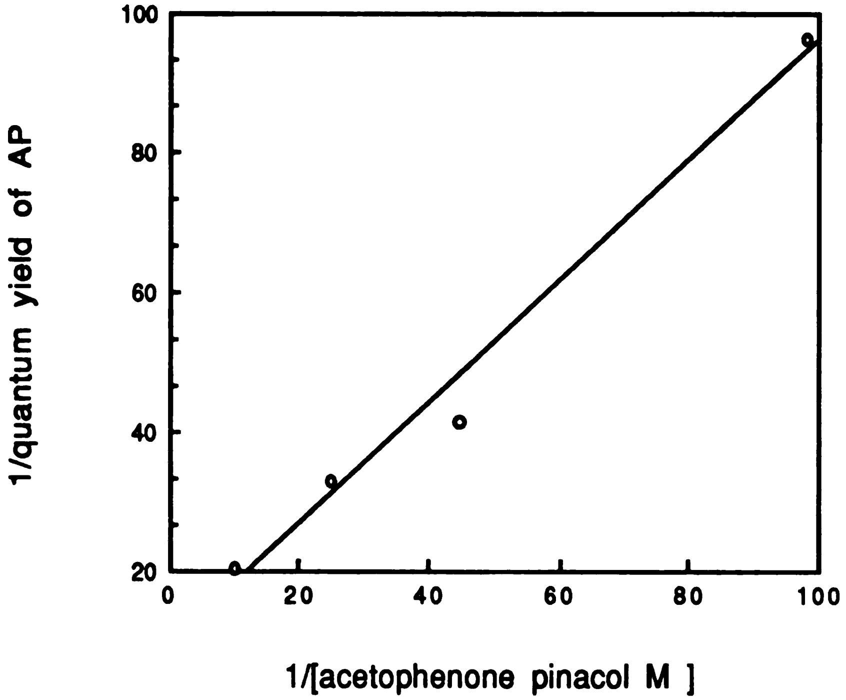


Figure 7: Reaction of 0.1M p-methoxyacetophenone with acetophenone pinacol in benzene:

Measurement of Equilibrium Constants

After irradiation of a mixture of two ketones (high concentration 0.05-0.5 M and equal amount) with 2-propanol (1 M) in degassed benzene at 313 nm, two semi-pinacol radicals were produced from two starting ketones. Three types of pinacol can occur by self and crossing combination reactions. Analyses were performed on a Varian 1400 gas chromatograph with the flame ionization detector and column DB-10 at 175° C.

The calculation of radical ratio from analysis of combination products is given by equation (11):

$$\frac{[\cdot AH]}{[\cdot KH]} = \frac{2[A_2H_2] + [AHKH]}{2[K_2H_2] + [AHKH]} \qquad (11)$$

All pinacol products were identified by preparative irradiation of ketone with 2-propanol. After recrystalization, the spectra of preparative pinacol products were compared with authentic data. The result, obtained by analysis of pinacols from irradiation, was compared with preparative products by GC. The SF value of cross pinacol was obtained by dividing the sum of the SF value from two pure pinacols. The experimental data are listed in Table 18 to 23. The summarization of radical ratio is listed in Table 6:

Table 6-1: Radical ratio of irradiation different ketones with 1M 2-propanol in benzene:

AP (M)	0.1	0.2	0.3
PP (M)	0.1	0.2	0.3
$(AH)_2$(M)	0.0033	0.0026	0.0024
(AHPH)(M)	0.0020	0.0014	0.0010
$(PH)_2$(M)	0.00024	0.00019	0.00018
·AH/·PH	3.4	3.6	3.6

AP (M)	0.10	0.15	0.2	0.30
ClAP (M)	0.05	0.05	0.1	0.10
$[AH]_2$(M)	0.00011	0.00022	0.00013	0.00019
[AHClAH](M)	0.00053	0.00069	0.00063	0.00058
$[ClAH]_2$(M)	0.00068	0.00046	0.00074	0.00046
·ClAH/·AH	2.5	1.4	2.4	1.6

continue

AP (M)	0.05	0.05	0.10	0.10
MeAP (M)	0.10	0.15	0.20	0.30
$(AH)_2$(M)	0.00040	0.00027	0.00038	0.00022
(MeAHAH)(M)	0.00063	0.00052	0.00063	0.00042
$(MeAH)_2$(M)	0.00021	0.00021	0.000092	0.00018
·AH/·MeAH	1.4	1.1	1.6	1.1

AP (M)	0.05	0.05	0.10	0.10
isBP(M)	0.10	0.15	0.20	0.30
$(AH)_2$(M)	0.00018	0.00013	0.00019	0.00013
(isBHAH)(M)	0.00076	0.00096	0.00086	0.00091
$(isBH)_2$(M)	0.00063	0.00011	0.00063	0.00012
·AH/·isBH	4.9	3.0	4.6	3.1

The value of equilibrium constants for hydrogen exchange can be calculated by equation (12):

$$K_e = \frac{k_{ex}}{k_{-ex}} = \frac{[K]\,[\cdot AH]}{[A]\,[\cdot KH]} \qquad (12)$$

Table 6-2: Calculation of equilibrium constants in hydrogen exchange reaction.

Reactants	Direction	K_e
AP/PP	AH·/PH·	3.5:1
AP/isBP	AH·/isBH·	9:1
AP/MeAP	AH·/MeAH·	3:1
AP/ClAP	AH·/ClAH·	1:5

Photoredox in ketone-semipinacol radical system

In the hydrogen exchange reactions, the samples were prepared in various concentrations of ketone and 0.2 M phenyl alcohol in degassed benzene, and irradiated in parallel for the same length of time at 313 nm. Analyses were performed on both varian 1400 and 3400 gas chromatographs, column DB-10 for pinacols, column DB-210 for exchange and disproportionation products. In all cases, all exchange products gave plots of [ketone quantum yields]$^{-1}$ versus [hydrogen donor]$^{-1}$. The experimental data are listed on Table 24, 27, 30, 33, and plotted in Figure 8, 10, 12 and 14, the slope and intercept are listed in Table 7.

Table-7: Results of photoredox reaction for ketones (varied concentration) and phenyl alcohol (0.2 M) in degassed benzene:

Reactants	slope	intercept
PP/AH_2	0.043	5.5
isBP/AH_2	0.024	7.1
MeAP/AH_2	0.046	8.3
AP/$ClAH_2$	0.050	5.1

The calculated rate constants for hydrogen exchange are listed as follows by using equation (13):

$$k_{ex} = \frac{\text{intercept}}{\text{slope}} \left(k_c I_a \Phi_{\cdot KH + \cdot AH} \right)^{1/2} \qquad (13)$$

The value of k_c is 2 X 10^9 $M^{-1}s^{-1}$[38], the light absorbances are from Table 24, 27, 30, 32; quantum yield for radicals is an average value from Table-13:

In PP/AH_2 system, radical ·AH exchange with PP:

$$k_{ex} = \frac{5.5}{0.043} (2 \times 10^9 \times 1.3 \times 10^{-6} \times 0.23)^{1/2} = 3.1 \times 10^3 M^{-1}s^{-1}$$

In isBP/AH_2 system, radical ·AH exchange with isBP:

$$k_{ex} = \frac{7.1}{0.024} (2 \times 10^9 \times 1.1 \times 10^{-6} \times 0.19)^{1/2} = 6.0 \times 10^3 M^{-1}s^{-1}$$

In MeAP/AH_2 system, radical ·AH exchange with MeAP:

$$k_{ex} = \frac{8.3}{0.046} (2 \times 10^9 \times 1.5 \times 10^{-6} \times 0.18)^{1/2} = 4.1 \times 10^3 M^{-1}s^{-1}$$

In AP/ClAH$_2$ system, radical ·ClAH exchange with AP:

$$k_{-ex} = \frac{5.1}{0.050} (2 \times 10^9 \times 0.74 \times 10^{-6} \times 0.20)^{1/2} = 1.7 \times 10^3 M^{-1}s^{-1}$$

because

$$K_e = \frac{k_{ex}}{k_{-ex}} = \frac{[AP]\,[\cdot ClAH]}{[ClAP]\,[\cdot AH]} = 0.2$$

The value of k_{ex} for radical •AH exchange with ClAP should be $9X10^3M^{-1}s^1$.

Several complementary experiments were accomplished to evaluate the extent of maximum quantum yields for hydrogen exchange reaction and the ratio of rate constants for triplet decay over hydrogen abstraction. In this study, varied concentrations of phenyl alcohol (0.1 to 1 M) were irradiated with certain concentration of ketone (0.05 M) in degassed benzene at 313 nm. The experimental results were listed on Table 26,29, 32 and plotted in Figure 9,11,13, the slope and intercept were listed in Table 8.

Table-8: Results of photoreduction for 0.05 M ketone with varied concentration of phenyl alcohol in degassed benzene:

Reactants	slope	intercept
isBP/AH_2	0.57	2.6
MeAP/AH_2	0.60	4.2
AP/$ClAH_2$	0.64	2.6

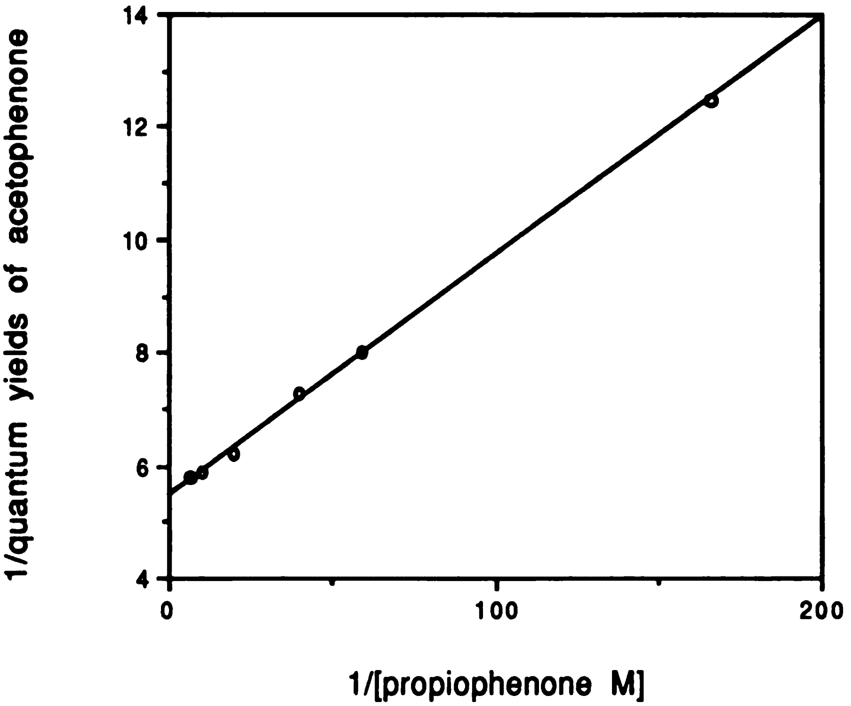


Figure 8: Quantum yields for acetophenone formation as a function of propiophenone concentration with 0.2M 1-phenylethanol in benzene.

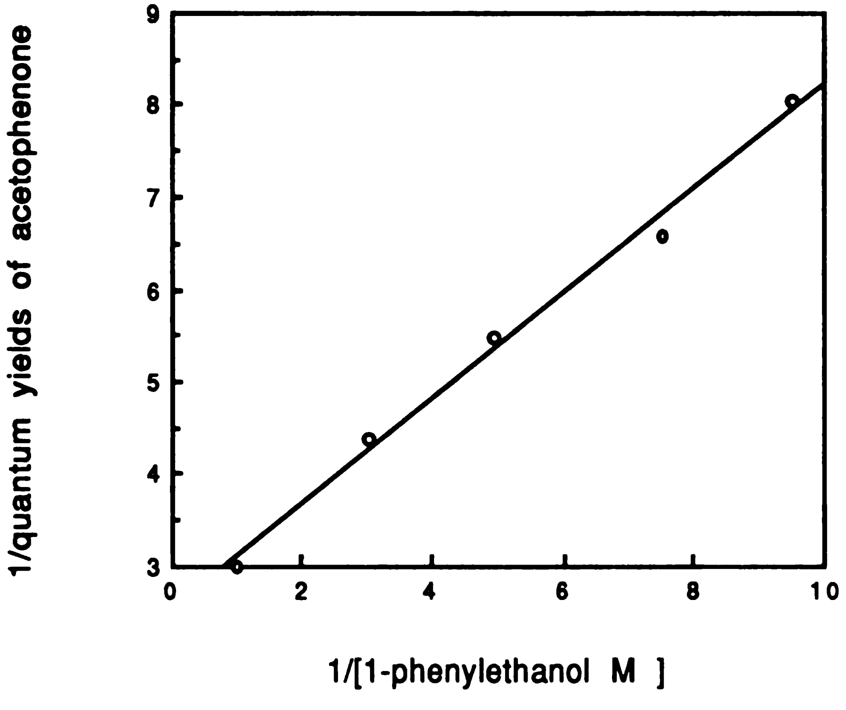


Figure 9: Quantum yields for acetophenone formation as a function of 1-phenylethanol concentration with 0.05M isobutyrophenone in benzene.

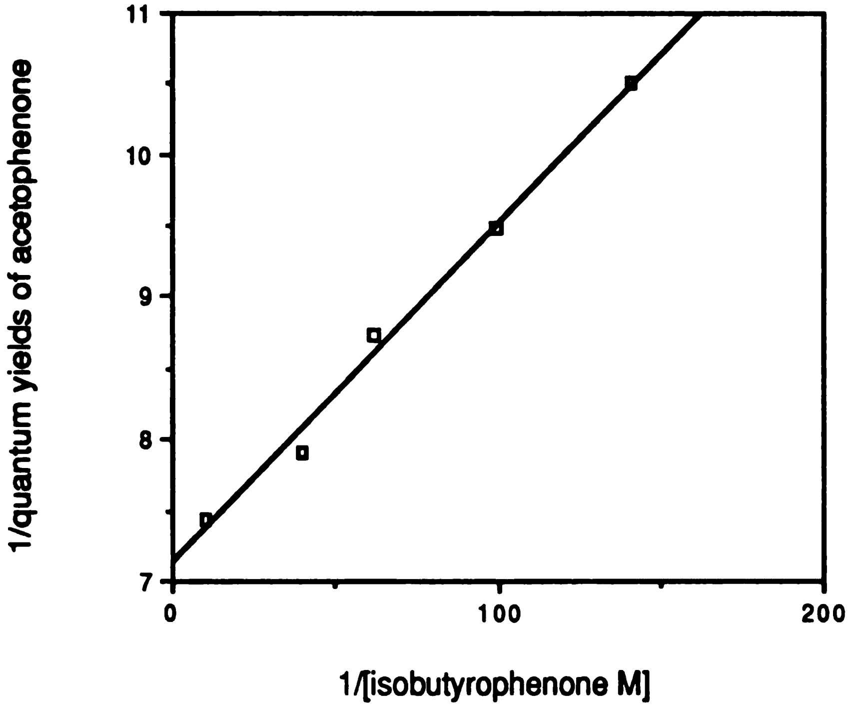


Figure 10: Quantum yields for acetophenone formation as a function of isobutyrophenone concentration with 0.2M 1-phenylethanol in benzene.

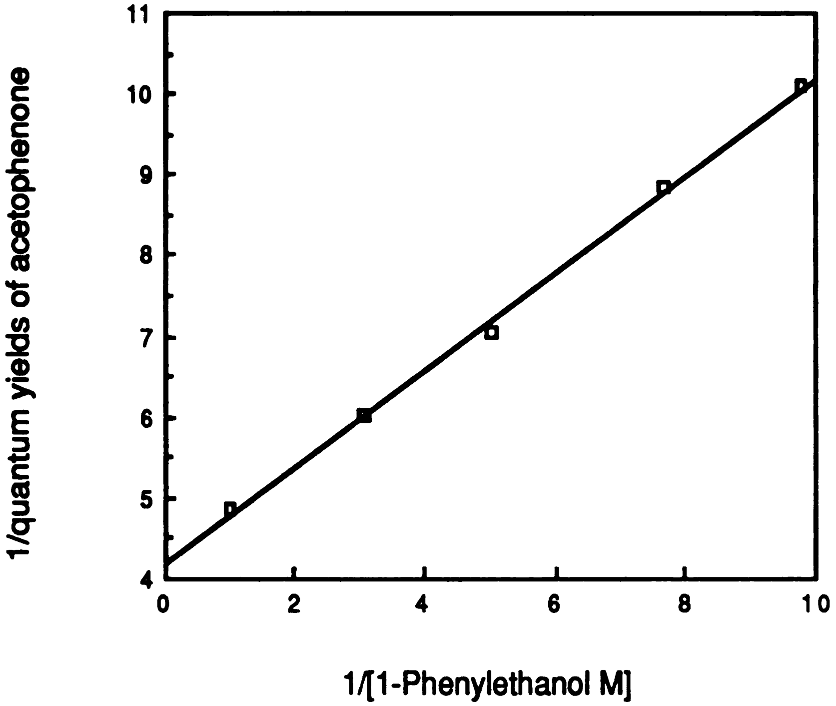


Figure 11: Quantum yields for acetophenone formation as a function of 1-phenylethanol concentration with 0.05 M p-methylacetophenone in benzene.

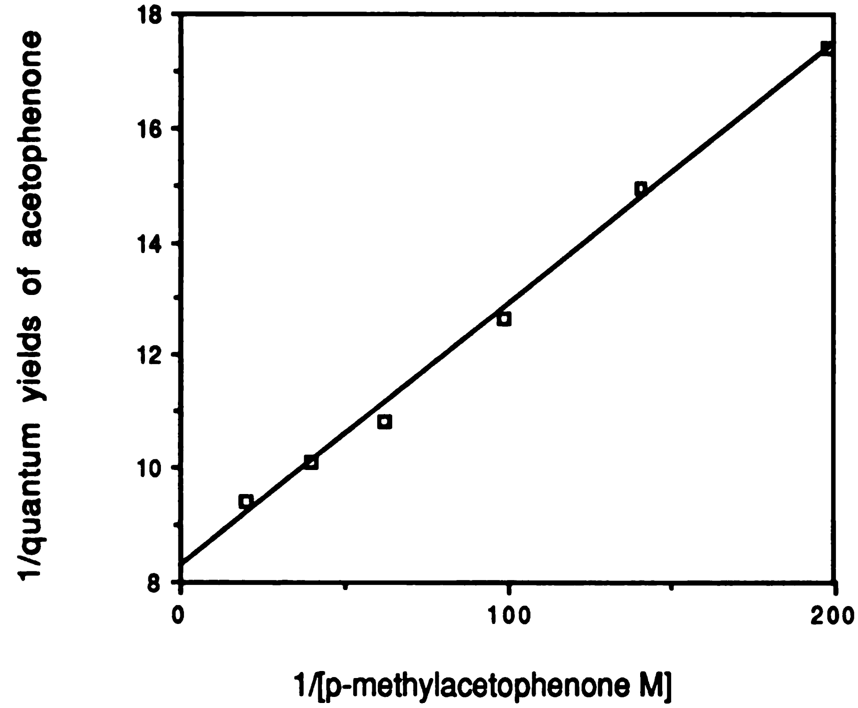


Figure 12: Quantum yields for acetophenone formation as a function of p-methylacetophenone concentration with 0.2M 1-phenylethanol in benzene.

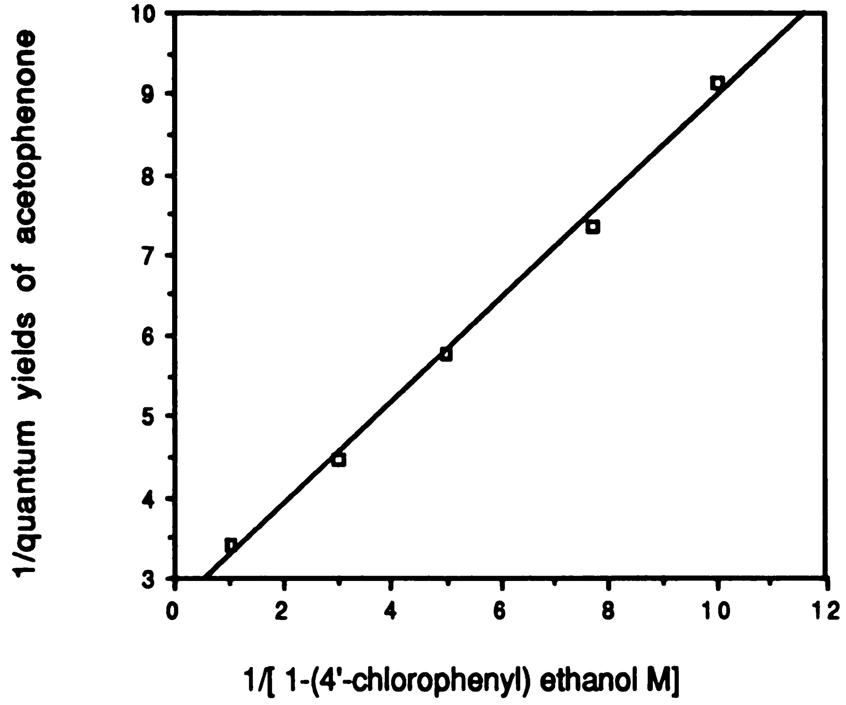


Figure 13: Quantum yields for acetophenone formation as a function of 1-(4'-chlorophenyl) ethanol concentration with 0.05M acetophenone in benzene.

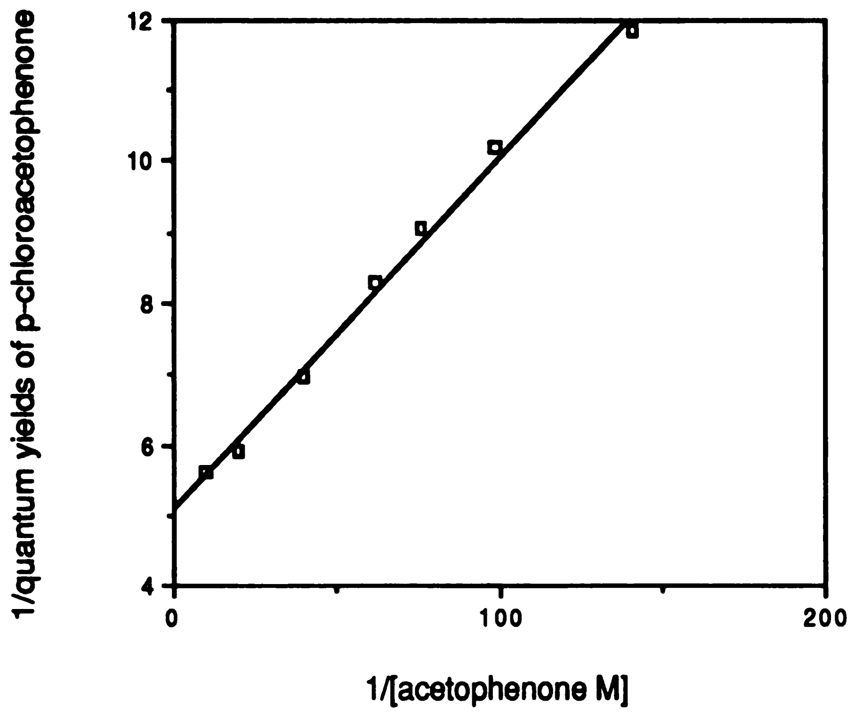


Figure 14: Quantum yields for p-chloroacetophenone formation as a function of acetophenone concentration with 0.2M 1-(4'-chlorophenyl) ethanol in benzene.

Discussion

Photoreduction of ketone by pinacols A comparison was made between undeuterated pinacol and deuterated pinacol. From the ratio of rate constants for triplet decay over hydrogen abstraction, it can be found that the hydroxy proton has no effect on the efficiency of the reaction. The pinacol-d_2 was 65% deuterated. The product acetophenone and its quantum yield are calculated in Table 16, 17. In all cases, all products gave linear plots of Φ^{-1} vs $[AH]_2^{-1}$. The slopes of the double reciprocal plots for the pinacols are shown in Figure 6 and Figure 7. Dividing the slope of the intercept gives k_d/k_r. The experimental results are listed in Table 9. In comparing the k_d/k_r of these reactions, it shows no isotope effect.

Table-9: Results for photoreduction of various ketones by acetophenone pinacol and acetophenone pinacol-d_2:

Reactants	Φ_{max}	K_d/k_r
$PP/[AH]_2$	0.053	0.040
$PP/[AD]_2$	0.044	0.043
$MeOAP/[AH]_2$	0.105	0.082

For the electron-donating group substituted ketone p-methoxyacetophenone, the reaction slows down, meaning the electron-donating group makes most molecules easily undergo a π, π* reaction and slows down the n, π* reaction.

Fate of radicals To understand the tendency of hydrogen exchange from semi-pinacol radical to ground state ketone, four groups (propiophenone and acetophenone; isobutyrophenone and acetophenone; p-methylacetophenone and acetophenone; p-chloroacetophenone and acetophenone) equilibrium constants of degenerate hydrogen exchange at a certain steady state have been measured. The mechanism of equilibrium is illustrated in Scheme 4:

$$A \xrightarrow{h\nu} {}^{3}A^{*}$$

$$K \xrightarrow{h\nu} {}^{3}K^{*}$$

$$K + {}^{3}A^{*} \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} A + {}^{3}K^{*}$$

$${}^{3}A^{*} \xrightarrow[\text{2-propanol}]{k_{HA}} \cdot AH$$

$${}^{3}K^{*} \xrightarrow[\text{2-propanol}]{k_{HK}} \cdot KH$$

$$A + \cdot KH \underset{k_{-ex}}{\overset{k_{ex}}{\rightleftharpoons}} K + \cdot AH$$

continue

$$\cdot KH + \cdot KH \xrightarrow{k_{ck}} [K_2H_2]$$

$$\cdot AH + \cdot AH \xrightarrow{k_{ca}} [A_2H_2]$$

$$\cdot KH + \cdot AH \xrightarrow{k_{cm}} [KHAH]$$

Scheme 4: equilibrium between two semi-pinacol radicals.

From different triplet energy of ketones, the equilibrium constant for triplet energy transfer can be deduced by equation (14).

$$\Delta G^{o} = - RT \ln K_{ET} \qquad (14)$$

Table-10: Calculated equilibrium constants of triplet energy transfer between different ketones.

$ketone_1$	E_T kcal/mol	$ketone_2$	E_T kcal/mol	K_{ET}^{a}
AP	74.1^{b}	PP	74.5^{c}	2.0
AP	74.1^{b}	BP	74.7^{d}	2.8
AP	74.1^{b}	MeAP	72.8^{e}	0.11
AP	74.1^{b}	ClAP	72.1^{f}	0.034

(a). In the equilibrium, take $ketone_1$ as product, $ketone_2$ as a starting material. (b). references {39}. (c). references {40}. (d). references {41}. (f). references {42}.

In the measurement of equilibrium constants, the rate constant of triplet decay for ketones is $k_d = 3 \pm 1 \times 10^5\ s^{-1}${16}. The rate constants of hydrogen abstraction are on the order of $10^5\ M^{-1}s^{-1}$ {15}, the rate constant of triplet energy transfer is $k_{et} = 10^9\ s^{-1}${43}, and the triplet energy of ketones should be very close. From the above data, the energy transfer is a fast step. The triplet decay and hydrogen abstraction steps are major competitive pathways. From the two competitive pathways, the originally formed radical ratio can be estimated.

Table-11: Estimation of originally formed radical ratio in the measurement of equilibrium constants for hydrogen exchange:

ketones	$k_d X10^5$ s^{-1}	$k_{HT} X10^5$ $M^{-1}s^{-1}$	radical pair	K_{ET}	ratio[a]	ratio[b]
AP	3.4[c]	6.8[c]				
	33%[d]	67%				
PP	3.2[c]	4.4[c]				
	42%	58%	AH·/PH·	2.0	2.4 : 1	3.5 : 1
isBP	3.4[c]	0.9[c]				
	79%	21%	AH·/isBH·	2.8	8.9 : 1	9 : 1
MeAP	3.0[e]	0.98[f]				
	75%	25%	AH·/MeAH·	0.11	1 : 3.4	3 : 1
ClAP	3.0[e]	1.6[f]				
	65%	35%	AH·/ClAH·	0.034	1 : 15	1 : 5

Footnote of Table-11:

(a). The starting ketones are of equal amount. The estimated radical ratio equals the ratio of percentage for hydrogen abstraction multiplied by K_{ET}.

(b). The ratios were measured from experiment.

(c). From references {15}.

(d). The percentages show the competition between k_d and k_{HT}.

(e). From references {16}, the rate constant of triplet decay is taken as same as acetophenone.

(f). The rate constant of hydrogen abstraction was estimated from relative rate constant of substituted valerophenone from references {10(a)}.

In equilibrium reaction, the concentration of ketones is 0.1-0.3M. The rate constant of triplet decay for ketones is $k_d = 3 \pm 1 \times 10^5 s^{-1}$ {16}, the rate of triplet decay is on the order of $10^4 Ms^{-1}$. The rate constant of triplet energy transfer is $k_{et} = 10^9 s^{-1}$ {43}, the rate of triplet energy transfer is on the order of $10^8 Ms^{-1}$. The rate constants of hydrogen abstraction are on the order of $10^5 M^{-1}s^{-1}$ {15}, the concentration of hydrogen donor 2-propanol is 1M, the rate of hydrogen abstraction is on the order of $10^4 Ms^{-1}$. As indicated from the above data, triplet energy transfer is a fast step, before triplet decay and hydrogen abstraction steps, the equilibrium of triplet energy transfer is established.

Within the experimental error, except for the radical pair of

AH•/MeAH•, all other estimated radical ratios are the same or very close to the ratios measured from experiments. The rate constants of hydrogen exchange from this research are on the order of $10^3 M^{-1}s^{-1}$. In the case of radical pair AH•/MeAH•, it is possible that the radical of MeAH• is consumed in the exchange reaction, so that the measured ratio is 10 times larger than the estimated ratio.

The value of the equilibrium constant for hydrogen exchange from experiment can be obtained by using equation (12).

The values of equilibrium constants were obtained by measuring of the radical combination product pinacols using equation (11). For the coupling products of radicals, a portion of them are cross-coupled product and another portion of them is self-coupling product. Because the differences of relative triplet energy between excited ketones, and the varied rate of reactions for hydrogen abstraction, and hydrogen exchange , actual semi-pinacol radicals were formed in unequal amounts.

Photoredox in ketone-Semipinacol Radicals System From the mechanism in Scheme 1, the rate constant of hydrogen exchange from semi-pinacol radical to ground state ketone can be deduced.

1. The efficiency of intermediate formation is :

$$\frac{k_{HT}(AH_2)}{k_{d_2} + k_{HT}(AH_2)} = \Phi_{\cdot KH}$$

2. The efficiency of product ketone (A) formed from exchange is:

$$\frac{k_{ex}(K)(\cdot AH) - k_{-ex}(A)(\cdot KH) + k_{dis'}(\cdot AH)^2 + k_{dis''}(\cdot KH)(\cdot AH)}{k_{ex}(K)(\cdot AH) - k_{-ex}(A)(\cdot KH) + k_{ca}(\cdot AH) + k_{cm}(\cdot KH)(\cdot AH) + k_{dis'}(\cdot AH)^2 + k_{dis''}(\cdot KH)(\cdot AH)}$$

In order to simplify analysis, it is helpful to make some approximations.

At the beginning, there was no exchange product ketone (A) and the starting ketone concentration was relatively high (K = 0.005-0.1M). The forward reaction was a major pathway. The conversion was kept lower than 10%, the final concentrations of ketone (A) were 0.0007-0.002M, so the backward exchange reaction k_{-ex} can be ignored.

Wagner has reported that the disproportionation for radical pairs is just 2.5%{44} for acetophenone, because most (·AH) radicals undergo the combination and exchange reactions. For the (·AH) radical, ignoring self disproportionation item $k_{dis'}(\cdot AH)^2$ and crossing disproportionation ite

ca

hy

k

item k_{dis}•(•AH)(•KH) should not have a large effect on the overall calculation.

After approximations, the efficiency of ketone formed from hydrogen exchange should be:

$$\frac{k_{ex}\,(K)}{k_{ex}\,(K) + k_{ca}(\cdot AH) + k_{cm}\,(\cdot KH)}$$

The overall quantum yield of ketone from exchange is:

$$\Phi_A = \Phi_{isc} X \Phi_{\cdot KH} \frac{k_{ex}\,(K)}{k_{ex}(K) + k_{ca}(\cdot AH) + k_{cm}(\cdot KH)}$$

$$\Phi_A^{-1} = \Phi_{isc}^{-1} X \Phi_{\cdot KH}^{-1} \left[\, 1 + \frac{k_{ca}\,(\cdot AH) + k_{cm}(\cdot KH)}{k_{ex}(K)} \right] \qquad (15)$$

At steady state:

$$I_a\Phi_{(AH)_2} = k_{ca}\,(\cdot AH)^2, \quad k_{ca} = 2 X 10^9 M^{-1} s^{-1\{38\}},$$

$$\frac{[\cdot KH]}{[\cdot AH]} = Z$$

$$= \frac{\text{products of [KH] from diproportionation and combination}}{\text{products of [}\cdot\text{AH] from combination}}$$

$$k_{ck} = \frac{I_a\Phi_{(KH)_2}}{(\cdot KH)^2}, \qquad k_{cm} = \frac{I_a\Phi_{(KHAH)}}{(\cdot KH)(\cdot AH)},$$

The estimated rate constants for combination reactions are listed as following:

Table-12: Estimated rate constants of combination reactions:

ketone (M)	AP0.0079(M)	PP 0.0060 (M)	isBP0.071(M)	MeAP0.071(M)
$I_aX10^{-7}E/Ls$	7.7	7.1	10	4.9
Φ_{KH_2}	0.0028	0.013	0.0032	-
$\Phi_{(AH)_2}$	0.0076	0.012	0.0098	0.051
$\Phi_{(KH)_2}$	0.023	0.048	0.039	-
$\Phi_{(KHAH)}$	0.036	0.050	0.036	0.038
$[\cdot AH]X10^{-9}$	1.7	2.1	2.2	3.5
Z	1.7	2.1	2.1	0.27
$[\cdot KH]X10^{-9}$	2.9	4.5	4.6	0.95
$k_{ck}M^{-1}s^{-1}X10^9$	2.1	1.7	1.8	-
$k_{cm}M^{-1}s^{-1}X10^9$	5.6	3.7	3.6	5.6

From Table-12, within experimental error, the rate constants of combination seem to be on the same order. It is possible to make an approximation:

$$k_{ca} = k_{cm} = k_{ck} = k_c = 2 \times 10^9 \, M^{-1}s^{-1}$$

Then equation (15) becomes:

$$\Phi_{A}^{-1} = \Phi_{isc}^{-1} \cdot \Phi_{\cdot KH}^{-1} \left\{ 1 + \frac{k_c [(\cdot AH) + (\cdot KH)]}{k_{ex}(K)} \right\} \qquad (16)$$

$$(\cdot AH + \cdot KH) = \left\{ \frac{I_a [\Phi_{KH2} + 2 X (\Phi_{(AH)2} + \Phi_{(KH)2} + \Phi_{(AHKH)})]}{k_c} \right\}^{1/2}$$

$$= \left(\frac{I_a \Phi_{\cdot KH + \cdot AH}}{k_c} \right)^{1/2}$$

At steady state, the sum of radicals should be constant. It can be verified by radical products from disproportionation and combination reactions in Table-13.

Table-13: Sum of the quantum yields from disproportionation and combination reactions: *

PP(M)	0.0060	0.017	0.025	0.05	0.10	0.15
$\Phi_{\cdot AH+\cdot PH}$	0.14	0.21	0.23	0.28	0.28	0.25

isBP(M)	0.0071	0.10	0.016	0.025	0.05
$\Phi_{\cdot AH+\cdot BH}$	0.22	0.21	0.21	0.20	0.14

MeAP(M)	0.0051	0.0071	0.010	0.016	0.025	0.051
$\Phi_{\cdot AH+\cdot MH}$	0.18	0.17	0.15	0.19	0.18	0.20

AP(M)	0.0079	0.010	0.013	0.016	0.025	0.051	0.10
$\Phi_{\cdot AH+\cdot ClAH}$	0.18	0.16	0.15	0.19	0.20	0.23	0.28

* $\Phi_{\cdot AH+\cdot KH} = \Phi_{KH_2} + 2 \times [\Phi_{(AH)_2} + \Phi_{(KH)_2} + \Phi_{(KHAH)}]$

From Table-13, within experimental error, the quantum yields of all radicals are constant, so the equation (16) becomes:

$$\Phi_{A}^{-1} = \Phi_{isc}^{-1} \cdot \Phi_{\cdot KH}^{-1} \left\{ 1 + \frac{(k_c I_a \, \Phi_{\cdot KH + \cdot AH})^{1/2}}{k_{ex} (K)} \right\}$$

$$\text{The intercept} = \Phi_{isc}^{-1} \cdot \Phi_{\cdot KH}^{-1}$$

$$\text{The slope} = \frac{\Phi_{isc}^{-1} \cdot \Phi_{\cdot KH}^{-1} \, (k_c I_a \, \Phi_{\cdot KH + \cdot AH})^{1/2}}{k_{ex}}$$

$$k_{ex} = \frac{\text{intercept}}{\text{slope}} \, (k_c I_a \, \Phi_{\cdot KH + \cdot AH})^{1/2}$$

This experiment using the steady state radical concentration for reaction provided a method to calculate the rate constant for hydrogen exchange from semi-pinacol radical to ground state ketone.

Recently, Steel and Cohen reported a similar study[2], they neglected the (·KH) self disproportionation, crossing disproportionation and crossing combination reactions, and deduced two approximate equations and all rate constants in their equations using literature data. In the first equation, they measured the benzopinacol quantum yields, comparing experimental data with the calculated model curves, and reported k_{ex} must lie between 3 X 10^4 $M^{-1}s^{-1}$ and 5 X 10^4 $M^{-1}s^{-1}$. In the second equation, they measured the benzopinacol and mixed pinacol quantum yields, and obtained

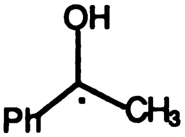
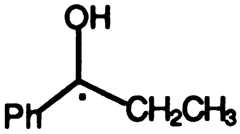
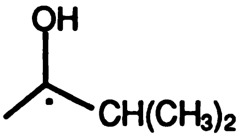
k_{ex} = (2.5 ± 0.5) X 10^4 $M^{-1}s^{-1}$. From both methods, they finally reported k_{ex} = (3.5 ± 1.5) X 10^4 $M^{-1}s^{-1}$.

Quantum yields for the hydrogen exchange, disproportionation, and combination products were determined in four groups of the photoreduction reactions: propiophenone by 1-phenylethanol; isobutyrophenone by 1-phenylethanol; p-methylacetophenone by 1-phenylethanol; and acetophenone by 1-(4'-chlorophenyl) ethanol. In these studies, the starting ketone began with a relatively low concentration of 0.005M and varied through a large range to 0.1M, the alcohol concentration was kept constant and relatively high (0.2M). According to the mechanism drawn in scheme 1, the products were: (1). alcohol corresponding to disproportionation of semi-pinacol radical from two-electron reduction of starting ketone; (2). ketone corresponding to hydrogen exchange from semi-pinacol radical by two-electron oxidization of the starting alcohol, (3). pinacols formed from the self coupling or cross coupling of two semi-pinacol radicals. In all cases, all exchange products gave plots of ketone's Φ^{-1} versus [hydrogen donor]$^{-1}$ (Table 24, 27, 30 and 33, Figure 8, 10, 12 and 14).

In the ketone-semipinacol photoredox reaction, there are three competitive reactions: hydrogen transfer from semi-pinacol radicals to ketone, disproportionation reaction, and combination reaction. In this research, the quantum yields of disproportionation reaction were low from 0.00002-0.07. The hydrogen exchange reaction and radical combination reaction seem to be the major competitive reactions.

Lewis[15] has reported the disproportionation/combination ratios for radical pairs of bimolecular hydrogen abstraction by triplet aryl alkyl ketones. (Table-14)

Table-14: Disproportionation/Combination Ratios for Radical Pairs

Radical pair	k_{dis}/k_{com}
	0.02
	0.17
	0.69

From Table-14, the relative rate constant of disproportionation reaction increases by increasing the size of the α-methyl substitution, which is consistent with the observation in this research.

The calculated ratio of rate constant for disproportionation over combination are listed in Table-15 by using equation (18)

$$k_{dis}/k_{com} = \Phi_{KH_2} /(2 \times \Phi_{(KH)_2} + \Phi_{(KHAH)}) \qquad (18)$$

Table-15: The ratio of rate constants for disproportionation over combination reactions: *

PP(M)	0.0060	0.017	0.025	0.05	0.10	0.15
k_{dis}/k_{com}	0.034	0.080	0.070	0.070	0.084	0.079

isBP(M)	0.0071	0.10	0.016	0.025	0.05
k_{dis}/k_{com}	0.089	0.095	0.086	0.13	0.14

MeAP(M)	0.0051	0.0071	0.010	0.016	0.025	0.051
k_{dis}/k_{com}	0.024	0.028	0.031	0.030	0.037	0.035

AP(M)	0.0079	0.010	0.013	0.016	0.025	0.051	0.10
k_{dis}/k_{com}	-	-	-	0.012	0.015	0.017	0.020

* Data are from Table 25, 28, 31, 34.

For the ketone that has α substituted groups, like isobutyrophenone, there is a significant steric effect. The quantum yields of combination reaction were lower than propiophenone. The quantum yields of disproportionation reaction were higher than propiophenone. The hydrogen transfer reaction was preferred and the rate constant of hydrogen exchange doubles that of propiophenone. The para-position electron withdrawing group like halogens can conjugate with the carbonyl group and cause electron density to move away from oxygen. This inductive effect should stabilize n,π^* state and its electron-donating resonance effect should stabilize the π, π^* transition. In the case of p-chloroacetophenone, there is a reversed equilibrium radical ratio. The reaction should be controlled so that the competitive absorption of light by produced ketone can be minimized. Almost no disproportionation product from starting ketone and self combination products from starting alcohol can be measured. The hydrogen exchange became the dominant pathway.

In the case of electron donating substitutes, (like p-methylacetophenone), the electron density moves from benzene ring to the carbonyl group. This substitution stabilizes the π, π^* triplet transition, so that the electron rich carbonyl group would not react like an electrophilic radical. The quantum yields of both combination and disproportionation were lower than that of propiophenone. The rate constant of exchange from semi-pinacol radical to ketone was 1.3 times that of propiophenone.

The rate constants of hydrogen exchange obtained in this research are on the order of 10^3 M^{-1} S^{-1}. These rate constants are slower than the rate constant of hydrogen exchange in benzophenone system measured by

Steel et al.{2}. It is not surprising, since the benzophenone has more bulky semi-pinacol radical, the rate constant of combination is 1 X 10^8 $M^{-1}S^{-1}${36} which is twenty times slower than the rate constant 2 X 10^9 $M^{-1}S^{-1}${38} of combination reaction for acetophenone. Therefore, it is possible that the rate constant of the hydrogen exchange in benzophenone system is faster than that in aryl alkyl ketone system.

Weiner{45} et al. have demonstrated that the products from crossing combination and disproportionation reactions were the products arising from solvent cage. All other products were produced from free radicals escaped from solvent cage. From the product distribution in Tables 25, 28, 31, 34, the cage products were 20-30% of the total radical products. The hydrogen exchange product was approximately 70% of total escaped products. This information indicated that most radicals products came from cage escaped free radicals, and because of the hydrogen bonding effect, the hydrogen exchange product was the major product of cage escaped products. Since the products of the cage reaction must be formed in their ground state, one electron must flip its spin. From these data, it is possible to estimate a value for thermally generated free radicals which formed in singlet radical pairs.

Several complementary experiments have been done by using certain amounts of ketone and varing amounts of alcohol to relate the fate of radical from photoreduction reaction. The ratio of rate constant for triplet decay over the rate constant of hydrogen abstraction and maximum quantum yields of acetophenone from hydrogen exchange were obtained.

CONCLUSION

The results of the research reported in this thesis have several conclusions regarding the photoreduction reaction. The main points are the steric effect and the substituent effect in the hydrogen exchange reaction.

The tendency of photoreduction for different ketones by alcohol has been understood by comparing the equilibrium constants of degenerate hydrogen exchange from semi-pinacol radicals to ground state ketone. At equilibrium, the radicals from electron-withdrawing group substituted and less bulky alkyl aryl ketone have higher ratios.

From the initial interaction of excited ketone with aromatic alcohol, the maximum quantum yield of the product from hydrogen exchange indicates that ketones with electron donating substituted ketone have less reactivity.

The rate constants of hydrogen exchange in ketone-semipinacol system have led to a greater understanding of the photoredox processes. It has clarified that the degenerate hydrogen exchange is an important individual step in the initial interaction of semi-pinacol radical with ground state ketone in the photoredox reaction. It has provided an independent method to calculate the kinetic parameters and a comprehensive experiment to separate the complicated aspects of the reaction.

Suggestion for further investigation

The hydrogen exchange is caused by the interaction of hydrogen bonding between semi-pinacol radical and ground state ketone. The solvent polarity should have a strong effect on the competitive reactions of exchange, combination, and disproportionation. The solvent can be changed from benzene to acetonitrile, pyridine, or neat alcohol such as 2-propanol. These solvent effects are unprecedented and should be investigated further. The study of temperature dependence{46} and the pH dependence{47} will help to explain the activation energy and the life time of radicals.

In the photoreduction of ketone by pinacols, the rate constants should be measured for ketones substituted with elecron-withdrawing groups (such as CF_3). Electron-donating groups (such as OCH_3) can be compared with the unsubstituted ketone by using 99% deuterated versus undeuterated pinacols. The substitutuent and isotope effect would assist in the understanding of the mechanism of hydrogen abstraction and the extent of the charge transfer reaction.

EXPERIMENTAL

Kinetics and calculation To understand excited state reactivity, it is necessary to make quantitative measurements of quantum yields and rate constants.

Calculation of the ratio for rate constant of triplet decay over hydrogen abstraction and maximum quantum yield for hydrogen exchange

From Figure 9, using equations (8), and (9), the value of rate constant for triplet decay over hydrogen exchange and maximum quantum yield can be obtained as following:

$K_d/K_r = 0.57/2.6 = 0.22$

$\Phi_{max} = 1/\text{intercept} = 1/2.5 = 0.40$

Correction of light absorption

At low concentration of reactant, when A<2, the light absorption was corrected as the following:[48]

I_0 = the intensity of the radiation energy striking on the sample

I = the intensity of the radiation energy transmitted from the sample

$T = I/I_0$ = transmittance

$A = \log(I_0/I)$ = absorbance (optical density)

$T_a = 1 - T = 1 - 10^{-A}$ = fraction of light absorbed

I_aT_a= the actual light absorbed after correction

Calculation of Quantum yields:

The amount of light absorbed (I_a in Einstein/liter) was determined by valerophenone actinometer. A benzene solution containing 0.10M valerophenone[37] as a standard was irradiated in parallel with the samples to be analyzed. The acetophenone concentration was calculated using the following equation:

acetophenone = (SF X standard X peak area of acetophenone)/(peak area of standard)

where SF is the standardization factor determined from the relative HPLC or GC peak area of the two compounds with known concentrations. From the concentration of acetophenone and the quantum yield of acetophenone formation (Φ_{ap}= 0.33 in benzene for 0.1M valerophenone), the amount of light absorbed can be calculated.

I_a = light absorbed = acetophenone/ (0.33)

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

Φ = quantum yield = [product]/I_a

Sample calculation:

Actinometer: 0.10M valerophenone
0.003M undecane (C_{11}), SF = 1.72

area of acetophenone/area of dodecane = 0.469

[acetophenone] = (SF X [C_{12}] X area of AP)/ area of C_{12}

[acetophenone] = 1.72 X 0.0110 X 0.469 = 0.00887M

I_a = light absorbed = 0.00887/0.33 = 0.0269 E/L

Φ = quantum yield = [product]/I_a = 0.33 for acetophnone

Sample: 0.050 M PP,
0.00456M dodecane (C_{12})
0.10M 1-phenylethanol
SF = 1.82 for acetophenone (AP) over dodecane (C_{12})

area of AP/area of dodecane = 0.205

[AP] = (SF X [C_{12}] X area of AP)/area of C_{12}

[AP] = 1.82 X 0.00456 X 0.205 = 0.00170 M

Φ_{AP} = [AP]/I_a = 0.00170/ 0.0269 = 0.063

Solvents

Benzene: (Baker) was purified by stirring over concentrated sulfuric acid .The sulfuric acid was changed every twenty-four hours until it remained clear . The benzene was then washed several times with water, several times with saturated sodium bicarbonate solution, and finally two times with water. The benzene was pre-dried with sodium sulfate and distilled from phosphorus pentoxide through a column packed with glass helices. The first 10% and the last 20% were discarded. (bP=80°C)

Hexane: (J.T.Baker) was purified by washing with concentrated sulfuric acid in a method similar to benzene, dried by magnesium sulfate and distilled over calcium hydride. The first and the last 10-20% were discarded.

Internal Standards

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

Undecane (C_{11}): (Aldrich) was purified in the same method as benzene and distilled under reduced pressure.

Dodecane (C_{12}): (Phillips) was purified in the same manner as benzene and distilled under reduced pressure.

Haxadecane (C_{16}): (Aldrich) was purified in the same manner as undecane.

2,2,4,4,6,8,8-Heptamethylnonane (C_{b16}): (Aldrich) was purified in the same manner as undecane.

Heptadecane (C_{17}): (Chemical Samples Co.) was purified in the same manner as undecane.

Octadecane (C_{18}): (Chemical Samples Co.) was washed with concentrated sulfuric acid and recrystallized from ethanol.

Nonadecane (C_{19}): (Chemical Samples Co.) was recrystalized from ethanol.

Hydrogen donors:

Acetophenone pinacol: was formed by preparative irradiation of 10ml acetophenone with 200ml 2-propanol in a 250 ml photochemical immersion well at 313nm for 48 hours. After removal of the solvent from the irradiation product, the solid residue was recrystallized several times from petroleum ether. (MP = 122°C) Spectra were compared with authentic data.{49} The reported melting point is 125°C{49}. ^{1}H-NMR (250 Hz, $CDCl_3$): $\delta = 1.5$ (s, 6H, $2CH_3$), $\delta = 2.6$ (s, 2H, 2OH) (was exchanged by D_2O), $\delta = 7.21$ (m, 10H, Phenyl). MS: 121 ($M^+/2$), 111 . IR: 3500 cm^{-1} (OH), 3300 cm^{-1}, 1270 cm^{-1}.

Acetophenonepinacol-d_2: To an oven dried 3-neck round bottom flask, flushed with argon, was added acetophenone pinacol. Benzene was distilled from sodium metal directly into the reaction flask. Butyllithium (4 equivalents) was injected. After stirring for 30 minutes in an ice bath, D_2O was added (10 equivalents). The organic layer was isolated and the solvent was removed to give a solid product. The solid was dissolved in dry hexane by refluxing, and a crystalline product , containing 65% deuterium , was obtained upon cooling. The low amount of deuterium incorporation was probably due to low quality D_2O .

The pinacol of low percentage deuteration was recrystallized in dry hexane, then dissolved in a 5 : 1 mixture of ethanol-d and D_2O, the solvent was removed and the solid was dissolved in ethanol-d, D_2O again, the crystal was dried by diffusion pump vacuum. The 99% deuterium pinacol-d_2 was obtained.

NMR spectrum showed no OH peak, and IR spectrum showed 99% OD peak at 2200 cm^{-1}, only 1% at 3500 cm^{-1}.

1-Phenylethanol: was prepared by stirring 5ml acetophenone with 2g H_4AlLi and 25ml dried ether in a 50ml round bottom flask for 24 hours. After removed of solvent, it was isolated by silica gel column. This procedure was repeated several times. G. C. analysis indicated that it was 100% pure, and it was finally distilled at reduced pressure. (BP 50°C/1mmHg) Spectra were compared with authentic data.{50} ^{1}H-NMR (250 Mz, $CDCl_3$): $\delta = 1.45$ (d, 3H, CH_3), $\delta = 1.89$ (s, 1H, OH) (was exchanged by D_2O), $\delta = 4.81$ (q, 1H, CH), $\delta = 7.21$ (s, 5H, Phenyl). The reported melting point is 204°C/745mm{50}.

1-(4'-Chlorophenyl)ethanol:{51} Grignard reagent was synthesized by dropping 10 ml distilled methyl iodide (baker) into 3 gram magnesium metal covered by 100 ml dried ether. The whole system was protected under argon. Then 10 gram dried 4-chlorobenzaldehyde dissolved in 30 ml dried ether were dropped in. The system was quenched in the usual manner. Because the system was in acidic condition, some elimition occurred{52} and there were always some p-chloroacetophenone being detected. The p-chloroacetophenone was reducted by aluminium isopropoxide.{53} 27 g (1mol) aluminium foil were placed in a 1-liter flask containing 300ml (3.9mol) 2-propanol dried by calcium oxide and 0.4 g of mercury chloride. The solution was stirred and refluxed until all metal had reacted. The excess 2-propanol was distilled to a 250 ml receiving flask until the temperature of distillate rose above 90°C, and then aluminium isopropoxide was distilled at 140-150°C/12mmHg. 5 Gram of 1-(4'-chlorophenyl)ethanol was stirred with 50ml aluminium isopropoxide for 24 hours. After removing solvent, final purification was accomplished by distillation under reduced pressure.(BP 55°C/1.1mmHg) Spectra were compared with authentic data.{54} ^{1}H-NMR (250 Mz, $CDCl_3$): $\delta = 1.31$ (d, 3H, CH_3), $\delta = 3.56$ (s, 1H, OH) (was exchanged by D_2O), $\delta = 4.64$ (q, 1H, CH), $\delta = 7.18$ (s, 5H, Phenyl). The reported melting point is 121°C/15mm{54}.

Reactants

Valerophenone: was prepared by Freidel-Crafts acylation of benzene. 10g valeric acid were placed in a three neck round bottom flask; 14 g redistilled thionyl chloride were dropped in the flask and refluxed for 40 mins. The valeryl chloride was isolated by distillation, bp 125-128°C. A 500 ml three necked flask with a reflux condenser was equipped with a mechanical stirrer and a dropping funnel; the top of the condenser was connected to a trap for absorbing the hydrogen chloride. 6g (0.045mol) anhydrous aluminium chloride and 100 ml benzene were placed in the flask with a cooling water bath; 5g valeryl chloride were added during 30 min. The mixture was refluxed for 2 hours before being cooled and poured to 200ml ice-water. The organic layer in a separatory funnel was washed with water, then saturated $NaHCO_3$, and then dried with magnesium sulfate. After work-up, the crude product was dried and distilled under reduced pressure. (BP = 105-110°C /2mm) .

Acetophenone: was purified by Dr. P. J. Wagner research group.

Propiophenone: (MC and B) was passed through alumina and then purified by distillation under reduced pressure. (BP 55-58°C/7mm). Spectra were compared with authentic data.{55} ^{1}H-NMR (250 Mz, $CDCl_3$): $\delta = 1.18$ (t, 3H, CH_3), $\delta = 2.94$ (q, 2H, CH_2), $\delta = 7.47$ (m, 3H, Phenyl), $\delta = 7.92$ (m, 2H, Phenyl). The reported melting point is 218°C{55}.

4'-Methylacetophenone: (Eastman Kodak) was purified by fractional distillation through 1-foot column packed with glass helices. One of the impurities, acetophenone was totally removed, and another impurity, 2'-methylacetophenone was reduced to 0.5 percent. The product was collected at 41.5°C / 2mmHg. Spectra were compared with authentic data.{56} ^{1}H-NMR (250 Mz, $CDCl_3$): δ = 2.32 (s, 3H, Phenyl CH_3), δ = 2.42 (s, 3H, carbonyl CH_3), δ = 7.09 (m, 2H, Phenyl), δ = 7.69 (m, 2H, Phenyl).

4'-(Trifluoromethyl)acetophenone: (Aldrich) was purified by distillation, hot water was used in the condenser to prevent the compound from condensing in the distillation head. (BP 78-80°C/8mm).
Spectra were compared with authentic data.{57} ^{1}H-NMR (250 Mz, $CDCl_3$): δ = 2.62 (s, 3H, CH_3), δ = 7.71 (m, 2H, Phenyl), δ = 8.08 (m, 2H, Phenyl).

Isobutyrophenone: was synthesized By Dr. Boli Zhou and purified by distillation under reduced pressure. (BP 54 °C /0.9mmHg). Spectra were compared with authentic data.{58} ^{1}H-NMR (250 Mz, $CDCl_3$): δ = 1.18 (d, 6H, $2CH_3$), δ = 3.47 (h, 1H, CH), δ = 7.33 (m, 3H, Phenyl), δ = 7.85 (m, 2H, Phenyl). The reported melting point is 91.5-93.5° C /7mm {58}.

<u>p-Methoxyacetophenone:</u> was prepared by Freidel-Crafts acylation of anisole by acetic anhydride. A 500 ml three necked flask with a reflux condenser were equipped with a mechanical stirrer unit and a dropping funnel; the top of the condenser was connected to a trap for absorbing the hydrogen chloride. 6 g (0.045mol) Anhydrous aluminium chloride and 5.4 ml (0.05mol) of anisole with 200ml CCL_4 were placed in the flask with a cooling water bath, the mixture was stirred and refluxed, 5.1g (4.7ml, 0.05mol) of redistilled acetic anhydride were added during 30 min, then refluxed for 2 hours. After cooling the reaction mixture was poured to 200ml ice-water and 50ml concentrated hydrochloric acid. The organic layer was separated in a separatory funnel, washed with water, then with saturated $NaHCO_3$, and dried with magnesium sulfate. After removing solvent, the crude product was crystallized several times from petroleum ether. (MP = 35-37°C) .
Spectra were compared with authentic data.{59} ^{1}H-NMR (250 Mz, $CDCl_3$):
$\delta = 2.56$ (s, 3H, CH_3), $\delta = 3.88$ (s, 3H, OCH_3), $\delta = 6.98$ (m, 2H, Phenyl), $\delta = 7.97$ (m, 2H, Phenyl).

Identification of photoproducts

Propiophenone pinacol: was formed by preparative irradiation of 10ml propiophenone with 200ml of 2-propanol in a 250 ml photochemical immersion well at 313nm for 48 hours. After removal of the solvent from the irradiation product, the solid residue was recrystallized several times from petroleum ether. (MP = 130-132°C)
Spectra were compared with authentic data.{60} ^{1}H-NMR (250 Mz, $CDCl_3$): $\delta = 0.6$ (t, 6H, 2CH_3), $\delta = 1.58$ (qd, 2H, CH_2), $\delta = 2.08$ (s, 2H, OH), $\delta = 2.30$ (qd, 2H, CH_2), $\delta = 7.2$ (s, 5H, Phenyl). The reported melting point is 133-134°C {61}

2,3-Bis(4-chlorophenyl)-2,3-butanediol: was formed by preparative irradiation of 2ml p-chloroacetophenone with 2ml 2-propanol in a pyrex test tube, sealed by a rubber stopper, deoxygenated with a steam of dry nitrogen passing through the solution by two needles (one entry, one out) for 20 minutes, then irradiated at 313nm for 48 hours. After removal of the solvent from the irradiation product, the solid residue was recrystallized several times from petroleum ether. (MP = 182-184°C)

^{1}H-NMR (250 Mz, $CDCl_3$){62}: $\delta = 1.54$ (s, 6H, 2CH_3COH),
$\delta = 2.2$ (s, 2H, 2OH) (was exchanged by D_2O), $\delta = 7.1$ (m, 8H, Phenyl).
MS: 135 (M/2, 155), 111 . IR: 3500 cm^{-1} (OH), 3000 cm^{-1}, 1500 cm^{-1}, 1100 cm^{-1}, 1000 cm^{-1}.

2.5-Dimethyl-3.4-diphenyl-3.4-hexanediol: was formed by preparative irradiation of 2ml isobutyrophenone with 2ml 2-propanol in a pyrex test tube, sealed by a rubber stopper, deoxygenated with a steam of dry nitrogen passing through the solution by two needles (one entry, one out) for 20 minutes, then irradiated at 313nm for 48 hours. After removal of the solvent from the irradiation product, the solid residue was recrystallized several times from petroleum ether.

^{1}H-NMR (250 Mz, $CDCl_3$){63}: $\delta = 0.34\text{-}0.37$ (d, J = 6.7 Hz; Me),
$\delta = 1.20\text{-}1.23$ (d, J = 6.4 Hz; Me), $\delta = 1.69\text{-}1.85$ (sept, J = 6.6 Hz; CH),
$\delta = 2.8$ (s, OH) (was exchanged by D_2O), 7.2-7.4 (m, Phenyl).

^{13}C-NMR: (250 Mz, $CDCl_3$) $\delta = 18,20$ (Me), 35 (CH), 84 (COH), 126, 126.5, 127.5, 143, (Phenyl).

MS: 149 (M/2, 100), 105, IR: 3600 cm^{-1}, 3500 cm^{-1} (OH); 3000 cm^{-1}, 1500 cm^{-1}, 1000 cm^{-1}, 750 cm^{-1}.

MP = 118-120°C, the reported melting point is 118-120°C{64}

2.3-Bis(4-methylphenyl)-2.3-butanediol: was formed by preparative irradiation of 2ml p-methylacetophenone with 2ml 2-propanol in a pyrex test tube, sealed by rubber stopper, deoxygenated with a steam of dry nitrogen passing through the solution by two needles (one entry, one out) for 20 minutes, then irradiated at 313nm for 48 hours. After removal of the solvent from the irradiation product, the solid residue was recrystallized several times from petroleum ether.

^{1}H-NMR (250 Mz, $CDCl_3$) {65}: $\delta = 1.53$ (s, 6H, $2CH_3COH$), $\delta = 2.32$ (s, 6H, $2CH_3$), $\delta = 2.1$ (s, 2H 2OH), (was exchanged by D_2O), $\delta = 7.0$-7.2 (m, 8H, Phenyl). MS: 135 (M/2, 85), 121(10) , IR: 3500 cm^{-1} (OH), 3000 cm^{-1}, 1500 cm^{-1}, 1100 cm^{-1}, 900 cm^{-1}. MP = 130-132°C.

2-Methyl-1-phenylpropanol: was synthesized from reducing isobutyrophenone by H_4AlLi. 100ml dried ether were placed in a three necked round bottom flask with a stirrer unit, condenser and dropping funnel. 3g lithium aluminium hydride were introduced to the flask, 10ml isobutyrophenone in a 30ml dried ether were added by the dropping funnel. The mixture was stirred for 2 hours before 20ml water were dropwise added in a ice-water bath. After the water layer was separated, the ethereal solution was dried by magnesium sulfate and evaporated, the residue was distilled under reduced pressure. (BP 50° C/2mmHg). Spectra were compared with authentic data.{66} ^{1}H-NMR (250 Mz, $CDCl_3$): $\delta = 1.25$ (d, 6H, $2CH_3$), $\delta = 3.41$ (d, 1H, CH), $\delta = 4.38$ (d, 1H, CH), $\delta = 7.30$ (m, 5H, Phenyl). MS: 150 (M^+), IR: 3600 cm^{-1}, 3500 cm^{-1} (OH), 3000 cm^{-1}, 1500 cm^{-1}, 1000 cm^{-1}. BP = 222-224°C.

1-(4'-Methylphenyl)ethanol: was synthesized from reducing p-methylacetophenone by H_4AlLi. 100ml dried ether were placed in a three necked round bottom flask with a stirrer unit, condenser, and dropping funnel. 3g lithium aluminium hydride were introduced to the flask, 10ml p-methylacetophenone in a 30ml dried ether were added by the dropping funnel. After stirring for 2 hours, 20ml water were dropwise added in a ice-water bath. After the water layer was separated, the ethereal solution was dried by magnesium sulfate and evaporated, the residue was distilled under reduced pressure. (BP 45° C/1.7mmHg). Spectra were compared with authentic data.{67}

^{1}H-NMR (250 Mz, $CDCl_3$): $\delta = 1.27$ (d, 3H, CH_3), $\delta = 2.26$ (s, 3H, CH_3), $\delta = 3.76$ (s, 1H, OH), $\delta = 4.60$ (q, 1H, CH), $\delta = 6.98$ (s, 2H, Phenyl), $\delta = 7.10$ (s, 2H, Phenyl). MS: 136 (M^+), IR: 3600 cm^{-1}, 3500 cm^{-1} (OH), 3000 cm^{-1}, 1500 cm^{-1}, 1000 cm^{-1}. BP = 180° C/20mmHg{67} .

p-Chloroacetophenone: was prepared by Freidel-Crafts acylation of chlorobenzene by acetic anhydride. A 500 ml three necked flask with a reflux condenser were equipped with a mechanical stirrer unit and a dropping funnel, the top of the condenser was connected to a trap for absorbing the hydrogen chloride. 6 g (0.045mol) aluminium chloride anhydrous and 5.6 ml (0.05mol) of chlorobenzene with 200ml CCL_4 were placed in the flask and the mixture was stirred and refluxed, 5.1g (4.7ml, 0.05mol) of redistilled acetic anhydride were added during 30 min, then refluxed for 2 hours. The mixture was cooled and poured into 200ml ice-water and 50ml concentrated hydrochloric acid. The organic layer was separated in a separatory funnel, washed with water, then with saturated $NaHCO_3$, and dried with magnesium sulfate. After removing solvent, the crude product was distilled under reduced pressure. (BP 48° C/1mmHg). Spectra were compared with authentic data.{68} ^{1}H-NMR (250 Mz, $CDCl_3$): $\delta = 2.49$ (s, 3H, CH_3), $\delta = 7.31$ (m, 2H, Phenyl), $\delta = 7.80$ (m, 2H, Phenyl).

1-Phenyl-1-propanol: was obtained from reducing propiophenone by H_4AlLi. 100ml dried ether were placed in a three necked round bottom flask with a stirrer unit, condenser and dropping funnel. 3g lithium aluminium hydride were introduced to the flask, 10ml propiophenone in 30ml dried ether were added by the dropping funnel. After stirring for 2 hours, 20ml water were dropwise added under cooling in a ice-water bath. After the water layer separated, the ethereal solution was dried by magnesium sulfate and removed. The residue was distilled under reduced pressure.

(BP 45° C/1.7mmHg). Spectra were compared with authentic data.{69}

^{1}H-NMR (250 Mz, $CDCl_3$): $\delta = 0.9$ (t, 3H, CH_3), $\delta = 1.7$ (q, 2H, CH_2), $\delta = 2.0$ (s, 1H, OH), $\delta = 4.5$ (t, 1H, CH), $\delta = 7.2$ (s, 5H, Phenyl).

Techniques

Glassware

All solutions were prepared with class A volumetric flasks and pipets. The volumetric ware was cleaned by soaking in hot soap water and boiling. This was followed by rinsing and soaking in hot distilled water, while changing water several times over a period of at least three days. Pyrex culture tubes used for irradiation were cleaned in the same manner. Syringes used for transfering solutions from volumetric flasks to culture tubes were cleaned in a manner similar to the volumetric ware. All glassware was dried in an oven at 140°C used only for analytical glassware to avoid contamination.

The Pyrex culture tubes (13X100mm) were drawn out by heating near the top so that a narrow constriction (approximately 3X50mm) was formed 30mm from the top of the tube.

Preparation of Samples

Solutions were made by weighing samples directly into volumetric flasks and diluting to the mark or pipetting from a stock solution , made in the above manner, into volumetric flasks and then being diluted. The latter method was used when a number of solutions were needed with the same component, such as an internal standard. A 2.8 ml aliquot of these solutions were then added to the constricted culture tubes by means of a 5cc syringe.

Degassing Procedure

The tubes prepared above were then attached to a vacuum line with diffusion pump capable of 10^{-4} Torr by means of size 00 one-hole rubber stoppers fitted to a manifold containing twelve stopcocks. The solutions were frozen in liquid nitrogen and the stopcocks opened. After pumping on the samples for 15 minutes the stopcocks were closed and the solutions allowed to warm to room temperature until completely thawed. The freeze-pump-thaw cycle was repeated four more times, after which the tubes were sealed using a torch while the samples were frozen.

Irradiation Procedure

All quantum yields were measured by parallel irradiation of samples and actinometer on a merry-go-round apparatus. The light source was a Hanovia medium-pressure mercury lamp with 313nm region isolated by means of a chemical filter . The chemical filter was a 0.0002M potassium chromate solution buffered by 1% potassium carbonate. The entire apparatus, merry-go-round and light source with filter, was immersed in a constant temperature bath at room temperature.

Preparative irradiation were performed in a photochemical immersion well. The light was filtered by a pyrex sleeve surrounding the lamp. The well had a capacity of 150 ml of solution and was fitted with a condenser to prevent loss of solvent. A stream of dry nitrogen was passed through the solution by a frit at the bottom of the well. For small amount preparative irradiation, was using a pyrex test tube, sealed by a rubber stopper. The stream of dry nitrogen was passed through the solution by two needles (one entry, another one out) for 20 minutes, then irradiated by a filtered light in a immersion well.

Analysis

Analysis was done by HPLC made of a Beckman 332 Gradient Liquid Chromatography System, equipped with a Du Pont 860 Instruments Column Compartment, Beckman Modal 110A pump, Perkin-Elmer Spectrophotometric LC-75 Ultraviolet-Visible Detector. The HPLC system was connected to a HP Hewlett Packard 6080 Integrating recorder. An Altex UltraspThere Si Absorption Phase Column was used. The flow rate was 1.0 , solvent ratio were 92% hexane , 8% ethyl acetate. The gas chromatography was Varian model 1440 and 3400 gas chromatography, employing flame ionization detectors. Model 1440 Gas chromatography was connected to either Hewlett-Packard 3393 A, or 3392 A Integrating recorder.

Two types of columns have been used for gas chromatography.

Column # 1- Magabore DB-1, 15 meter in length
Column # 2- Magabore DB-210, 15 meter in length

For AH_2, PH_2, AP, PP, BH_2, MH_2, column was DB-210, temperature 60°C 10 minutes, then 170°C 3 minutes; for PClAP, column was DB-210, temperature 60°C 8 minutes, 95°C 8 minutes,then 170°C 3 minutes; for pinacols, column was DB-1, temperature was 175°C.

Spectroscopic Measurements

^{1}H NMR spectra were recorded on either a Varian T-60 or a Bruker WM-250 Fourier Transform Spectrometer.

Infrared spectra were recorded on a Niclet IR/442 Spectrometer.

Ultraviolet-visible spectra were recorded on a Shimadzu UV-160 Spectrometer.

Mass spectra were recorded on a Finigan 4000 GC/MS.

References

1. (a) P. J. Wagner, "Chemistry of Excited Triplet Organic Compounds", Topics in Current Chemistry **1976** *66* 1

   (b) Scaiano, J. C., J. Photochem., 81 **1973/74** *2.* 81
2. Colin Steel and Saul G. Cohen, J.Phys. Chem. **1988** *92* 6574
3. Giering, L., Berger, M., Steel, C., J. Am. Chem. Soc., **1974** *96* 953
4. C. M. Previtali and J. C. Scaiano, J. Chem. Soc., Perkin Trans. II, **1972** 1667, 1672
5. C. Walling and M. J. Gibian, J. Am. Chem. Soc., **1965** *87* 3361
6. W. Herkstroeter, A. A. Lamola and G. S. Hammod, J. Am. Chem. Soc., **1964** *86* 4537
7. (a) C. Walling, "Free Radicals in Solution" John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 2

   (b) G. L. Esteban, J. A. Karr, and A. F. Trotman-Dickenson, J. Chem. Soc., **1963** 3873
8. P. Gray and A. Williams, Chem. Rev., **1959** *59* 239
9. Lewis, F. D., Jonhnson, R. W., kory, D. R., J. Am. Chem. Soc., **1974** *96* 6100
10. (a) P. J. Wagner, A. E. Kampainen, and H. N. Schott, J. Am. Chem. Soc., **1973** *95,* 5604

    (b) P. J. Wagner, and A. E. Kampainen, J. Am. Chem. Soc., **1968** *90* 5896
11. P. J. Wagner, Accts. Chem. Res., **1971** *4* 168

12. P. J. Wagner, and E. Siebert, J. Am. Chem. Soc., **1981** *103* 7329

13. N. C. Yang, R. Dusenberg, Mol. Photochem., **1969** *1* 159

14. N. C. Yang, R. Dusenberg, J. Am. Chem. Soc., **1968** *90* 5899

15. F. D. Lewis, J. G. Magyar, J. Org. Chem., **1972** *37* 2102

16. F. D. Lewis, Tetrahedron Letters **1970** *16* 1373

17. D. E. Pearson, M. Y. Moss Tetrahedron Letters **1967** *39* 3791

18. E. S. Huyser and D. C. Neckers, J. Am. Chem. Soc., **1963** *85* 3641

19. Jeandrau, J. P.; Gramain, J. C.; Lamaire, J.; J. Chem. Res., Synop. **1979** 186; J. Chem. Res., Miniprint **1979** 2240

20. Lutz, H.; Duval, M. C.; Breheret, E.; Lindqvist, L. J. Phys. Chem. **1972** *76* 821

21. Scaiano, J. C., J. Am. Chem. Soc., **1980** *102* 5902

22. P. J. Wagner, Tet. Lett. **1967** *18* 1753

23. (a) G.Ciamician and P.Silber, Chem. Ber., **1900** *33* 2911
    (b) G.Ciamician and P.Silber, Chem. Ber., **1900** *34* 1530

24. G. S. Hammond, W. M. Moore, J. Am. Chem. Soc., **1959** *81* 6334

25. P. Colman, A. Dunne, M. F. Quinn, J. Chem. Soc. Faraday trans., **1976** *72* 2605

26. W. D. Cohen, Rec. Trav. Chim. Pays-Bas. **1920** *39* 243

27. Ch. Weizman, E. Bergman, Y. Hirshberg, J. Am. Chem. Soc., **1938** *60* 1530

28. V. Franzen, Justus. Liebigs Ann. Chem. **1960** *631* 1

29. D. I. Schuster, P. B. Karp, J. Photochem., **1980** *12* 333

30. H. Yoshia and T. Warashina, Bull. Chem. Soc. Jpn., **1971** *44* 2950

31. G. O. Schenck, G. Behrens and E. Roselius, Tetrahedron Letters **1970** 5185

32. J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Paterson G. Recktenwald and R. B. Martin, J. Am. Chem. Soc., **1959** *81* 1068

33. G. L. Closs and D. R. Paulson, J. Am. Chem. Soc., **1970** *92* 7229

34. Paul, H., Segaud, C. Int. J. Chem. Kinet. **1980** *12* 637

35. McCracken, D. D.; Dorn, W. S. Numerical Methods and Fortran Programming; Wiley: New York, 1964; pp 144.

36. Naguib, Y. M. A.; Cohen, S. G.; Steel. C. J. Am. Chem. Soc., **1985** *108* 128

37. P. J. Wagner, P. A. Kelso and R. G. Zeep, J. Am. Chem. Soc., **1972** *94* 7480

38. P. J. Wagner unpublished work.

39. N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, Ruth Dusenbery, J. Am. Chem. Soc., **1967** *89* 539

40. S. L. Murov, Ph. D. Thesis, Univ. of Chicago, 1966

41. J. N. Pitts, D. R. Burley, J. C. Mani and A. D. Broadbent, J. Am. Chem. Soc., **1968** *90* 5900

42. D. R. Arnoold, "Advances in Photochemistry", Vol. 6, Wiley, New York, **1968**, p. 301.

43. P. J. Wagner, Irene E. Kochevar, and A. E. Kamppainen, J. Am. Chem. Soc., **1972** *94,* 7489

44. P. J. Wagner and A. E. Puchalski, J. Am. Chem. Soc., **1980** *102* 7138

45. (a) B. M. Monroe, S. A. Weiner and G. S. Hammond, J. Am. Chem. Soc., **1968** *90* 1913

(b) B. M. Monroe, S. A. Weiner, J. Am. Chem. Soc., **1969** *91* 450

46. E. A. Lissi, J. C. Scaiano, et al., J. Am. Chem. Soc., **1983** *105* 1856

47. R. A. Caldwell, et al., J. Am. Chem. Soc., **1985** *107* 5166

48. Robert B. Fischer and Dennis G. Peters, "Quantitative Chemical Analysis" W. B. Saunders Company, Philadelphia London Toronto 1968

49. H. Agahigian, Can. J. Chem. **1963**, *41,* 194

50. The Aldrich library of NMR spectra p. 921-C.

51. Lester. A. Brooks, J. Am. Chem. Soc. **1944**, *66,* 1295

52. Dar'eva and Miklukhin, J. Gen. Chem. **1959** *29,* 620 (USSR)

53. Hanai, J. Chem. Soc. (Japan) **1944** *62,* 1208

54. The Sadtler standard spectra, NMR 2615

55. The Sadtler standard spectra, NMR 34

56. The Sadtler standard spectra, NMR 10188

57. The Sadtler standard spectra, NMR 13807

58. The Sadtler standard spectra, NMR 10447

59. The Sadtler standard spectra, NMR 10243

60. Dieter. Sebach Chem. Ber. **1977** *110(6),* 2316

61. W. A. Mosher, N. D. Heindel, J. Org. Chem., **1963** *28,* 2145

62. Angelo. Clerici and Ombreta. Porta, J. Org. Chem., **1985** *50(1),* 80

63. Peter. Weyerstalh. Chem. Ber. **1982** *115* 3697

64. A. Claus, J. Prakt. Chem. **1892** *46* 474

65. Angelo. Clerici and Ombretta. Porta, J. Org. Chem., **1985** *50(1),* 80

66. Rolf. H. Prager. Aust. J. Chem., **1977** *30(1),* 151

67. The Sadtler standard spectra, NMR 2629, Grating IR 4714

68. The Sadtler standard spectra, NMR 18007, Grating IR 272

69. The Aldrich library of NMR spectra p. 923-B

APPENDIX

This section contains the raw experimental data from which the results were obtained. The concentrations of reactants and standards are listed. The product to standard peak ratios were obtained from gas chromatographic analysis. The G. C. conditions are given in each table.

The valerophenone actinometry was measured on column DB-1 at 75° C.

The product yields, given as concentrations, are calculated from the peak area ratios and the appropriate response factors, which are also listed. A sample calculation is included in the kinetics and calculation section. From the product yields and the amount of light absorbed by the samples, as determined by valerophenone actinometry, the quantum yields were determined. The quantum yields, the radical ratio, the amount of light absorbed, the ratio of peak area from analysis, and the G. C. response factor are listed here.

Table-16: Results for the photoreduction of 0.1 M propiophenone with acetophenone pinacol $[AH]_2$ and acetophenone pinacol-d_2 $[AD]_2$, measured by HPLC, flow rate1.0, solvent ratio: 92% hexane with 8% ethyl acetate, irradiation 3 hours, $I_a = 0.31$ E/L, $SF_{AP/\gamma\text{-}P} = 1.2$,

Actinometer: 0.11M valerophenone, 0.0044M γ-phenylbuteronitrile

$[AH]_2$(M)	AP/γ-P*	[AP](M)	Φ_{AP}
0.010	0.060	0.0033	0.011
0.014	0.77	0.0042	0.013
0.021	1.1	0.0059	0.019
0.10	2.0	0.011	0.036
$[AD]_2$(M)			
0.010	0.47	0.0026	0.0083
0.014	0.64	0.0035	0.011
0.020	0.79	0.0043	0.014
0.040	1.2	0.0067	0.022
0.10	1.8	0.0096	0.031

* peak area ratio

Table-17: Results for the photoreduction of 0.1 M p-methoxyacetophenone with acetophenone pinacol $[AH]_2$, measured by HPLC, flow rate1.0, solvent ratio: 92% hexane with 8% ethyl acetate, irradiation 4.5 hours,
I_a = 0.90 E/L, $SF_{AP/\gamma\text{-}P}$= 1.2,
Actinometer: o.10M valerophenone, 0.0054M γ-phenylbuteronitrile(γ-P)

$[AH]_2$(M)	AP/γ-P*	[AP]	Φ_{AP}
0.010	1.42	0.0094	0.010
0.022	3.3	0.022	0.024
0.040	4.1	0.027	0.030
0.10	6.7	0.045	0.050

* peak area ratio

Table-18: Radical ratio in the reaction of acetophenone (AP) and propiophenone (PP) with 2-propanol (1 M) in benzene:

column DB-1 temperature 165°C, C_{19} = 0.0012M, I_a = 0.020 E/L

$SF_{(AH)2/C19}$ = 1.4, $SF_{(AHPH)/C19}$ = 1.3, $SF_{(PH)2/C19}$ = 1.1

$SF_{AP/C11}$ = 1.7, irradiation 4 hours

AP (M)	0.05	0.1	0.5
PP (M)	0.05	0.1	0.5
$(AH)_2/C_{19}$*	2.1	2.4	0.91
$(AHPH)/C_{19}$*	1.4	1.5	0.85
$(PH)_2/C_{19}$*	0.38	0.24	0.10
$(AH)_2$(M)	0.0045	0.0040	0.0015
(AHPH)(M)	0.0022	0.0023	0.0013
$(PH)_2$(M)	0.00050	0.00031	0.00014
$\Phi_{(AH)2}$	0.18	0.20	0.075
$\Phi_{(AHPH)}$	0.11	0.12	0.065
$\Phi_{(PH)2}$	0.025	0.015	0.0065
·AH/·PH	2.9	3.4	2.8

* peak area ratio

VP = 0.11(M), C_{11} = 0.0013(M), AP/C_{11} = 3.3, 3.2, 2.4, 2.4.

Table 19: Radical ratio in reaction of acetophenone and propiophenone with 2-propanol (1M) in benzene,
column DB-1 temperature 165°C, C_{18} = 0.00099M, I_a = 0.021 E/L
$SF_{(AH)_2/C18}$ = 1.2, $SF_{(AHPH)_2/C18}$ = 1.1, $SF_{(PH)_2/C18}$ = 1.0,
$SF_{AP/C11}$ = 1.7, irradiation 5 hours.

AP (M)	0.1	0.2	0.3
PP (M)	0.1	0.2	0.3
$(AH)_2/C_{18}$*	2.8	2.2	2.0
$(AHPH)/C_{18}$*	1.8	1.3	1.1
$(PPH)_2/C_{18}$*	0.29	0.21	0.19
$(AH)_2$(M)	0.0033	0.0026	0.0024
(AHPH)(M)	0.0020	0.0014	0.0010
$(PH)_2$(M)	0.00024	0.00019	0.00018
$\Phi_{(AH)2}$	0.16	0.12	0.11
$\Phi_{(AHPH)}$	0.0093	0.068	0.064
$\Phi_{(PH)2}$	0.013	0.0093	0.0088
·AH/·PH	3.4	3.6	3.6

VP = 0.11(M), C_{11} = 0.015(M), AP/C_{11} = 0.27, 0.29,
C_{11} = 0.014(M), AP/C_{11} = 0.28, 0.27.

* peak area ratio

The radical ratio of two ketones with different concentrations of 2-propanol was measured to ensure no effect for radical ratio from varied concentrations of hydrogen donor.

Table-20: Radical ratio in reaction of (0.1M) acetophenone and (0.2M) propiophenone with different concentrations of 2-propanol in benzene: column DB-1 temperature 165°C, C_{18} = 0.0011M, I_a = 0.012 E/L $SF_{(AH)2/C18}$ = 1.2, $SF_{(AHPH)2/C18}$ = 1.1, $SF_{(PH)2/C18}$ = 1.0, $SF_{AP/C11}$ = 1.7, irradiation 5 hr.

2-Prop (M)	1.0	1.5	2.1
$(AH)_2/C_{18}$*	0.70	0.73	0.77
$(AHPH)/C_{18}$*	0.90	0.94	0.99
$(PH)_2/C_{18}$*	0.28	0.30	0.31
$(AH)_2$(M)	0.00092	0.00096	0.0010
(AHPH)(M)	0.0011	0.0011	0.0012
$(PH)_2$(M)	0.00029	0.00031	0.00032
$\Phi_{(AH)2}$	0.072	0.076	0.080
$\Phi_{(AHPH)}$	0.0848	0.0884	0.0926
$\Phi_{(PH)2}$	0.024	0.025	0.026
·AH/·PH	1.74	1.74	1.74

VP = 0.11(M), C_{11} = 0.016(M), AP/C_{11} = 0.14, 0.14, 0.13, 0.14.

* peak area ratio

Table-21: Radical ration for reaction of acetophenone and p-chloroacetophenone with (1M) 2-propanol in benzene:
Column DB-1, temperature 175°C, C_{18} = 0.00055M, I_a = 0.015 E/L
$SF_{(AH)2/C18}$ = 1.2, $SF_{(ClAHAH)2/C18}$ = 1.3, $SF_{(ClAH)2/C18}$ = 1.4,
$SF_{AP/C11}$ = 1.7, irradiation 5.5 hr.

AP (M)	0.05	0.10	0.15	0.2	0.24	
ClAP (M)	0.05	0.10	0.15	0.2	0.24	---
$(AH)_2/C_{18}$*	0.062	0.033	0.031	0.026	0.023	
$(ClAHAH)/C_{18}$*	0.65	0.67	0.67	0.61	0.57	
$(ClAH)_2/C_{18}$*	1.4	1.5	1.5	1.4	1.3	
$(AH)_2$(M)	0.000041	0.000022	0.000020	0.000017	0.000015	
(ClAHAH)(M)	0.00046	0.00047	0.00047	0.00044	0.00040	
$(ClAH)_2$(M)	0.0011	0.0012	0.0012	0.0011	0.0010	
$\Phi_{(APH)2}$	0.0027	0.0015	0.0014	0.0011	0.0010	
$\Phi_{(ClAHAH)}$	0.033	0.031	0.031	0.029	0.0027	
$\Phi_{(ClAH)2}$	0.067	0.08	0.08	0.073	0.067	
·ClAH/·AH	4.3	5.6	5.6	5.5	5.5	

VP = 0.1(M), C_{11} = 0.0017(M), AP/C_{11} = 0.51, 0.52, 0.52, 0.51.

* peak area ratio

Table-22: Radical Ratio for reaction of acetophenone and p-methylacetophenone with 1M 2-propanol in benzene,
Column DB-1, temperature 170°C, C_{18} = 0.00034M,
$SF_{(AH)_2/C18}$ = 1.2, $SF_{(AHMH)_2/C18}$ = 1.3, $SF_{(MH)_2/C18}$ = 1.4,

AP (M)	0.05	0.10	0.15	0.25	0.45
MeAP (M)	0.05	0.10	0.15	0.25	0.45
$(AH)_2/C_{18}$*	3.2	1.7	1.8	1.6	0.87
$(MeAHAH)/C_{18}$*	2.0	0.95	0.99	0.91	0.48
$(MeAH)_2/C_{18}$*	0.13	0.043	0.054	0.056	0.033
$(APH)_2$(M)	0.0013	0.00065	0.00067	0.00051	0.00031
(MeAHAH)(M)	0.00088	0.00041	0.00043	0.00043	0.00025
$(MeAH)_2$(M)	0.000062	0.000020	0.000026	0.000027	0.000016
·AH/·MeAH	3.4	3.8	3.6	2.9	3.0

* peak area ratio

Table-23: Radical Ratio in reaction of acetophenone with different ketones and 1M 2-propanol in benzene, irradiation 5.5 hr, Column DB-1,Temperature 170°C, C_{18} = 0.00044M, $SF_{AP/C11}$ = 1.7, $SF_{(AH)2/C18}$ = 1.2, $SF_{(AHMH)2/C18}$ = 1.3, $SF_{(MH)2/C18}$ = 1.4, $SF_{(ClAHAH)2/C18}$ = 1.2, $SF_{(ClAH)2/C18}$ = 1.4, $SF_{(BHAH)2/C18}$ = 1.15, $SF_{(isBH)2/C18}$ = 1.1,

AP (M)	0.10	0.15	0.2	0.30
ClAP (M)	0.05	0.05	0.1	0.10
$(AH)_2/C_{18}^*$	0.21	0.43	0.25	0.37
$(ClAHAH)/C_{18}^*$	1.0	1.3	1.2	1.1
$(ClAH)_2/C_{18}^*$	1.1	0.75	1.2	0.74
$[AH]_2$(M)	0.00011	0.00022	0.00013	0.00019
[AHClAH](M)	0.00053	0.00069	0.00063	0.00058
$[ClAH]_2$(M)	0.00068	0.00046	0.00074	0.00046
$\cdot$ClAH/$\cdot$AH (k_e)	2.5	1.4	2.4	1.6

continue

AP (M)	0.05	0.05	0.10	0.10
MeAP (M)	0.10	0.15	0.20	0.30
$(AH)_2/C_{18}$*	0.79	0.53	0.75	0.43
$(MeAHAH)/C_{18}$*	1.1	0.91	1.1	0.80
$(MeAH)_2/C_{18}$*	0.34	0.34	0.15	0.30
$(AH)_2$(M)	0.00040	0.00027	0.00038	0.00022
(MeAHAH)(M)	0.00063	0.00052	0.00063	0.00042
$(MeAH)_2$(M)	0.00021	0.00021	0.000092	0.00018
·AH/·MeAH (k_e)	1.4	1.1	1.6	1.1

AP (M)	0.05	0.05	0.10	0.10
isBP(M)	0.10	0.15	0.20	0.30
$(AH)_2/C_{18}$*	3.5	2.5	3.6	2.5
$(isBHAH)/C_{18}$*	1.5	1.9	1.7	1.8
$(isBH)_2/C_{18}$*	0.13	0.23	0.14	0.24
$(AH)_2$(M)	0.00018	0.00013	0.00019	0.00013
(isBHAH)(M)	0.00076	0.00096	0.00086	0.00091
$(isBH)_2$(M)	0.000063	0.00011	0.00068	0.00012
·AH/·isBH (k_e)	4.9	3.0	4.6	3.1

* peak area ratio

Table-24: Quantum yields for acetophenone (AP) formation as a function of propiophenone concentration in benzene: I_a = 0.0161 E/L,

Irr. 3.5 hous, Column DB-210,Temperature 60°C, 10 min, 170°C, 5 min, $SF_{AP/C11}$ = 1.7, $SF_{Ap/C12}$ = 1.8, C_{12} = 0.0016M, (AH_2) = 0.2 M.

Before irradiation, the sample containing $2X10^{-4}M$ acetophenone, the calculation was done by subtracting starting AP from each sample.

PP(M)	0.0060	0.017	0.025	0.050	0.10	0.15
A	0.40	0.95	1.34	>2	>2	>2
T_a@	0.60	0.89	0.95	1	1	1
I_aT_a	0.0097	0.014	0.015	0.016	0.016	0.016
AP/C_{12}*	0.36	0.70	0.81	0.97	1.03	1.0
AP(M)	0.00077	0.0018	0.0021	0.0026	0.0027	0.0028
A°/AP	20%	10%	9%	7%	7%	7%
Φ_{AP}	0.080	0.13	0.14	0.16	0.17	0.17

VP = 0.10(M), C_{11} = 0.0017(M), AP/C_{11} = 0.57, 0.58, 0.57.

* peak area ratio , @ percentage of light absorbed

Table-25: Quantum yield and radical ratio for reaction of propiophenone with 0.2M 1-phenylethanol in benzene:

Column DB-210,Temperature 60°C, 10 min, 170°C, 5 min,for AP and PH_2,

Column DB-1, Temperature 175°C, for pinacols,

C_{12} = 0.0016M, C_{18} = 0.00080M, $SF_{AP/C_{12}}$ = 1.8, $SF_{PH_2/C12}$ = 2.3,

$SF_{(AH)_2/C_{18}}$ = 1.2, $SF_{(AHPH)/C18}$ = 1.1, $SF_{(PH)2/C18}$ = 1.0, $SF_{AP/C_{11}}$ = 1.7.

PP(M)	0.00601	0.0170	0.0251	0.0501	0.100	0.150
PH_2/C_{12}*	0.012	0.034	0.053	0.068	0.085	0.070
PH_2(M)	0.000044	0.00013	0.00020	0.00025	0.00031	0.00026
Φ_{PH2}	0.0028	0.012	0.013	0.016	0.020	0.017
Φ_{AP}	0.079	0.12	0.14	0.16	0.17	0.17
$(AH)_2/C_{18}$*	0.13	0.11	0.038	0.019	-	-
$(AHPH)/C_{18}$*	0.49	0.69	0.67	0.56	0.36	0.27
$(PH)_2/C_{18}$*	0.51	1.2	1.6	2.2	2.3	2.2
$(AH)_2$(M)	0.00013	0.00011	0.000036	0.000018	-	-
(AHPH)(M)	0.00043	0.00061	0.00059	0.00049	0.00032	0.00024
$(PH)_2$(M)	0.00038	0.00090	0.0012	0.0016	0.0017	0.0016
$\Phi_{(AHAH)}$	0.0076	0.0062	0.0022	0.0011	_	-
$\Phi_{(AHPH)}$	0.036	0.035	0.034	0.029	0.018	0.014
$\Phi_{(PHPH)}$	0.023	0.057	0.073	0.10	0.11	0.10

* peak area ratio

Table-26: Quantum yields of acetophenone as a function of 1-phenylethanol concentration with 0.05 M isobutyrophenone in benzene:

Column DB-210,Temperature 60°C, 10 min, 170°C, 5 min, irradiation 8 hr, C_{12} = 0.0024M, $SF_{AP/C_{12}}$ = 1.8, $SF_{AP/C_{11}}$ = 1.7, I_a = 0.022E/L

(AH_2)(M)	AP/C_{12}*	AP(M)	Φ_{AP}
1.00	1.7		
	1.70	0.0073	0.33
0.33	1.2		
	1.2	0.0050	0.23
0.20	0.94		
	0.92	0.0040	0.18
0.13	0.77		
	0.78	0.0033	0.15
0.11	0.64		
	0.63	0.0027	0.12

VP = 0.1, C_{11} = 0.00071, AP/C_{11} = 5.8, 5.9, 5.8, 5.9.

* peak area ratio

Table-27: Quantum yields for acetophenone (AP) formation as a function of isobutyrophenone concentration in benzene: $(AH_2) = 0.2$ M
Column DB-210: Temperature : 60°C, 10 min, 170°C, 5 min,
$C_{12} = 0.0011$M, $SF_{AP/C_{12}} = 1.8$, $SF_{AP/C_{11}} = 1.7$, irradiation 3.5 hr, $I_a =$ 0.014E/L

isBP(M)	0.0071	0.010	0.016	0.025	0.050
A	0.48	0.64	0.97	1.5	>2
T_a@	0.67	0.77	0.89	0.97	1
T_aI_a	0.0090	0.011	0.012	0.013	0.014
AP/C_{12}*	0.43	0.55	0.69	0.83	0.91
AP(M)	0.00086	0.0011	0.0014	0.0017	0.0018
Φ_{AP}	0.096	0.11	0.12	0.13	0.14

VP = 0.1, $C_{11} = 0.0033$, $AP/C_{11} = 0.77, 0.79, 0.78, 0.78$.

* peak area ratio, @ percentage of light absorbed

Table-28: Quantum yield and radical ratio for reaction of isobutyrophenone with 0.2M 1-phenylethanol in benzene:
Column DB-210,Temperature 60°C, 10 min, 170°C, 5 min,for AP and BH_2,
Column DB-1, Temperature 175°C, for pinacols, I_a = 0.014E/L
C_{12} = 0.0011M, C_{18} = 0.00039M, $SF_{AP/C12}$ = 1.8, $SF_{BH2/C12}$ = 1.5,
$SF_{(AH)2/C18}$ = 1.2, $SF_{(AHBH)/C18}$ = 1.15, $SF_{(isBH)2/C18}$ = 1.1.

isBP(M)	0.0071	0.0100	0.016	0.025	0.050
BH_2/C_{12}	0.11	0.12	0.11	0.17	0.16
BH_2(M)	0.00018	0.00024	0.00022	0.00028	0.00026
Φ_{BH2}	0.013	0.014	0.014	0.021	0.019
Φ_{AP}	0.096	0.097	0.12	0.13	0.14
$(AH)_2/C_{18}$*	0.24	0.24	0.079	0.12	-
$(AHBH)/C_{18}$*	1.0	1.1	1.1	0.96	0.30
$(isBH)_2/C_{18}$*	1.0	1.3	1.7	1.9	2.0
$(AH)_2$ (M)	0.00011	0.00011	0.000036	0.000053	-
(AHBH)(M)	0.00045	0.00049	0.00049	0.00043	0.00013
$(isBH)_2$(M)	0.00043	0.00056	0.00073	0.00082	0.00086
$\Phi_{(AHAH)}$	0.012	0.010	0.0030	0.0041	_
$\Phi_{(AHBH)}$	0.050	0.045	0.041	0.033	0.0096
$\Phi_{(BHBH)}$	0.048	0.051	0.061	0.063	0.061

* peak area ratio

Table-29: Quantum yields of acetophenone as a function of 1-phenylethanol concentration with 0.05 M p-methylacetophenone in benzene:

Column DB-210,Temperature 60°C, 10 min, 170°C, 5 min, I_a =0.022 E/L

C_{12} = 0.0041M, $SF_{AP/C_{12}}$ = 1.8, $SF_{AP/C_{11}}$ = 1.7, irradiation 8 hrs

(AH_2)	AP/C_{12}*	AP	Φ_{AP}
(M)		(M)	
0.10	0.30		
	0.29	0.0022	0.099
0.13	0.34		
	0.33	0.0025	0.11
0.20	0.42		
	0.41	0.0031	0.14
0.33	0.50		
	0.48	0.0036	0.17
1.0	0.61		
	0.60	0.0045	0.21

VP = 0.1, C_{11} = 0.00077, AP/C_{11} = 5.7, 5.4, 5.5, 5.3.

* peak area ratio,

Table-30: Quantum yields for acetophenone (AP) formation as a function of p-methylacetophenone concentration in benzene: $(AH_2) = 0.2$ M Column DB-210,Temperature 60°C, 10 min, 170°C, 4 min, $C_{12} = 0.0031$M, $SF_{AP/C_{12}} = 1.8$, $SF_{AP/C_{11}} = 1.7$, irradiation 4 hr, $I_a = 0.022$ E/L

MeAP -(M)-	A	T_a@	T_aI_a	AP/C_{12}*	AP (M)
0.0051	0.38	0.58	0.013	0.13	0.00072
0.0071	0.54	0.71	0.015	0.18	0.0010
0.010	0.76	0.83	0.018	0.25	0.0014
0.016	1.2	0.94	0.020	0.34	0.0019
0.025	1.8	0.98	0.021	0.38	0.0021
0.051	>2	1	0.022	0.41	0.0023

VP = 0.1, $C_{11} = 0.0016$, $AP/C_{11} = 2.7, 2.6, 2.7, 2.7$.

* peak area ratio, @percentage of light absorbed

Table-31: Quantum yield and radical ratio for reaction of p-methylacetophenone with 0.2M 1-phenylethanol in benzene:

Column DB-210,Temperature 60°C, 10 min, 170°C, 4 min,for AP and MH_2,

Column DB-1, Temperature 175°C, for pinacols,

$C_{12} = 0.0031M$, $C_{18} = 0.00032M$, $SF_{AP/C_{12}} = 1.8$, $SF_{MH_2/C_{12}} = 1.4$,

$SF_{(AH)_2/C_{18}} = 1.2$, $SF_{(AHMH)/C_{18}} = 1.3$, $SF_{(MH)_2/C_{18}} = 1.4$

MeAP(M)	0.0051	0.0071	0.010	0.016	0.025	0.051
I_a	0.013	0.015	0.018	0.020	0.021	0.022
MH_2/C_{12}*	0.0073	0.012	0.017	0.024	0.032	0.035
MH_2(M)	0.000030	0.000050	0.00007	0.00010	0.00013	0.00015
Φ_{MH_2}	0.0024	0.0032	0.0038	0.0050	0.0063	0.0067
Φ_{AP}	0.057	0.067	0.079	0.092	0.099	0.11
$(AH)_2/C_{18}$*	0.45	0.34	0.26	0.39	-	-
$(AHMH)/C_{18}$*	1.8	1.3	0.59	0.78	0.55	0.38
$(MH)_2/C_{18}$*	0.70	1.3	2.2	3.4	3.7	4.5
$(AH)_2$(M)	0.00017	0.00013	0.00010	0.00015	-	-
(AHMH)(M)	0.00069	0.00054	0.00025	0.00032	0.00023	0.00016
$(MH)_2$(M)	0.00031	0.00058	0.00099	0.0015	0.0017	0.0020
$\Phi_{(AH)_2}$	0.013	0.0098	0.0053	0.0048	-	-
$\Phi_{(AHMH)}$	0.053	0.036	0.014	0.016	0.011	0.0073
$\Phi_{(MHMH)}$	0.024	0.039	0.055	0.076	0.079	0.092

* peak area ratio

Table-32: Quantum yields of p-chloroacetophenone formation as a function of 1-(4'-chlorophenyl) ethanol concentration with 0.05 M acetophenone in benzene: Column DB-210,Temperature 60°C,4 min, Temperature 95°C, 8 min, 170°C, 3 min, $C_{17} = 0.0079M$, $SF_{ClAP/C_{17}} = 2.2$, $SF_{AP/C_{11}} = 1.7$, irradiation 8.5 hr, $I_a = 0.0135$ E/L

$ClAH_2$ (M)	$ClAP/C_{17}$*	ClAP (M)	Φ_{ClAP}
0.1	0.089		
	0.086	0.0015	0.11
0.13	0.11		
	0.10	0.0018	0.14
0.2	0.14		
	0.14	0.0023	0.17
0.33	0.18		
	0.18	0.0030	0.22
1.0	0.23		
	0.23	0.0040	0.29

VP = 0.1, $C_{11} = 0.0013$, $AP/C_{11} = 2.0, 2.1, 1.9, 2.0$.

* peak area ratio

Table-33: Quantum yields for p-chloroacetophenone (ClAP) formation as a function of acetophenone concentration in benzene: $(ClAH_2) = 0.2$ M, $I_a = 0.0146$ E/L Column DB-210,Temperature 60°C,8 min, Temperature 95°C, 8 min, 170°C, 3 min, $C_{17} = 0.0078$M, $SF_{ClAP/C_{17}} = 2.2$, $SF_{AP/C_{11}} = 1.7$, irradiation 5.5 hr.

(AP) -(M)	A	T_a@	T_aI_a	$ClAP/C_{17}$*	ClAP (M)
0.0071	0.50	0.68	0.0099	0.046	0.00078
0.010	0.68	0.79	0.012	0.068	0.0011
0.013	0.84	0.85	0.013	0.082	0.0014
0.016	1.0	0.91	0.014	0.095	0.0016
0.025	1.4	0.96	0.014	0.12	0.0020
0.051	>2	1	0.015	0.15	0.0025
0.10	>2	1	0.015	0.15	0.0026

VP = 0.1, $C_{11} = 0.0016$, $AP/C_{11} = 1.7, 1.8, 1.9, 1.8$.

* peak area ratio, @ percentage of light absorbed

Table-34: Quantum yield and radical ratio for reaction of acetophenone with 0.2M 1-(4'-chlorophenyl) ethanol in benzene: Column DB-210, for ClAP and AH_2, Column DB-1, for pinacols, $C_{16'} = 0.0035M$, $C_{17} = 0.0079M$, $C_{18} = 0.00053M$, $SF_{ClAP/C_{17}} = 2.2$, $SF_{AH_2/C_{16'}} = 2.1$, $SF_{(AH)_2/C_{18}} = 1.2$, $SF_{(AHClAH)/C_{18}} = 1.2$, $SF_{(ClAH)_2/C_{18}} = 1.4$

AP(M)	0.0079	0.010	0.013	0.016	0.025	0.051	0.10
I_a	0.0099	0.012	0.012	0.013	0.014	0.015	0.015
AH_2/C_{b16}*	-	-	-	0.0033	0.0051	0.0074	0.011
AH_2(M)	-	-	-	0.000024,	0.000037,	0.000054,	0.000081
Φ_{AH_2}	-	-	-	0.0019	0.0027	0.0037	0.0054
Φ_{ClAP}	0.084	0.98	0.11	0.12	0.14	0.17	0.18
$(AH)_2/C_{18}$*	0.82	0.88	1.0	1.4	1.8	2.4	3.0
$(AHClAH)/C_{18}$*	0.59	0.60	0.52	0.57	0.51	0.38	0.25
$(AH)_2$(M)	0.00052	0.00056	0.00064	0.00089	0.0011	0.0015	0.0019
(AHClAH)(M)	0.00038,	0.00038	0.00033	0.00036	0.00032	0.00024,	0.00016
$\Phi_{(AH)_2}$	0.051	0.047	0.049	0.065	0.079	0.10	0.13
$\Phi_{(AHClAH)}$	0.038	0.032	0.028	0.028	0.023	0.016	0.011

*peak area ratio

Table-35: GC Response Factors

Compounds	Standard	Condition	SF
acetophenone	g-butyrophenylacetonitrile	HPLC	1.2
	dodecane(C_{12})	# 2- 60°C	1.8
	undecane(C_{11})	# 1- 75°C	1.7
1-phenylpropanol	dodecane (C_{12})	# 2- 60°C	2.4
1-phenylethanol	2,2,4,4,6,8,8-heptamethylnonane ($C_{16'}$)	# 2- 60°C	2.1
isobutyrobenzyl alcohol	dodecane (C_{12})	# 2- 60°C	1.5
p-chloroacetophenone	Heptandecane(C_{17})	# 2- 95°C	2.2
1-(4'-methylphenyl) ethanol	dodecane (C_{12})	# 2- 60°C	1.4
acetophenone pinacol	octadecane(C_{18})	# 1- 175°C	1.2
	nonadecane (C_{19})	# 1- 175°C	1.4

continue

propiophenone pinacol	octadecane(C_{18})	# 1- 175°C	1.0
	nonadecane(C_{19})	# 1- 175°C	1.1
ClAP pinacol	octadecane(C_{18})	# 1- 175°C	1.4
MeAP pinacol	octadecane(C_{18})	# 1- 175°C	1.4
isBP pinacol	octadecane (C_{18})	# 1- 175°C	1.1