1959

Excitation mechanisms in photoreduction of ketones

William Marshall Moore
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EXCITATION MECHANISMS IN PHOTOREDUCTION OF KETONES

by

William Marshall Moore

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

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Ames, Iowa

1959
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INTRODUCTION

Solution photochemistry has entered a new phase of development within the last ten years. The energy required for kinetic study in solution has been supplied by the advent of high intensity mercury arc lamps and extremely high intensity flash units. Light intensities with the mercury arcs have been increased a thousand fold over those used for vapor phase photochemistry. Flash units have increased the light energy by a million fold (for short periods of time) over low intensity light sources.

Numerous organic photochemical reactions are known, and more are being discovered. The recent interest shown by organic chemists in the photochemical rearrangements of natural products\(^1,2\) has emphasized the lack of knowledge concerning excited molecules. Vapor phase photochemistry, although thoroughly studied\(^3,4\), has had limited application to organic photochemical mechanisms. In the vapor phase, the light absorbed is usually converted into vibrational

energy which leads to fragmentation of the molecule. Reactions of the excited molecule in solution are: hydrogen abstraction, addition, and rearrangement, with fragmentation assuming a minor role.

The necessity for a basic mechanistic approach to solution photochemistry becomes apparent after a brief scan of the available literature. This research was carried out in an effort to contribute to the basic understanding of solution photochemistry.

Absorption spectroscopy has furnished much information concerning the properties of excited molecules. There have been few attempts to correlate this information with photochemical mechanisms. A notable exception is the work of Norrish and others in the field of flash photolysis. The present research program was pursued with an underlying desire to bridge the gap between chemical reactivity and the nature of the excited molecule.

Electronic absorption and emission spectroscopy has blossomed since 1945 when Lewis and Calvin, and Lewis, Calvin, and Kasha, demonstrated that phosphorescence was caused by a triplet to singlet transition. Now, assignments

5 R. G. W. Norrish, Quart. Revs., 10, 149 (1956).
have been given to the absorption and emission spectra of many compounds containing most of the functional groups.

Several types of transitions are possible, but from practical and energy considerations, only two of these transitions have much chemical importance. They are the \( \pi \rightarrow \pi^* \) transitions and the \( \eta \rightarrow \pi^* \) transitions of carbonyl groups and other conjugated systems containing hetero-atoms with unshared electrons.

The transition of an electron from a pi bonding orbital to a pi antibonding orbital is designated a \( \pi \rightarrow \pi^* \) transition. It is a space allowed transition and possesses a large molar extinction coefficient (approximately \( 10^4 \)). Photochemical studies involving this transition have been limited. The use of unfiltered light for photochemical reactions induced by the \( \pi \rightarrow \pi^* \) transition has clouded its significance. The problem of developing filter systems which are practical for the 2000-3000 Å region has dampened interest in this transition.

The transition of an electron from a nonbonding orbital to a pi antibonding orbital is designated as an \( \eta \rightarrow \pi^* \) transition. It is a space forbidden transition and possesses a small molar extinction coefficient (approximately 100). It might well be called "the photochemical transition". The moderate energy requirement for the transition (3000-5000 Å) has made it popular for photochemical synthesis and hence-
forth kinetic study.

Platt\(^8\) has developed the following notation which is being generally accepted, since much symbolic confusion has arisen in the field. An \(\psi \rightarrow \psi^*\) transition allowed by local symmetry is termed \(^1W \leftrightarrow ^1A\), and an \(\psi \rightarrow \psi^*\) transition forbidden by local symmetry is termed \(^1U \leftrightarrow ^1A\). The corresponding triplet states are \(^3W\) and \(^3U\).

McClure and Hanst\(^9\) have studied the absorption and emission spectra of a single crystal of benzophenone at 20°K. The absorption spectrum contains a \(^1U \leftrightarrow ^1A\) transition with the 0-0 band at 26580 cm\(^{-1}\), and the carbonyl stretching frequency is 1240 cm\(^{-1}\) in the upper state. The emission spectrum, which is excited by ultraviolet radiation, is probably due to the \(^3U \rightarrow ^1A\) transition with the 0-0 band at 23800 cm\(^{-1}\), and the carbonyl stretching frequency in the ground state is 1740 cm\(^{-1}\).

Gilmore, Gibson, and McClure\(^10\) determined the absolute quantum yield of fluorescence and phosphorescence for a number of compounds including benzophenone. In solid solution at 77°K., using exciting light of 2650 A., a phosphorescence

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quantum yield of 0.7-0.8 was found for benzophenone. No fluorescence was observed. The lifetime of the triplet state was calculated to be 0.008 sec.

Kasha\textsuperscript{11}, in a discussion of $\pi \rightarrow \pi^*$ transitions, has suggested that the transition of the excited singlet to the triplet state could compete successfully with fluorescence and internal conversion of the singlet to the ground state, if the intersystem crossing lies near the bottom of the potential energy curve of the excited singlet state.

From spectroscopic evidence, the following picture can be constructed for the $\pi \rightarrow \pi^*$ transition of benzophenone. An electron from the nonbonding p orbital on the oxygen of the carbonyl group is excited by light of 3450 A. to the antibonding pi orbital with conservation of spin. Intersystem crossing to the triplet state is favorable, and occurs within several molecular vibrations ($10^{-12}$ sec.). During this interval the C-O bond lengthens due to bond weakening by the antibonding orbital. At low temperatures the triplet state returns to the ground singlet by radiation and collisional deactivation. From the high quantum yield observed for the phosphorescence of benzophenone, one must conclude that all excited molecules pass through the triplet state, since collisional deactivation would not be able to compete

with fluorescence, and any molecule left in the excited singlet state would probably return to the ground state by radiation.

The literature concerning the photochemistry of benzophenone has been reviewed by Baker; therefore, only the work that is pertinent to the present study will be mentioned.

Porter developed the method of flash photolysis which is being used by several investigators at the present time. It involves the triggering of a bank of condensers to furnish a high energy spark. This flash has a duration of 20 to 40 micro-seconds. Then a spectroscopic flash of lower intensity is automatically triggered at a preset interval after the first flash, and the transient absorption spectra are observed with a spectrograph. This method has been successful in locating the triplet absorption spectra of many organic compounds in solution. Once the transient absorption spectra have been identified, the rate of decay of one of the bands can be followed with an oscilloscope.

Employing the method of flash photolysis, Porter and


Windsor\textsuperscript{14} studied anthracene and found that the lifetime of the triplet state was dependent on the solvent, independent of anthracene concentration up to $10^{-3}\text{M}$, easily excited to higher triplet levels, and quenched by oxygen. The decay of the triplet state followed first order kinetics with $k_1$ equal to $1.1 \times 10^4$ sec.$^{-1}$. The rate constant for quenching by oxygen was $3 \times 10^9$ liter mole$^{-1}$ sec.$^{-1}$. It was argued that the triplet state was deactivated intramolecularly by internal conversion to the ground state. In some manner, more viscous solvents inhibit the internal conversion producing slower rate constants.

Livingston\textsuperscript{15}, using the flash technique, was able to identify the triplet absorption spectra of chlorophyll-a and chlorophyll-b. The decay rate of the triplet for chlorophyll-b was found to be linearly dependent on the concentration of chlorophyll-b. Apparently, quenching by solute is more specific than quenching by solvent. This agrees with the observation of Calvin and Dorough\textsuperscript{16} that triplet state quenching of porphyrin-like molecules is a difficult and specific process.

\begin{itemize}
  \item \textsuperscript{15}R. Livingston, J. Am. Chem. Soc., 77, 2179 (1955).
  \item \textsuperscript{16}M. Calvin and G. D. Dorough, J. Am. Chem. Soc., 70, 699 (1948).
\end{itemize}
Bridge and Porter\textsuperscript{17} have applied the flash photolysis technique to an actual photochemical reaction in an attempt to determine the chemically reactive state. The photoreduction of duroquinone in liquid paraffin was chosen since the various transient absorption spectra were easily separated and identified, and the lifetime of the triplet state was measurable. It was observed that the formation of the radical was independent of the rate of disappearance of the triplet state, indicating that it was not involved in the photoreduction. Unfiltered light was employed so all transitions above the quartz cut-off were excited. Although the choice of the system for study may have been unfortunate, the method certainly has promise for the investigation of photochemical reactions.

In 1944, Bäckström\textsuperscript{18} investigated the oxidation processes occurring during the photoreduction of benzophenone in alcohol. Solutions of benzophenone in various alcohols were shaken with oxygen in the presence of light of the 3660 Å region. The oxidation proceeded at approximately the same rate in ethyl alcohol, isoamyl alcohol, isopropanol, and benzhydrol. The rate was three times faster in benzyl alcohol than in any of the other alcohols. The rate of oxida-


\textsuperscript{18}H. L. J. Bäckström, "The Svedberg Memorial Volume", Almquist and Wiksells Boktryckeri, Uppsala, Sweden (1944).
tion was faster in air than in oxygen for all of the alcohols except benzyl alcohol. Oxygen was consumed at a constant rate during the photolysis, and the oxidation was definitely not a chain process. The quantum yield in the oxidation of isopropanol in the presence of benzophenone was 0.5 at 20° and 1 atm. of oxygen. Product analysis indicated that quantitative yields of acetone and hydrogen peroxide were obtained from the reaction. A careful study of the benzophenone-isopropanol system showed that the rate of oxidation was approximately inversely proportional to the oxygen pressure, and approximately proportional to the concentration of isopropanol. t-Butyl alcohol served as the diluent in the determination of the dependence of the rate on isopropanol concentration. The results indicated that the following reaction scheme was feasible. In the absence of air, a quantum yield of 0.5 should be obtained for the

\[
\begin{align*}
(1) \quad & (C_6H_5)_2CO + h\nu \rightarrow (C_6H_5)_2CO^* \\
(2) \quad & (C_6H_5)_2CO^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2COH + (CH_3)_2COH \\
(3) \quad & 2 (C_6H_5)_2COH \rightarrow (C_6H_5)_2(\text{OH})C-C(\text{OH})(C_6H_5)_2 \\
(4) \quad & 2 (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + (CH_3)_2CO \\
(5) \quad & (C_6H_5)_2CO^* + O_2 \rightarrow (C_6H_5)_2CO + O_2 \\
(6) \quad & (C_6H_5)_2COH + (CH_3)_2COH + O_2 \rightarrow (C_6H_5)_2CO + (CH_3)_2CO + H_2O_2 \\
\end{align*}
\]

formation of benzpinacol and acetone. Reaction (5) accounted for the inverse dependence of rate on concentration of oxygen,
since (5) competes with (2). Reaction (6) proceeds at such a rate that (3) and (4) are unable to compete.

The benzophenone-isopropanol system has recently been reinvestigated\textsuperscript{19}. The quantum yields for production of benzpinacol and acetone and for the disappearance of benzophenone were determined at 3660 A. and 3130 A. in the presence and absence of oxygen. The quantum yield for benzophenone was 1.0 for an average of five runs in nitrogen flushed solutions. The quantum yield for acetone was 0.92, and was independent of the amount of dissolved oxygen. The quantum yield for benzpinacol was 0.93 in oxygen free solutions, but dropped to zero in oxygen saturated solutions. Hydrogen peroxide was produced in the oxygen saturated solutions. Pitts, et al. suggested a mechanism to account for these results which differs from that of Backstrom in that step (4) is replaced by step (7). It is evident from this study, that the quantum yield for the production of the chemically reactive state must be one. A colored intermediate was observed during the photolysis in the absence of oxygen, which was destroyed on contact with air. The intermediate was not identified, and its place in the reaction scheme could only

be suggested.

Baker\textsuperscript{12} has investigated the benzophenone-toluene system using light of the 3660 Å region. The products from the photoreduction are benzpinacol, bibenzyl, and benzylidiphenylcarbinol. Oxidation occurred, but the reaction was carried out to sufficient conversion to minimize this effect. Product distribution was accounted for by random coupling of diphenylhydroxymethyl and benzyl radicals. The quantum yield was relatively insensitive to changes in: temperature, light intensity, and concentration of benzophenone. In varying the concentration of toluene, with benzene as the inert solvent, it was found that a plot of the inverse of the quantum yield versus the ratio of benzene to toluene concentration gave a linear function. The following mechanism accounted for the results.

\begin{align*}
\text{(8)} & \quad (C_6H_5)_2CO + hv \rightarrow (C_6H_5)_2CO^* \\
\text{(9)} & \quad (C_6H_5)_2CO^* + C_6H_5CH_3 \rightarrow (C_6H_5)_2COH + C_6H_5CH_2 \\
\text{(10)} & \quad (C_6H_5)_2CO^* + C_6H_5CH_3 \rightarrow (C_6H_5)_2CO + C_6H_5CH_3 \\
\text{(11)} & \quad (C_6H_5)_2CO^* + C_6H_6 \rightarrow (C_6H_5)_2CO + C_6H_6 \\
\text{(12)} & \quad 2(C_6H_5)_2COH \rightarrow (C_6H_5)_2(OH)C-C(0H)(C_6H_5)_2 \\
\text{(13)} & \quad (C_6H_5)_2COH + C_6H_5CH_2 \rightarrow (C_6H_5)_2(OH)C-CH_2C_6H_5 \\
\text{(14)} & \quad 2C_6H_5CH_2 \rightarrow C_6H_5CH_2CH_2C_6H_5
\end{align*}

A steady state treatment of the kinetics gave the following rate law, where $\varnothing_B$ is the quantum yield for disa-
pearance of benzophenone. The subscripts of the rate

\[
\phi_B = \frac{k_9 \text{ (toluene)}}{(k_9 + k_{10})\text{ (toluene)} + k_{11} \text{ (benzene)}}
\]

costants correspond to the number of the reaction. Inversion of Equation 15 gave Equation 16. The intercept (2.85)

\[
\frac{1}{\phi_B} = 1 + \frac{k_{10}}{k_9} + \frac{k_{11} \text{ (benzene)}}{k_9 \text{ (toluene)}}
\]

of the forementioned plot is \((1 + \frac{k_{10}}{k_9})\), and the slope (2.81) is \(k_{11}/k_9\). These values indicate that toluene is as effective as benzene in deactivating the excited state, and this caused the low quantum yield for the photoreduction.

Baker concluded that the reactive state was the triplet state, since numerous collisions between excited benzophenone molecules and toluene molecules must occur before either deactivation or hydrogen abstraction takes place.

Spectroscopic evidence suggests that all excited benzophenone molecules are easily converted to the triplet state, which phosphoresces or is deactivated by collisions with other molecules. Photochemical evidence suggests that only one excited state is responsible for the hydrogen abstraction reaction, and that the limit for the quantum yield is one.
EXPERIMENTAL

Materials

Alumina

Alumina (80-200 mesh, Chicago Apparatus Co.) was activated by allowing it to stand under ethyl acetate for several days. The alumina was filtered, washed first with water and then methanol, and then was dried \textit{in vacuo} at room temperature.

Benzene

Benzene (Reagent Grade, thiophene free, Baker and Adamson) was used without further purification. It was stored over sodium when moisture was undesirable.

Benzhydrol

Benzhydrol (Reagent Grade, Matheson, Coleman, and Bell) was dissolved in hot ligroin (b.p. 60-70°), and the solution was filtered. Upon cooling, benzhydrol crystallized in white needles, which were recrystallized from ligroin to give a product with melting point 65-66° (uncorrected).

Benzophenone

Benzophenone (Reagent Grade, Matheson, Coleman, and Bell) was used without further purification.
Benzoquinone

Benzoquinone (Eastman Yellow Label, Eastman Kodak Co.) was dissolved in hot ligroin (b.p. 60-70°), and the solution was filtered. Upon cooling, yellow needles formed, which were recrystallized from ligroin to give a product with melting point 114-115° (uncorrected).

t-Butyl alcohol

t-Butyl alcohol (Reagent Grade, Matheson, Coleman, and Bell) was allowed to stand over anhydrous magnesium sulfate for several hours. The mixture was filtered, the t-butyl alcohol was fractionally distilled, and the fraction boiling at 82° was collected, melting point, 24.8°.

Chloranil

Chloranil (Eastman White Label, Eastman Kodak Co.) was recrystallized twice from glacial acetic acid and dried in vacuo, melting point, 295-297° (uncorrected).

Cumene

Cumene (Eastman White Label, Eastman Kodak Co.) was washed five times with concentrated sulfuric acid in a ratio of 10:1, once with water, once with 10% sodium carbonate, once again with water, and dried over anhydrous magnesium sulfate. The cumene was then fractionally distilled from
sodium, the fraction boiling at 150-152° was collected and stored over sodium. A vapor phase chromatograph of the purified cumene indicated the presence of 1.6% of low boiling impurity.

**Cyclohexane**

Cyclohexane (Spectrophotometric Grade, Matheson, Coleman, and Bell) was used without further purification.

**α-Deuterobenzhydrol**

(α-Deuterobenzhydrol$^{20}$ was prepared by the reduction of benzophenone with lithium aluminum deuteride (96.6% pure, Metal Hydrides Corp.) in anhydrous diethyl ether. The reaction was carried out under nitrogen, and stoichiometric amounts of reactants were used. The yield obtained was 85% based on the deuteride. The product was recrystallized twice from ligroin (b.p. 60-70°) to give white needles, melting point 69-70° (uncorrected). A comparison of the infrared spectra of benzhydrol and α-deuterobenzhydrol showed them to be identical, except that the C-H band at 2850 cm.$^{-1}$ was completely shifted to 2110 cm.$^{-1}$. This agrees well with the calculated shift for the stretching frequency from a C-H to

---

a C-D bond. Deuterium analyses in triplicate on the product gave values of 0.85, 1.0, and 1.0 deuterium atoms per molecule.

**Erbium dipivaloylmethide**

Erbium dipivaloylmethide, Er(DPM)$_3$, was prepared by dissolving erbium oxide (Lindsay Chemical Div.) in dilute hydrochloric acid, adding an equal volume of ethanol, and then excess dipivaloylmethane. Dimethylformamide was added until a homogeneous solution was obtained. Dilute ammonium hydroxide was then added until the solution became neutral. Pink erbium dipivaloylmethide precipitated, was filtered off, and the precipitate was extracted with ligroin. Evaporation of the ligroin extract produced pink crystals, melting point 145-150°C. Further purification was not successful due to decomposition of the chelate. The ultraviolet spectrum of Er(DPM)$_3$ consisted of two absorption maxima at 3750 A. (extinction coefficient of 92) and 2840 A. (extinction coefficient of 28,000).

---

$^{21}$J. Warkentin, California Institute of Technology, Pasadena, Calif. Data from deuterium analyses. Private communication. 1959.

$^{22}$Dipivaloylmethane was prepared by Mr. Kenneth Johnson, Iowa State University of Science and Technology, Ames, Iowa.
**Ferric dipivaloylmethide**

Ferric dipivaloylmethide, Fe(DPM)_3, was prepared by dissolving ferric chloride and excess sodium acetate in 50% ethanol-water mixture, followed by the addition of dipivaloylmethane. A red precipitate of Fe(DPM)_3 formed immediately, and was filtered off and extracted with ligroin. Evaporation of the ligroin extract produced red cubic crystals. The material was recrystallized from dimethylformamide to give a product, melting point 161-162°C (uncorrected). The molecular weight was 642 as determined by cryoscopic measurements in benzene. Theoretical molecular weight is 605. The ultraviolet spectra gave absorption maxima at 2730 Å (extinction coefficient of 30,000), 3540 Å (extinction coefficient of 4400), and 4230 Å (extinction coefficient of 3300). Calculated for FeC_{33}H_{57}O_{6}: C, 65.5; H, 9.4; and ash, 13.2. Found: C, 65.39; H, 9.42; and ash, 13.28.

**Gadolinium dipivaloylmethide**

Gadolinium dipivaloylmethide was prepared by the method described for erbium dipivaloylmethide.

**Isopropanol**

Isopropanol (Reagent Grade, Matheson, Coleman, and Bell) was used without further purification.
Lanthanum dipivaloylmethide

Lanthanum dipivaloylmethide, La(DPM)₃, was prepared by the method described for erbium dipivaloylmethide. The chelate was recrystallized from dimethylformamide to give a product, melting point 114-115°. Calculated for LaC₃₃H₅₇O₆: C, 57.6; H, 8.3; and ash, 23.6. Found: C, 55.28; H, 8.71; and ash 19.64. If dimethylformamide was assumed to be the contaminant, the mole ratio of dimethylformamide to La(DPM)₃ would be 1 to 3, and would give the material an apparent molecular weight of 536. Cryoscopic measurements in benzene gave a molecular weight of 553. Theoretical molecular weight for La(DPM)₃ is 688. Attempted removal of the residual solvent by heating or sublimation resulted in decomposition of the chelate. This was true for all the rare earth chelates prepared, and rendered purification very difficult. The compound obtained from the sublimation had a melting point of 219-221° (uncorrected).

Lead tetraacetate

Lead tetraacetate (Reagent Grade, Matheson, Coleman, and Bell) was dissolved in hot glacial acetic acid and the lead oxide was filtered off. White needles of lead tetraacetate formed on cooling. The solution was filtered, and the crystals were immediately dissolved in glacial acetic acid to produce the desired concentration.
Samarium dipivaloylmethide

Samarium dipivaloylmethide was prepared by the method described for erbium dipivaloylmethide. Sublimation of the product gave a white powder, melting point, 188-91° (uncorrected). Decomposition during the sublimation was troublesome.

Toluene

Toluene (Reagent Grade, Baker and Adamson) was used without further purification.

Other Chemicals

Other chemicals used for the filter systems and analytical procedures were Reagent Grade, and were used without further purification.

Apparatus

Photochemical reactor

A new type of photochemical reactor was designed and constructed which employed the use of mirrors in the optical system. A previously existing reactor\textsuperscript{12} was used for the preliminary work in this investigation. It consisted of a mercury arc lamp, the light from which was collimated by a thick plano-convex quartz lens. The collimated beam, after
passing through the reactor, was focused on a thermopile by a lens identical to the one mentioned. The lenses formed the windows of a constant temperature bath, which contained the holders for the filters and reaction cell.

Features which were designed and achieved in the new reactor that made it superior to the old one were: (1) increased light intensity (approximately twice that of the old reactor using the same type lamp), (2) more uniform cross-section of the collimated light beam, (3) the length of the collimated beam easily varied, (4) a wider spectral range, (5) adjustment of optical system with lamp in operation, (6) exact alignment of all units in the system, (7) complete protective shielding for the optical system and lamp, and (8) light scattering reduced to a minimum.

Suggestions and ideas for the design of the photochemical reactor were obtained from several sources. The arrangement of the components used in the photochemical reactor is shown in Figure 1. The basic simplicity of the system is immediately evident.

The light source was a Westinghouse (SAH 800-C) 800 watt short arc, medium pressure, mercury lamp. The spectral

\[ \text{References} \]


distribution of relative energy\textsuperscript{25} (in arbitrary units) contains maxima at: 5500-6000 A. (60), 4000-4500 A. (25), 3600-3800 A. (60), and 3000-3200 A. (25). No data were given for lower wavelengths. The advantages of this lamp over other high intensity lamps are: a short arc length (8 mm.) for focusing, no cooling equipment required, long lifetime of lamps (rated at 500 hours), and no expensive starting equipment needed (a tesla coil is sufficient).

The collecting mirror was a spherical, 2.5 inch diameter mirror with a focal length of 1.5 inches, and was placed three inches from the lamp. Light intensities are increased up to 50\% through the use of a collecting mirror.

The collimating and focusing mirrors were identical off-axis parabolic mirrors, 4 inches in diameter, focal length of 5 inches, and an off-axis angle of 34°. The circle of confusion tolerance was 0.010 inches. The lamp and the thermopile were placed at the focal points of these mirrors.

All three of the mirrors were constructed\textsuperscript{26} from fused quartz, surfaced with aluminum, and overcoated with SiO. The thermopile (Eppley Laboratories, Newport, R. I.) was a single junction, constantan-manganin element with a circular


\textsuperscript{26}The mirrors were specially made by J. Unertl Optical Co., 3551 East St., Pittsburgh, Pa.
Figure 1. Schematic diagram of photochemical reactor

(a) Mercury arc lamp
(b) Collecting mirror
(c) Collimating mirror
(d) Water cell
(e) Filter cell
(f) Glass filter
(g) Light stop
(h) Reaction cell
(i) Focusing mirror
(j) Thermopile
receiver 1/8 inch in diameter. The sensitivity was calibrated to be 0.0054 microvolts per microwatt per cm². The thermopile case was water jacketed to prevent heating of the cold junction. It was specially made for high radiation intensities up to 2 watts per cm², which corresponds to $3 \times 10^{17}$ quanta per sec. at 3660 Å. Output from the thermopile was determined by a portable potentiometer (Rubicon No. 2732, Rubicon Co., Philadelphia, Pa.) with a range of 0 to 161 millivolts.

Accessory equipment for the lamp were an inductive ballast (No. 1301, Nothelfer Winding Laboratories, Trenton, N. J.), and a voltage regulator (Model IE 205, Superior Electric Co., Bristol, Conn.). Optimum operating conditions for the lamp were 70 volts at 11.8 amperes furnished by the ballast. A tesla coil was used to start the lamp, with an open circuit potential of 150 volts on the lamp.

Alignment and support for all the components of the reactor were accomplished by the construction of a lathe bed type optical bench. Two steel channels 100 cm. in length, were spaced 4 inches apart with the arms of the beams positioned to form a cavity between them. They were then welded together by cross members. Two 1 inch square steel rails

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27The thermopile was calibrated by Eppley Laboratories with a lamp calibrated by the National Bureau of Standards.
were welded to the tops of the arms of the beams spaced three inches apart. One rail was cut in the form of an inverted V on a large Planer, and the other rail was milled flat. The optical bench was supported by three leveling screws, and the whole assembly rested on two concrete pillars, which were one foot in diameter and stood three feet high.

The design of the optical bench permitted commercial carriages (Nos. S1230R, S1230L, and S1231, Gaertner Scientific Corp., Chicago, Ill.) to be used to support holders for the components placed in the light path. The cavity formed by the channels allowed for easy adjustment of the carriages from below.

The large mirrors were placed in cylindrical holders, cut, and bored to fit. Felt pads surrounded the mirrors to prevent any stress from the cylinder on the mirror. Three plungers in the rear of the holder provided for the correct positioning of the mirror, while clips attached to the outer surface of the holder kept the mirror in place. Two horizontal pivot screws held the cylindrical holder to a vertical plate, and the holder was spring loaded against the plate. This allowed for centering of the holder with the pivot screws, and angular adjustment in the vertical plane. The vertical plate was mounted on a cylindrical steel plunger, 2 inches in diameter, which fit into a specially constructed carriage. This was arranged in a manner such that the face
of the mirror was centered over the axis of rotation of the plunger. Angular rotation in the horizontal plane was accomplished by this arrangement. The plunger could be raised or lowered by a screw from under the carriage.

Also attached to the mirror carriage was a steel plate that extended out from the carriage and furnished support for the lamp at the collimating mirror end and the thermopile at the focusing end. This plate could be rotated, and the axis of rotation coincided with the axis of rotation of the plunger. On the plate, at the appropriate distance, was placed a double dovetail slide, which supported the mount for the lamp or thermopile, as the case might be.

The design of the mirror mount, carriage, and base plate, permitted the optical system to be mounted on two carriages, and made for easy focusing of the off-axis optics.

The support for the light source also served as support for the collecting mirror. Vertical adjustments for these components were possible.

A protective box, constructed of steel, surrounded the light source, collecting mirror, and collimating mirror. The box was silver soldered to the steel platform extending from the carriage. It was designed so that none of the vital adjustments mentioned were eliminated. This was accomplished by means of sliding doors and knobs extending through the shield. The box was rendered light tight, except for a
ventilation hole in the bottom, and a chimney on top to dissipate heat.

A total of 22 adjustments were necessary to focus the optical system. The large mirrors were centered in their holders, so that a vertical center line tangent to the face of the mirror was in line with the axis of rotation of the plunger in the carriage. This was accomplished by means of a height gage and the table of a Mill. The components were placed at the correct height above the optical bench with the height gage. Premarked center lines on the carriages aided in making crude adjustments. Visual focusing of the optical system proved to be very helpful. Final adjustments were made with the lamp in operation, and the thermopile at its maximum reading.

Two V blocks were designed to hold the filter cells, glass filters, and reaction cells. One was constructed to hold cells four inches in diameter, and the other to hold cells 2-1/2 inches in diameter. The V blocks were made of aluminum, and held in place by a 19 mm. rod extending from the bottom and fitting into the commercial carriages. Adjustments were made with a collar on the rod and a set-screw on the carriage.

The cell holders that fit into the V blocks were made from brass cylinders which were bored, threaded, and faced on the outside. A metal retaining ring screwed into the holder enabling cells of different thickness to be accom-
modated. Flanges extended from the sides of the holders, allowing the holder to be fastened into the V block with screws.

A holder for glass filters was designed to fit into the large V block. It was furnished with a spring loaded slide that could accommodate filters of different thickness.

The entire collimated light beam was enclosed by a tube except where the V blocks were located. This tube enclosed the focusing mirror, and contained a hole to allow the light beam to strike the thermopile which was not covered. All parts that were in the light path were anodized, black nickel plated, or painted a dull black to minimize light scattering. The entire unit was very compact, occupying a space 4 feet by 2 feet.

Figure 2 shows the reactor from the side as seen by the operator. Figure 3 is a top view of the lamp housing (with the top removed) showing the collecting mirror, lamp, and collimating mirror.

Photolysis cells

Two types of cells\(^{28}\) were designed for the photochemical reactor. Both types were constructed of fused quartz with optically flat faces.

\(^{28}\)The cells were specially constructed by Thermal American Fused Quartz Co., 18-20 Salem St., Dover, N. J.
Figure 2. Side view of photochemical reactor

The lamp housing is on the left, the reaction cell in the middle, and the thermopile on the right.
Figure 3. Top view of lamp housing

The top of the lamp housing has been removed exposing the lamp, collecting mirror, and collimating mirror.
One type of cell was 10 cm. in diameter, and was 2 cm. thick. Two outlet tubes were provided, separated by an angle of 90°. These cells were used for the water cell and filter solutions. They could be employed as reaction cells when higher light intensities were desirable, and degassing was not necessary.

The other type of cell, hereafter designated the reaction cell, had more critical specifications. Degassing of the reaction cell was a prerequisite in many experiments. A smaller optical face was necessary to withstand the stresses created during degassing procedures, but at the same time, sufficient volume was desired for the various analyses which were performed on the photolyzed solutions. These requirements were met by a cell 64 mm. in diameter and 25 mm. thick. It was attached to a manifold tube by means of two outlet tubes. The manifold was situated approximately one inch from the cell and was parallel to a tangent of the cylindrical cell. The two ends of the manifold terminated in quartz to Pyrex seals. One end was connected to a degassing tube made of Pyrex, and the other end served as the outlet.

Filter Systems

Several filter systems\(^{29}\) have been found to be adequate

for this photochemical reactor. A water cell was placed in front of the filter cell to remove infrared radiation. An increase in the temperature changed the absorption spectra of some of the filter solutions; therefore, a stream of air was directed on the face of the cell. Some of the solutions deteriorated in the light beam, and thus a flow system was necessary for these systems.

The flow system consisted of a reservoir (7 liter capacity), which was gravity fed through an inlet tube to the bottom of the four inch diameter cell. The photolyzed solution was siphoned from the top and drained into a bucket. The flow rate was controlled by a needle valve at the drainage end. Flow rates of 300-500 ml. per hour were usually required to stabilize the thermopile reading.

The filter system with a maximum at 3660 A. was mainly used in this investigation. A 2.0 cm. solution of copper sulfate pentahydrate in water (400 g. per liter), and a Corning filter 7-51 (5970) constituted the system. The half-height width of the transmission band was 500 A. The mercury emission line at 3130 A. was completely excluded as shown in Figure 4. Except for this region, the system absorbs light from 2000 A. to 7000 A. Corning filters 7-60 and 7-37 gave a narrower band width with a corresponding lower light intensity.

The system with a transmission maximum at 3130 A. con-
Figure 4. Filter system for 3660 Å.

- Corning filter 7-51 (5970)
- CuSO$_4$·5H$_2$O (400 g. per liter), 2 cm. layer

Filter system

/// Relative light energy from the mercury arc lamp

---

Figure 5. Filter system for 3130 Å.

- Potassium acid phthalate (2.5 g. per liter), 2 cm. layer
- NiSO$_4$·6H$_2$O (690 g. per liter), and CoSO$_4$·7H$_2$O (220 g. per liter), 2 cm. layer

Filter system

/// Relative light energy from the mercury arc lamp
sisted of a 2.0 cm. solution of nickel sulfate hexahydrate (690 g. per liter) and cobaltous sulfate heptahydrate (220 g. per liter) in water, and a solution of potassium acid phthalate in water (2.5 g. per liter) in a 2.0 cm. layer. A flow system was necessary for the potassium acid phthalate. The half-height width of the band was 300 A. as shown in Figure 5, and the mercury emission line at 3660 A. was completely excluded. Small transmission maxima existed at 5750 A. (14%), and 9000 A. (32%). The light from these two regions did not affect the actinometer.

Two systems of minor importance in this investigation, but of potential value in the future had transmission maxima located at 4200 A. and 2650 A. The system at 4200 A. consisted of potassium permanganate in water (0.21 g. per liter) in a 2.0 cm. layer (see Figure 6). Troublesome transmission maxima exist at lower and higher wavelengths. These can be eliminated by any one of several glass filters. The system at 2650 A. consisted of potassium permanganate in water (0.21 g. per liter) in a 2.0 cm. layer, and nickel sulfate hexahydrate in water (400 g. per liter) in a 2.0 cm. layer (see Figure 7). A transmission maximum exists at 4750 A. It can be eliminated with a Corning filter 7-54, but at the price of reduced transmission at 2650 A. A flow system was necessary for the potassium permanganate solution in both of these systems.
Figure 6. Filter system for 4200 A.
- Potassium permanganate (0.21 g. per liter), 2 cm. layer

/// Relative light energy from the mercury arc lamp

Figure 7. Filter system for 2650 A.
- Potassium permanganate (0.21 g. per liter), 2 cm. layer
- NiSO$_4$·6H$_2$O (400 g. per liter), 2 cm. layer
- Filter system
Reagent Grade chemicals were used for the preparation of all filter solutions, and the solutions were changed periodically. Spectrophotometric analysis was used to determine when solutions were deteriorating.

**Actinometry**

Actinometry has always been troublesome to quantitative photochemistry. No new method was developed in this investigation, but a technique long employed in vapor phase photochemistry was adapted to solution photochemistry. This method involves the use of a secondary actinometer, whose absorption characteristics closely resemble those of the system studied.

Uranyl oxalate\(^{30}\), the primary actinometer, gave very consistent rate data, but complete absorption of the useful light was not obtained with the cells used, and absorption corrections were necessary. These corrections were calculated from the thermopile readings for incident light and residual light. A ratio of the difference between these two readings for the unknown solution and the actinometer gave the correction factor. This ratio approached 2.5 for the comparison of benzophenone and uranyl oxalate absorptions. It should be mentioned at this point that thermopile readings intro-

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duced errors of 10% or more. This was apparently due to variations in the characteristics of the lamp (i.e., movement of the arc over the electrode surfaces). These variations gave no overall change in the light intensity, as indicated by the consistent rates obtained for uranyl oxalate decomposition; but this made the corresponding thermopile readings very erratic. It was decided that a different method of actinometry was necessary.

It was fortunate that Pitts, et al., were studying the photoreduction of benzophenone in isopropanol at this time. Employing uranyl oxalate as an actinometer, they found that the quantum yield for this system was approximately one. They also found that the quantum yield was dependent upon the amount of oxygen present. The mechanism for this reaction has been mentioned previously.

A quantum yield of one for benzophenone in isopropanol was verified in the following experiments. The quantum yield of benzophenone in toluene based on the benzophenone-isopropanol actinometer was equal to the quantum yield based on the uranyl oxalate actinometer. The same relationship was found to be true for the benzophenone-cumene system.

However, the rate of benzophenone disappearance was found to be the same in the presence or absence of oxygen. This was in apparent disagreement with Pitts, et al. Upon closer scrutiny, it can be rationalized that, because
of the much higher light intensities employed in this investigation, oxygen effects became negligible. The justification for this statement is evident in the mechanism presented in the Discussion. Also, the higher concentration of radicals favored radical combination, rather than the hydrogen transfer step (7) proposed by them. The rate of the reaction seemed to decrease with higher conversions. This was attributed to insufficient stirring of the photolyzed solutions.

Although benzophenone-isopropanol is not an ideal actinometer, no absorption corrections were necessary, and the consistency of resulting quantum yield determinations seemed to justify its application.

The amount of benzophenone photolyzed was determined spectrophotometrically with a Beckman DU Spectrophotometer. The absorbance was measured between 3600 A. and 3400 A. at intervals of 50 A. The un photolyzed solution was used as the standard, and its absorbance was measured at the same time as the photolyzed solution. This procedure eliminated errors in the wavelength setting and small errors in the concentration of the solutions. This method was accurate to one percent at sufficient conversion of benzophenone.
Analytical Procedures

Product analysis for benzophenone-cumene system

Preliminary to any definitive study of a reaction mechanism, it is desirable to account for all the reactants in terms of products. Since this had not been done for the photoreduction of benzophenone in cumene, such a study was initiated. The results of the product analysis parallel those found by Baker\textsuperscript{12}, and probably form a general pattern for the photoreduction of benzophenone in aromatic hydrocarbons.

Solutions of benzophenone (0.5 M; 1.0 M; and saturated) in cumene were prepared, and placed in Pyrex tubes. The tubes were degassed\textsuperscript{31} three times to a pressure of $10^{-3}$ mm. and sealed. The tubes were placed in the sunlight for more than a month (during the summer). White crystals began ap-

\textsuperscript{31}The degassing procedure consisted of cooling the solution until the vapor pressure was very low. Liquid nitrogen or dry ice-isopropanol solutions were ordinarily used for cooling. It was found desirable not to freeze the solution to be degassed, since this often resulted in shattering of the tube. The tube was connected to a high velocity vacuum system by means of a stopcock. The tube containing the cold solution was evacuated and then the stopcock was closed. The solution was then allowed to warm to room temperature. After the solution equilibrated with the surroundings, it was again cooled, the stopcock was opened, the tube was evacuated, the stopcock was closed, and the solution was warmed. This was repeated (usually three times was sufficient) until two successive cycles produced little pressure change in the tube.
pearing after the tubes had been outside for a week.

The tube containing the photolyzed solution was opened, the contents were placed in a distilling flask, and the solvent was removed under reduced pressure. The residue was mixed with ligroin (b.p. 60-70°), and allowed to stand overnight. The precipitate that formed was removed by filtration through a fritted crucible, dried and weighed. It was easily identified as benzpinacol with melting point of 186° (dec.). The ligroin was removed by evaporation to leave a viscous, pleasant smelling oil. An infrared spectrum of the oil indicated a hydroxyl band at 3600 cm.$^{-1}$. The addition of methanol to this oil caused the formation of a white precipitate, melting point, 117-118°. The infrared spectrum showed no hydroxyl band, but indicated a gem-dimethyl band at 1370 cm.$^{-1}$. It was identified as 1,2-dimethyl-1,2-diphenylbutane, melting point, 115°. This compound would result from the combination of two dimethylphenylmethyl radicals.

The remaining oil was now assumed to be 1,1,2-triphenyl-2-methyl-1-propanol, which would form from the combination of a dimethylphenylmethyl radical and a diphenylhydroxymethyl radical. It was not possible to prove the structure of the oil at that time, since complete removal of the hydrocarbon

had not been accomplished. Although several solvents were tried in an attempt to separate the compounds by crystallization, it was necessary to resort to chromatography. The hydrocarbon came through after a few fractions of ligroin had passed through an alumina column. Diethyl ether eluted the remaining oil. Complete and quantitative separation of the two components was accomplished in this manner.

Infrared spectra of the oil showed a strong hydroxyl band at 3600 cm.\(^{-1}\), and gem-dimethyl bands at 1360-1380 cm.\(^{-1}\). The proposed tertiary alcohol had never been prepared, and an attempt to purify the oil by distillation resulted in decomposition. After standing for several months, the oil began to crystallize. It was then possible to recrystallize the compound from ethanol by seeding. The compound was a pleasant smelling white solid, melting point, 62° (uncorrected). Calculated for \(\text{C}_{22}\text{H}_{21}\text{O}\): C, 87.6; H, 7.3. Found: C, 88.0; H, 7.49. The photochemical reaction provides a method for synthesizing hindered tertiary alcohols which are difficult to prepare by other methods\(^{33}\).

A lead tetraacetate oxidation was performed on one of the photolyzed solutions to determine the amount of benz-

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pinacol present. More lead tetraacetate was consumed than was indicated by the gravimetric analysis of benzpinacol. Upon examination, it was found that both cumene and 1,1,2-triphenyl-2-methyl-1-propanol reacted with lead tetraacetate. The reaction with cumene was no surprise, but the oxidation of a tertiary alcohol was quite novel.

An investigation of the reaction between lead tetraacetate and 1,1,2-triphenyl-2-methyl-1-propanol showed that the oxidation was quantitative, and followed second order kinetics. Infrared spectra of the products indicated an ester band at 1730 cm\(^{-1}\), a carbonyl band at 1660 cm\(^{-1}\), and gem-dimethyl bands at 1360-1380 cm\(^{-1}\). Benzophenone was identified as the ketone by the formation of the 2,4-dinitrophenylhydrazone (m.p. 240-242°), and determined quantitatively by spectrophotometric analysis. The other product was identified as \(\alpha\)-cumylacetate by comparison of the infrared spectra with a known sample of the acetate.

\(^{34}\)Benzpinacol was oxidized quantitatively to benzophenone by lead tetraacetate in glacial acetic acid\(^{12,35}\). The excess lead tetraacetate was reduced with potassium iodide, and the iodine liberated was titrated with sodium thiosulfate. The standard iodiometric titration was complicated by the formation of lead iodide (yellow precipitate). Also, a clean end-point was difficult to obtain because of the resulting two phase mixture (iodine was absorbed by the organic layer). The formation of lead iodide was prevented by the addition of excess sodium acetate, and, near the end-point, excess potassium iodide was added to form the \(I_3^-\) complex ion in the aqueous layer.

\(^{35}\)R. Criegee, Ber., 64B, 264 (1931).
$\text{d-Cumylacetate was prepared by the esterification of dimethylcarbinol with acetic anhydride. The oxidation of 1,1,2-triphenyl-2-methyl-1-propanol by lead tetraacetate is shown in the following equation.}$

$$\text{Pb(OAc)}_4 + (\text{C}_6\text{H}_5)_2\text{C-C(C}_6\text{H}_5)\text{CH}_3 \rightarrow (\text{C}_6\text{H}_5)_2\text{CO} + (\text{C}_6\text{H}_5)\text{C-0Ac} + \text{CH}_3\text{Pb(OAc)}_2 + 2\text{HOAC}$$

Mosher and Neidig\textsuperscript{36} found that benzpinacolyl alcohol was oxidized by lead tetraacetate to give triphenylcarbinol and benzaldehyde. The reaction was neither quantitative nor simple, since elimination reactions competed. This was the only analogous reaction found in the literature.

Incorporating this reaction into the analytical procedure, the following scheme was used to analyze most of the sunlight reactions: (1) removal of the cumene by distillation at reduced pressure to leave a residue of benzpinacol, 1,2-dimethyl-1,2-diphenylbutane, and 1,1,2-triphenyl-2-methyl-1-propanol, (2) extraction of residue with ligroin to precipitate the benzpinacol, (3) gravimetric determination of the benzpinacol, (4) complete removal of ligroin by distillation under reduced pressure, (5) gravimetric determination of the residue, (6) dilution of the residue to a known volume

\textsuperscript{36}W. A. Mosher and H. A. Neidig, \textit{J. Am. Chem. Soc.}, 72, 4452 (1950).
with ligroin, (7) spectrophotometric analysis on an aliquot from (6) for residual benzophenone, (8) titration of an aliquot from (6) by lead tetraacetate for determination of the tertiary alcohol, and (9) chromatographic separation of an aliquot from (6) for gravimetric determination of the tertiary alcohol and the hydrocarbon. Although not every step was followed in the analyses, usually a sufficient combination of steps were used to determine all the quantities. Table 1 shows the results obtained in the sunlight reactions. It should be mentioned that no evidence was found for disproportionation. The results indicated that the radicals show no preference in combination and that statistical distribution is observed (i.e., half of the radicals combine with like radicals, and half combine with different radicals).

No cage effect was observed. This would be an ideal situation for a cage effect, since two radicals are formed in a solvent cage, and might be expected to combine before diffusion occurred. It is possible that an unobservable cage effect could occur in which the radicals re-exchange the hydrogen atom and return to their original form. This would account for a quantum yield of less than one.

**Quantitative analysis of benzophenone-cumene solutions**

It was necessary to modify the procedure used for the product analysis, so that routine analysis of photolyzed
Table 1. Product analysis for sunlight reactions of benzophenone and cumene

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Concentration of Benzophenone</th>
<th>0.5 M</th>
<th>0.5 M</th>
<th>1.0 M</th>
<th>Sat'd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzpinacol</td>
<td>3</td>
<td></td>
<td>12.1 mmol</td>
<td>12.7 mmol</td>
<td>24.3 mmol</td>
<td>35.4</td>
</tr>
<tr>
<td>1,2-dimethyl-1,2-diphenyl butane</td>
<td>9</td>
<td></td>
<td>12.1 mmol</td>
<td>12.7 mmol</td>
<td>---</td>
<td>31.7</td>
</tr>
<tr>
<td>1,1,2-Triphenyl 2-methyl-1-propanol</td>
<td>8</td>
<td></td>
<td>30.0 mmol</td>
<td>---</td>
<td>24.3 mmol</td>
<td>---</td>
</tr>
<tr>
<td>1,1,2-Triphenyl 2-methyl-1-propanol</td>
<td>9</td>
<td></td>
<td>28.7 mmol</td>
<td>---</td>
<td>48.7 mmol</td>
<td>---</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>7</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>---</td>
</tr>
<tr>
<td>Benzophenone used</td>
<td></td>
<td></td>
<td>53. mmol</td>
<td>50.7 mmol</td>
<td>100 mmol</td>
<td>---</td>
</tr>
</tbody>
</table>

| Ratio benzpinacol/benzophenone | 0.23 | 0.25 | 0.24 | 0.18^a |

^aAmount of benzophenone used was estimated from the products.
solutions could be performed.

The photolyzed solution was divided into aliquot portions. One aliquot was used to determine the amount of benzophenone spectrophotometrically. Another aliquot was distilled under reduced pressure to remove the cumene. The residue was dissolved in benzene and diluted to 100 ml. with benzene. Aliquots were taken from this solution for a lead tetraacetate oxidation. From these two determinations, all the quantities could be calculated using two equations and two unknowns.

\[ X \text{ (moles alcohol)} + Y \text{ (moles pinacol)} = \text{Moles from lead tetraacetate oxidation} \]

\[ X + 2Y = \text{Moles of benzophenone photolyzed} \]

An alternate procedure was to dissolve the residue from the first distillation in ligroin, precipitate the benzpinacol, and determine it gravimetrically. Then the ligroin solution was diluted to a known volume, and aliquots were taken for the lead tetraacetate determination of alcohol present.

Quantitative analysis of benzophenone in other systems

Benzophenone was always determined spectrophotometrically. Benzpinacol was determined by the lead tetraacetate oxidation if the solution was free of interfering substances,
or gravimetrically if sufficient conversion of benzophenone was achieved.
RESULTS

General

The original plan of investigation was to continue the type of program begun by Baker\textsuperscript{12} concerning the photoreduction of benzophenone in various hydrogen donors. The logical step from the investigation of toluene was to proceed to cumene, which is known to be a better hydrogen donor in free radical reactions. From the work done by Baker, several facts were evident: (1) slight temperature changes did not affect the quantum yields, (2) a change in wavelength from 3660 Å to 3130 Å produced a small but measurable decrease in the quantum yield of benzophenone, (3) quantum yield dependence on light intensity was small, (4) quantum yield dependence on concentration of benzophenone was small, (5) quantum yield dependence on concentration of hydrogen donor was measurable and corresponded to a proposed rate law, and (6) different hydrogen donors gave different limiting quantum yields. These are the variables which were thought to make the photochemical study possible. The first four variables are very important in the study of vapor phase photochemistry, but offered slight aid for this investigation. Left were variables (5) and (6) as the methods available for probing the photochemical reaction.

Although a product analysis, quantitative determination
of products and reactants, and quantum yield studies were performed on the benzophenone-cumene system, other variables were found which proved to be more fruitful. Since no systematic method existed for a photochemical study in solution, the investigative pathways were not always well marked.

More consistent rate data were possible after an examination was made on the temperature increase produced in the filter solutions and the reaction solution in the absence of a constant temperature bath. It was found that in one hour the temperature of a nickel sulfate solution increased: 30° when placed directly in the light path; 20° when a water cell was placed in front of the solution; and only 10° when the solution cell was cooled by a stream of air. The reaction cell containing benzophenone in toluene had a temperature increase of 3° over a two hour period when placed in the path of filtered light. Temperature measurements were made with an iron-constantan thermocouple. It was concluded that a water bath was not necessary for cooling of the various cells, but that air cooling of the filter solution was desirable. This eliminated corrections for light absorbed by the water bath.

The sequence of cells was; (1) a water cell, 2.0 cm. thick, (2) one or more filter solution cells, 2.0 cm. thick, (3) a glass filter, (4) a light stop with hole of desired diameter, and (5) the reaction cell.
Benzophenone-Toluene System

Baker\textsuperscript{12}, in his study of the photoreduction of benzophenone by toluene, was not able to remove oxygen from the system. The validity of corrections for light intensity were also in doubt. When new cells were perfected, several runs were made to determine the quantum yield of benzophenone in toluene. The data are presented in Table 2.

The result obtained in the run with a degassed solution confirms the assumption made by Baker that oxygen effects were overcome by sufficient conversion of benzophenone (approximately 20\%). Baker found the quantum yield to be 0.35 for 0.1 M benzophenone in toluene at 3660 A. The quantum yield under the same conditions was found (Table 2) to be 0.39. This small difference is attributed to the method of correcting for light absorbed by the water bath. At 3130 A., Baker found the quantum yield to be 0.21. The quantum yield under the same conditions was found to be 0.35 (Table 2). This discrepancy is attributed to the inadequate filter system employed by Baker. He used nickel sulfate and copper sulfate for the filter system. A transmission band occurs at 5000 A., for that system which is stronger than the band at 3130 A. Uranyl oxalate absorbs light to beyond 5000 A., and has a quantum yield of 0.4 at this wavelength. Therefore the available light for benzophenone would be much less than indicated by the actinometer, and would give low values.
Table 2. Photoreduction of benzophenone in toluene

<table>
<thead>
<tr>
<th>Filter system wavelength maximum</th>
<th>Initial concentration benzophenone (molarity)</th>
<th>Percent conversion of benzophenone</th>
<th>Light intensity absorbed quanta/sec. (x 10^{-17})</th>
<th>Quantum yield benzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>3660 A.</td>
<td>0.10</td>
<td>33.2</td>
<td>3.5</td>
<td>0.39^a</td>
</tr>
<tr>
<td>3660 A.</td>
<td>0.10</td>
<td>70.2</td>
<td>4.0</td>
<td>0.40^a</td>
</tr>
<tr>
<td>3660 A.</td>
<td>0.10</td>
<td>41.7</td>
<td>1.1</td>
<td>0.40^a</td>
</tr>
<tr>
<td>3660 A.</td>
<td>0.10</td>
<td>24.3</td>
<td>4.3</td>
<td>0.38^a</td>
</tr>
<tr>
<td>3660 A.</td>
<td>0.10</td>
<td>26.6</td>
<td>4.3</td>
<td>0.38^a</td>
</tr>
<tr>
<td>3660 A.</td>
<td>0.10</td>
<td>21.6</td>
<td>2.3</td>
<td>0.36^a</td>
</tr>
<tr>
<td>3130 A.</td>
<td>0.10</td>
<td>34.6</td>
<td>1.3</td>
<td>0.35^a</td>
</tr>
<tr>
<td>3130 A.</td>
<td>0.10</td>
<td>21.4</td>
<td>1.3</td>
<td>0.35^a</td>
</tr>
<tr>
<td>3130 A.</td>
<td>0.10</td>
<td>38.2</td>
<td>1.5</td>
<td>0.36^a</td>
</tr>
<tr>
<td>3130 A.</td>
<td>0.050</td>
<td>20.3</td>
<td>1.5</td>
<td>0.33^a</td>
</tr>
<tr>
<td>3130 A.</td>
<td>0.050</td>
<td>18.9</td>
<td>1.5</td>
<td>0.36^a</td>
</tr>
</tbody>
</table>

^aBased on uranyl oxalate.

^bBased on benzophenone-isopropanol system.

^cSolution was degassed.

Benzophenone-Cumene System

Results found for the photoreduction of benzophenone in cumene are given in Table 3. The system was very analogous to the benzophenone-toluene system, and only confirmed the mechanism proposed by Baker^12 for that system. The effect
Table 3. Photoreduction of 0.1 M benzophenone in cumene with light of 3660 A.

<table>
<thead>
<tr>
<th>Percent conversion of benzophenone</th>
<th>Light intensity absorbed quanta/sec. (x 10^-17)</th>
<th>Quantum yield benzophenone</th>
<th>Ratio of benzpinacol to benzophenone</th>
<th>Ratio of alcohol to benzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.4</td>
<td>3.4</td>
<td>.22^b</td>
<td>.18</td>
<td>.64</td>
</tr>
<tr>
<td>28.2</td>
<td>3.4</td>
<td>.19^b</td>
<td>.22</td>
<td>.56</td>
</tr>
<tr>
<td>15.1^c</td>
<td>2.4</td>
<td>.21^b</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>89.3^c</td>
<td>2.3</td>
<td>.74^b</td>
<td>.23</td>
<td>--</td>
</tr>
<tr>
<td>48.2^c</td>
<td>2.3</td>
<td>.69^b</td>
<td>.23</td>
<td>.55</td>
</tr>
<tr>
<td>19.3^c</td>
<td>4.3</td>
<td>.70^d</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

^a1,1,2-triphenyl-2-methyl-1-propanol.

^bQuantum yield was calculated with uranyl oxalate actinometer.

^cSolution was degassed.

^dQuantum yield was calculated with benzophenone-isopropanol actinometer.

Of oxygen in the benzophenone-cumene system has not been explained. The cumene used for the degassed runs was different than that used for the air runs, which was unfortunate. The low quantum yield in the presence of air could be attributed to: impurities in the cumene; oxidation of the cumene; or efficient quenching by oxygen. The low quantum yield of the one degassed run could be attributed to a leak in the tube after degassing, or to impure cumene.
The photoreduction of benzophenone in alcohols was not originally meant to be included in this investigation, but circumstances caused a change in the program.

The use of the photoreduction of benzophenone in isopropanol as an actinometer has been discussed. Table 4 shows the results for the rate of disappearance of benzophenone. For all the runs listed, the amount of light absorbed was approximately the same. Different reaction cells were used, and different amounts of benzophenone were photolyzed. The only correlation seemed to be that the rate decreased as the percent conversion of benzophenone increased. Since the solutions were not stirred, depletion of benzophenone and relatively large concentrations of product near the cell face would account for the decrease in rate. Although the average rate was $629 \times 10^{-6}$ mole liter$^{-1}$ min.$^{-1}$, the value chosen for actinometry was $640 \times 10^{-6}$ mole liter$^{-1}$ min.$^{-1}$ since the largest cluster of points surrounded that point. Special attention should be given to the lack of correlation between degassed solutions and air solutions.

The precision in the rate data is not as good as would be desired for an actinometer, but since no correction was needed for the difference in light absorbed, the accuracy of the method was superior to the uranyl oxalate actinometer.

The lead tetraacetate assay$^{34}$ for determination of benz-
Table 4. Photoreduction of 0.1 M benzophenone in isopropanol at 3660 A.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Percent conversion benzophenone</th>
<th>Relative absorbance&lt;sup&gt;a&lt;/sup&gt; (thermopile)</th>
<th>Rate of benzophenone&lt;sup&gt;b&lt;/sup&gt; (mol. 1. (^{-1}) min(^{-1}) x 10^6)</th>
<th>Ratio benzpinacol to benzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>19.7</td>
<td>31</td>
<td>655</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>21.6</td>
<td>34</td>
<td>617</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>20.4</td>
<td>28</td>
<td>600</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>20.5</td>
<td>29</td>
<td>640&lt;sup&gt;c&lt;/sup&gt;</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>20.0</td>
<td>29</td>
<td>645</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>20.5</td>
<td>28</td>
<td>640</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>35.4</td>
<td>23</td>
<td>553</td>
<td>--</td>
</tr>
<tr>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>47.6</td>
<td>26</td>
<td>535</td>
<td>.35</td>
</tr>
<tr>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>39.9</td>
<td>26</td>
<td>713</td>
<td>.39</td>
</tr>
<tr>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>20.0</td>
<td>27</td>
<td>633</td>
<td>.31</td>
</tr>
<tr>
<td>3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>23.1</td>
<td>26</td>
<td>762</td>
<td>--</td>
</tr>
<tr>
<td>4&lt;sup&gt;d&lt;/sup&gt;</td>
<td>22.6</td>
<td>27</td>
<td>754</td>
<td>.32</td>
</tr>
<tr>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>36.6</td>
<td>26</td>
<td>585</td>
<td>.39</td>
</tr>
<tr>
<td>4&lt;sup&gt;d&lt;/sup&gt;</td>
<td>33.6</td>
<td>28</td>
<td>620</td>
<td>.39</td>
</tr>
</tbody>
</table>

<sup>a</sup>Difference between incident light reading and residual light reading on the thermopile.

<sup>b</sup>Benzpinacol was determined gravimetrically.

<sup>c</sup>Rate corresponds to 4.3 x 10\(^{17}\) quanta per sec. assuming the quantum yield is one.

<sup>d</sup>Solution was degassed.
pinacol was not successful in benzophenone-isopropanol system; therefore, when benzpinacol was determined, it was done gravimetrically. Formation of hydrogen peroxide in the air solutions could have been the source of difficulty in the lead tetraacetate oxidation. Also, if some mixed pinacol were formed, it would react with lead tetraacetate. The ratio of benzpinacol formed to benzophenone used never exceeded .40 (the theoretical ratio is .50). The indication that some diphenylhydroxymethyl radicals are not dimerizing was given by one complete analysis. A lead tetraacetate assay on that sample gave a benzpinacol to benzophenone ratio of 0.56, and the gravimetric analysis gave 0.39. Since that sample was degassed, the difference could not be attributed to hydrogen peroxide. The other possibility for termination of radicals would be diphenylhydroxymethyl radicals reacting with dimethylhydroxymethyl radicals. The combination of these two radicals has not been confirmed, but at the high light intensities employed, the coupling would be feasible and might compete with the reaction between benzophenone and dimethylhydroxymethyl radicals, which has been proposed\(^19\).

If the cell containing benzophenone in isopropanol were transferred to the spectrophotometer immediately after photolysis, the disappearance of an absorbing intermediate at 3900 A. could be followed. The rate of disappearance was second order. The intermediate did not decompose in de-
gassed solutions until they were exposed to air. These ob-
ervations confirm the results of Pitts, et al., who sug-
gested that the intermediate might be the free radical
\((C_6H_5)_2OC(OH)(C_6H_5)_2\).

Benzophenone-Benzhydrol System

From the investigation of the photoreduction of benzop-
phenone in toluene and cumene, the chemistry of the reac-
tion appeared to be straightforward and offered no new in-
formation as to the actual mechanism of the hydrogen abstrac-
tion process. Although the oxidation processes and the
formation of the intermediate in isopropanol are not elu-
cidated, they must follow the primary act and will not
contribute to the interpretation of it.

Examination of the photoreduction of benzophenone in
benzhydrol was initiated with the purpose of reducing the
chemistry of the reaction to a minimum. Oxygen was still
expected to be a nuisance, but all radicals should terminate
with the formation of benzpinacol.

During a brief survey of the benzophenone-benzhydrol
system in benzene, the quantum yield was found to vary over
a wide range while the concentration of benzhydrol varied
from zero to 1.0 M. Benzene is inert as a hydrogen donor.
Since the concentration of benzhydrol was kept low, the
concentration of benzene could be considered approximately
constant. Benzhydrol was the most efficient hydrogen donor tested, and further investigation was deemed desirable.

The concentration of benzhydrol was varied from 1.0 M to 0.030 M, and the photoreduction was carried out in the presence of air and in degassed solutions. No attempt was made to keep the solutions saturated with air. Table 5 shows the results of these experiments.

The efficiency of the hydrogen abstraction process is apparently hindered by the presence of oxygen. The quantum yield in the presence of oxygen at a constant benzhydrol concentration was dependent upon the percent conversion of benzophenone, as demonstrated in runs containing, 1.0 M, 0.96 M, and 0.96 M benzhydrol. Apparently some oxidation occurred\(^{18}\), and, as the oxygen was depleted, the quantum yield increased, approaching the limiting value found for the degassed solutions.

No intermediate was observed during the photoreduction of benzophenone with benzhydrol, which indicates that the structure of the intermediate suggested by Pitts, \textit{et al.}\(^{19}\) was incorrect, since it should have readily formed in this system.

The quantum yields marked (c) in Table 5 were determined in runs made in the regular reaction cells, and those marked (e) were runs made in 1.0 cm. thick spectrophotometer cells. The light intensity absorbed by the small cells was one-tenth
Table 5. Photoreduction of 0.1 M benzophenone with benzhydrol in benzene at 3660 A.

<table>
<thead>
<tr>
<th>Molarity benzhydrol</th>
<th>Percent conversion benzophenone</th>
<th>Quantum yield benzophenone</th>
<th>Ratio of benzpinacol to benzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>11.0</td>
<td>0.57&lt;sup&gt;c&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>0.96</td>
<td>18.1</td>
<td>0.58&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>0.96</td>
<td>42.9</td>
<td>0.75&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>0.48</td>
<td>36.6</td>
<td>0.64&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>0.50</td>
<td>44.3</td>
<td>0.72&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.08</td>
</tr>
<tr>
<td>0.29</td>
<td>16.3</td>
<td>0.53&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>0.10</td>
<td>18.5</td>
<td>0.26&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>0.045</td>
<td>6.4</td>
<td>0.12&lt;sup&gt;c&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>0.029</td>
<td>9.6</td>
<td>0.075&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>1.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>56.1</td>
<td>0.97&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.93</td>
</tr>
<tr>
<td>0.20&lt;sup&gt;e&lt;/sup&gt;</td>
<td>34.9</td>
<td>0.78&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.00</td>
</tr>
<tr>
<td>0.70&lt;sup&gt;e&lt;/sup&gt;</td>
<td>20.5</td>
<td>0.52&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.11</td>
</tr>
<tr>
<td>0.050&lt;sup&gt;e&lt;/sup&gt;</td>
<td>18.1</td>
<td>0.45&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.96</td>
</tr>
<tr>
<td>0.040&lt;sup&gt;e&lt;/sup&gt;</td>
<td>16.6</td>
<td>0.41&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.99</td>
</tr>
<tr>
<td>0.030&lt;sup&gt;e&lt;/sup&gt;</td>
<td>10.4</td>
<td>0.29&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.16</td>
</tr>
</tbody>
</table>

<sup>a</sup>Quantum yield was calculated with benzophenone-isopropanol actinometer.

<sup>b</sup>Lead tetraacetate assay was employed for the benzpinacol determination.

<sup>c</sup>Light intensity absorbed was $4.3 \times 10^{17}$ quanta per sec.

<sup>d</sup>Light intensity absorbed was $3.3 \times 10^{16}$ quanta per sec.

<sup>e</sup>Solution was degassed.
of that absorbed by the regular cells, but due to the difference in volume, the rate was twice as fast in the small cells. Quantum yields determined at the same concentration of benzhydrol in both types of cell are the same within experimental error.

The quantum yield was determined for the photoreduction of benzophenone with \( \alpha \)-deuterobenzhydrol. Table 6 gives the essential data for that system. The run marked (F) was made by Mr. Robert Foss.

Table 7 demonstrates the independence of the quantum yield with respect to the nature of solvent for the benzophenone-benzhydrol system. Again, notice should be made of

Table 6. Photoreduction of 0.1 M benzophenone with \( \alpha \)-deuterobenzhydrol in benzene at 3660 A.

<table>
<thead>
<tr>
<th>Molarity ( \alpha )-deuterobenzhydrol</th>
<th>Percent conversion benzophenone</th>
<th>Quantum(^a) yield benzophenone</th>
<th>Ratio of benzpinacol to benzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10(^c)</td>
<td>25.5</td>
<td>0.41(^d)</td>
<td>1.00</td>
</tr>
<tr>
<td>0.050(^c)</td>
<td>12.9</td>
<td>0.24(^d)</td>
<td>1.10</td>
</tr>
<tr>
<td>0.030(^c)(F)</td>
<td>10.0</td>
<td>0.16(^d)</td>
<td>----</td>
</tr>
</tbody>
</table>

\(^a\)Quantum yield was calculated with benzophenone-isopropanol actinometer.

\(^b\)Lead tetraacetate assay was employed for the benzpinacol determination.

\(^c\)Solution was degassed.

\(^d\)Light intensity absorbed was \( 4.3 \times 10^{17} \) quanta per sec.
Table 7. Photoreduction of 0.1 M benzophenone with 1 M benzhydrol in various solvents at 3660 A.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Percent conversion benzophenone</th>
<th>Quantum\textsuperscript{a} yield benzophenone</th>
<th>Reactivity of solvent in the photoreduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>18.1</td>
<td>0.58\textsuperscript{b}</td>
<td>None</td>
</tr>
<tr>
<td>Benzene</td>
<td>42.9</td>
<td>0.75\textsuperscript{b}</td>
<td>None</td>
</tr>
<tr>
<td>t-Butyl alcohol</td>
<td>15.</td>
<td>0.49\textsuperscript{b}</td>
<td>None</td>
</tr>
<tr>
<td>t-Butyl alcohol</td>
<td>27.1</td>
<td>0.74\textsuperscript{b}</td>
<td>None</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>25.</td>
<td>0.61\textsuperscript{b}</td>
<td>None</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Quantum yield was calculated with benzophenone-isopropanol actinometer.

\textsuperscript{b}Light intensity absorbed was $3.3 \times 10^{16}$ quanta per sec.

The dependence of quantum yield on percent conversion. All these runs were made in 1.0 cm. thick spectrophotometer cells in the presence of air.

Table 8 shows the effect of a paramagnetic chelate, ferric dipivaloylmethide, on the quantum yield for the benzophenone-benzhydrol system.

The Effect of Chelates on the Quantum Yield of Benzophenone

Benzophenone was photoreduced in the presence of paramagnetic chelates in the anticipation of changing the quantum yield. This presumption was verified as shown in Tables 8, 9, 10, and 11.
Table 8. Photoreduction of 0.1 M benzophenone with benzhydrol and 10^{-4}M ferric dipivaloylmethide in benzene at 3660 Å.

<table>
<thead>
<tr>
<th>Molarity benzhydrol</th>
<th>Percent conversion benzophenone</th>
<th>Quantum yield benzophenone</th>
<th>Ratio of $\phi_b$ (with chelate) to $\phi_b$ at same M. benzhydrol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10$^b$</td>
<td>28.0</td>
<td>0.54$^c$</td>
<td>----$^d$</td>
</tr>
<tr>
<td>0.050$^b$(F)</td>
<td>18.8</td>
<td>0.29$^c$</td>
<td>0.65</td>
</tr>
<tr>
<td>0.030$^b$</td>
<td>9.6</td>
<td>0.21$^c$</td>
<td>0.71</td>
</tr>
</tbody>
</table>

$^a$Quantum yield was calculated with benzophenone-isopropanol actinometer.

$^b$Solution was degassed.

$^c$Light intensity absorbed was $4.3 \times 10^{17}$ quanta per sec.

$^d$A corresponding quantum yield was not available.

Table 9 demonstrates the effect of various chelates on the photoreduction of benzophenone in tblue. In the case of ferric dipivaloylmethide, the quantum yield was dependent on the concentration of chelate. Ferric, samarium, and erbium dipivaloylmethides, which are paramagnetic, reduced the quantum yield of benzophenone. Aluminum dipivaloylmethide, which is diamagnetic, did not alter the quantum yield. Ferric dipivaloylmethide possesses an absorption maximum at 3660 Å, which became troublesome at higher concentrations. Samarium and erbium dipivaloylmethides do not possess this maximum, and are potentially more suitable for experimentation. The discrepancy in the value for the standard quantum
Table 9. Photoreduction of 0.1 M benzophenone in toluene in the presence of chelate at 3660 A.

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Molarity of chelate</th>
<th>Percent conversion benzophenone</th>
<th>Quantum yield of benzophenone</th>
<th>Ratio of $\Phi_B$ (with chelate) to $\Phi_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>--------</td>
<td>21.6</td>
<td>0.36$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(DPM)$_3^a$</td>
<td>$4 \times 10^{-5}$</td>
<td>18.9</td>
<td>0.27$^b$</td>
<td>0.75$^c$</td>
</tr>
<tr>
<td>Fe(DPM)$_3^a$</td>
<td>$4 \times 10^{-5}$</td>
<td>17.8</td>
<td>0.27$^b$</td>
<td>0.75$^c$</td>
</tr>
<tr>
<td>Fe(DPM)$_3^a$</td>
<td>$8 \times 10^{-5}$</td>
<td>25.6</td>
<td>0.27$^b$</td>
<td>0.75$^c$</td>
</tr>
<tr>
<td>Fe(DPM)$_3^a$</td>
<td>$2 \times 10^{-3}$</td>
<td>7.9</td>
<td>0.08$^b$</td>
<td>0.22$^c$</td>
</tr>
<tr>
<td>Al(DPM)$_3^a$</td>
<td>$4 \times 10^{-5}$</td>
<td>21.9</td>
<td>0.35$^b$</td>
<td>0.97$^c$</td>
</tr>
<tr>
<td>--------</td>
<td>24.3</td>
<td>0.41$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(DPM)$_3$</td>
<td>$7 \times 10^{-5}$</td>
<td>19.2</td>
<td>0.33$^d$</td>
<td>0.80$^e$</td>
</tr>
<tr>
<td>Fe(DPM)$_3^a$</td>
<td>$1 \times 10^{-3}$</td>
<td>2.5</td>
<td>0.07$^d$</td>
<td>0.17$^e$</td>
</tr>
<tr>
<td>Sm(DPM)$_3$</td>
<td>$1 \times 10^{-4}$</td>
<td>21.5</td>
<td>0.36$^d$</td>
<td>0.88$^e$</td>
</tr>
<tr>
<td>Er(DPM)$_3$</td>
<td>$9 \times 10^{-5}$</td>
<td>25.6</td>
<td>0.35$^d$</td>
<td>0.85$^e$</td>
</tr>
</tbody>
</table>

$^a$Solution was degassed.

$^b$Quantum yield was calculated with uranyl oxalate actinometer.

$^c$Ratio was calculated from quantum yield of 0.36.

$^d$Quantum yield was calculated with benzophenone-isopropanol actinometer.

$^e$Ratio was calculated from quantum yield of 0.41.
Table 10. Photoreduction of 0.1 M benzophenone in the presence of ferric dipivaloylmethide at 3660 A.

<table>
<thead>
<tr>
<th>Hydrogen donor</th>
<th>Molarity Fe(DPM)$_3$</th>
<th>Percent conversion benzophenone</th>
<th>Quantum yield benzophenone</th>
<th>Ratio of $\Phi_B$ (with chelate) to $\Phi_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropanol</td>
<td>$5 \times 10^{-5}$</td>
<td>25.6</td>
<td>1.0$^a$</td>
<td>1.0</td>
</tr>
<tr>
<td>Cumene$^b$</td>
<td>$5 \times 10^{-5}$</td>
<td>22.6</td>
<td>0.61$^a$</td>
<td>0.87$^c$</td>
</tr>
<tr>
<td>Toluene</td>
<td>$7 \times 10^{-5}$</td>
<td>19.2</td>
<td>0.33$^a$</td>
<td>0.80$^d$</td>
</tr>
</tbody>
</table>

$^a$Quantum yield was calculated with benzophenone-isopropanol actinometer.

$^b$Solution was degassed.

$^c$Ratio was calculated from quantum yield of 0.70.

$^d$Ratio was calculated from quantum yield of 0.41.

Table 11. Photodecomposition of ferric dipivaloylmethide at 3660 A.

<table>
<thead>
<tr>
<th>System</th>
<th>Molarity Fe(DPM)$_3$</th>
<th>Percent conversion Fe(DPM)$_3$</th>
<th>Quantum yield Fe(DPM)$_3$</th>
<th>Visible change in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone-toluene</td>
<td>$2 \times 10^{-3}$</td>
<td>70.</td>
<td>0.01</td>
<td>Green ppt.</td>
</tr>
<tr>
<td>Benzophenone-toluene</td>
<td>$1 \times 10^{-3}$</td>
<td>30.</td>
<td>0.01</td>
<td>Green ppt.</td>
</tr>
<tr>
<td>Toluene</td>
<td>$4 \times 10^{-4}$</td>
<td>10</td>
<td>0.001</td>
<td>Fading of color</td>
</tr>
<tr>
<td>Benzophenone-toluene</td>
<td>$4 \times 10^{-5}$</td>
<td>87.</td>
<td>0.001</td>
<td>Fading of color</td>
</tr>
<tr>
<td>Benzophenone-benzhydrol</td>
<td>$1 \times 10^{-4}$</td>
<td>70.</td>
<td>0.001</td>
<td>Fading of color</td>
</tr>
<tr>
<td>Benzophenone-cumene</td>
<td>$5 \times 10^{-5}$</td>
<td>56.</td>
<td>0.001</td>
<td>Fading of color</td>
</tr>
</tbody>
</table>
yield was attributed to differences in experimental conditions, and not to the actinometry as it might appear. The experiments were conducted with different reactors, with different light intensities, and with different correction factors.

Table 10 summarizes the dependence of the effect of the iron chelate on the hydrogen donor. As the hydrogen donor became more efficient, the effect of the chelate was reduced.

During the series of experiments employing ferric dipivaloylmethide, the chelate apparently decomposed, as evidenced by the fading of the yellow chelate color. Several spectrophotometric determinations of the decomposition were made, utilizing the absorption maximum at 4250 Å. The results are presented in Table 11.

In concentrated solutions of the chelate, the formation of a green precipitate was noticed during the photolysis. One run was degassed, and after the photolysis had proceeded for an hour, the reaction cell was removed from the light path. In addition to the green flocculent precipitate, the yellow color of ferric dipivaloylmethide had completely faded. When the cell was opened to the air and shaken a few times, the green precipitate disappeared, and the yellow color returned. Analysis showed that 30% of the chelate had decomposed.
Miscellaneous Reactions

Chloranil and benzoquinone were photolyzed in the presence of toluene at 4200 Å and 3650 Å. No reaction was evidenced as determined spectrophotometrically.

Benzophenone was photolyzed in the presence of s-butyl benzene, cyclohexene, p-nitrocumene and p-isopropyl anisole. Benzophenone was photoreduced in each solution. The reactions were performed to examine the synthetic possibilities of the reaction.

Association between Benzophenone and Benzhydrol

Cryoscopic measurements were performed to determine the degree of association between benzophenone and benzhydrol. A Beckman Freezing Point Apparatus was used for the determination. Benzene was used for the solvent and ice water was used for coolant. The cryoscopic constant for benzene is 5.7. Benzene (Reagent Grade) was stored over sodium, freezing point, 5.3°.

A solution of benzophenone (0.116 molal) and benzhydrol (0.116 molal) in benzene gave a freezing point depression of 1.115 degrees. The apparent molecular weight was 217. A solution of benzophenone in benzene (0.218 molal) gave a freezing point depression of 1.10 degrees. The apparent molecular weight was 206. A solution of benzhydrol in benzene (0.216 molal) gave a freezing point depression of
0.98 degrees. The apparent molecular weight was 232. The actual molecular weight of benzophenone is 182, and of benzhydrol is 184. Since benzhydrol dimerized to such a large degree, it was felt that cryoscopic measurements would not yield a reliable association constant for the benzophenone-benzhydrol system.

The ultraviolet spectra for 0.01 M benzophenone; in benzene gave a maximum at 3430 A., in t-butyl alcohol gave a maximum at 3340 A., and with 1.0 M benzhydrol in benzene gave a maximum at 3410 A. If it is assumed that the benzophenone in benzene is free from association, and that the benzophenone in t-butyl alcohol is entirely complexed, the molar extinction coefficients from these spectra can be used to solve simultaneous equations for the percent of complexed molecules in the mixed spectrum from the benzhydrol solution. With this method, 45% of the benzophenone was calculated to be complexed. An absorption curve was then calculated for 45% of complexed benzophenone and 55% free benzophenone. It was found to match the experimental curve for benzophenone in benzhydrol very nicely as shown in Table 12.
Table 12. Absorption spectrum for 0.01 M benzophenone with 1.0 M benzhydrol in benzene

<table>
<thead>
<tr>
<th>Wavelength in angstroms</th>
<th>Extinction coefficient (complexed)</th>
<th>Extinction coefficient (free)</th>
<th>Absorbance (observed)</th>
<th>Absorbance (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200</td>
<td>136</td>
<td>82</td>
<td>1.05</td>
<td>1.06</td>
</tr>
<tr>
<td>3250</td>
<td>145</td>
<td>95</td>
<td>1.18</td>
<td>1.17</td>
</tr>
<tr>
<td>3300</td>
<td>155</td>
<td>116</td>
<td>1.35</td>
<td>1.34</td>
</tr>
<tr>
<td>3400</td>
<td>153</td>
<td>127</td>
<td>1.40</td>
<td>1.39</td>
</tr>
<tr>
<td>3450</td>
<td>141</td>
<td>128</td>
<td>1.37</td>
<td>1.35</td>
</tr>
<tr>
<td>3500</td>
<td>121</td>
<td>115</td>
<td>1.20</td>
<td>1.19</td>
</tr>
<tr>
<td>3550</td>
<td>99</td>
<td>106</td>
<td>1.07</td>
<td>1.04</td>
</tr>
<tr>
<td>3600</td>
<td>74</td>
<td>90</td>
<td>0.85</td>
<td>0.83</td>
</tr>
<tr>
<td>3700</td>
<td>30</td>
<td>47</td>
<td>0.41</td>
<td>0.40</td>
</tr>
</tbody>
</table>
From the experimental results, it was possible to develop a unified theory for the fate of excited benzophenone molecules. The theory will be discussed in connection with the benzophenone-benzhydrol system, followed by an elaboration of the benzophenone-toluene system. The theory should be generally applicable to all photoreductions involving ketones, and with modification may be used for all photoredox reactions of ketones. The methods employed may be of interest to solution photochemistry in general.

The following mechanism is specific for the photoreduction of benzophenone in a benzene solution of benzhydrol. However, the mechanism is applicable to most systems with some modification.

Filtered light of the 3660 A. region produces the $\eta \rightarrow \pi^*$ transition of benzophenone mentioned previously. The concentration of benzophenone (0.10 M) gave an absorbance of 40, which was sufficient for complete light absorption, and therefore the rate of the conversion from the ground singlet to the excited singlet was equal to the light intensity absorbed ($I_a$).

\[
B + h \nu \xrightarrow{\eta \rightarrow \pi^*} B^1 \]  
(B is benzophenone)

The excited singlet can be deactivated by several pathways: (1) radiative transition to the ground singlet (flu-
orescence); (2) collisional deactivation by other molecules; (3) intersystem crossing to the triplet state; and (4) chemical reaction with other molecules.

Since quantum yields of one have been observed, chemical reactivity must be able to compete with all other processes under favorable conditions. The short lifetime of the singlet state ($10^{-8}$ - $10^{-6}$ sec.) indicates that some long-lived state may be the chemically reactive species. For the present, it will be assumed that intersystem crossing to the triplet state is very efficient and that the transition is complete.

(2) \[ \text{B}_1 \rightarrow \text{B}_3 \quad k_{\text{is}} \]

The rate for reaction (1) and (2) will be designated $\phi I_a$, and $\phi'$ is assumed to be one due to the preceding discussion. It is the quantum yield for formation of the triplet state.

Deactivation processes for the triplet state are the same as those for the singlet state, but the details vary considerably. Neither fluorescence nor phosphorescence have been observed for benzophenone in solution, but phosphorescence has been observed at low temperatures ($77^\circ$K)\textsuperscript{10}. It seems safe to exclude all radiative processes from the mechanism, but the lack of fluorescence should be kept in mind. This leaves only collisional and chemical deactivation.
Chemical reactivity in this system is limited to hydrogen abstraction as proven by product analysis. The excited benzophenone molecule acts like a reactive free radical due to its partially vacant p orbital, and is capable of abstracting hydrogen from other molecules, thus forming two free radicals which are relatively stable.

$$\text{(3)} \quad B^3 + BH_2 \longrightarrow 2 BH^* \quad k_r$$

Benzhydrol is designated by BH$_2$ and diphenylhydroxymethyl radical by BH$^*$. Collisional deactivation of the excited molecule can be accomplished by any molecular species in solution. The solvent will be an important deactivator due to its large concentration. Benzhydrol and benzophenone can also de-

$$\text{(4)} \quad B^3 + C_6H_6 \longrightarrow B + C_6H_6 \quad k_s$$

$$\text{(5)} \quad B^3 + B \longrightarrow 2 B \quad k_b$$

$$\text{(5a)} \quad B^3 \longrightarrow B \quad k_d$$

$$\text{(6)} \quad B^3 + BH_2 \longrightarrow B + BH_2 \quad k_h$$

activate the excited state. Steps (4) and (5) can be combined where it is convenient into a single step (5a), represented by a first order rate constant $k_d$. In the absence of other contaminates, no further reactions are likely, with the exception of radical combination.
In the presence of oxygen, the mechanism becomes more complicated. Oxygen is known to be a good quencher for both the excited singlet and triplet states.\(^{(7)}\)

\[
(8) \quad B^3 + O_2 \rightarrow B + O_2 \quad k_q
\]

\[
(8a) \quad B^1 + O_2 \rightarrow B^3 + O_2 \quad k_{1\rightarrow 3}
\]

Oxygen is thought to promote the conversion of the excited singlet state to the triplet state, since it has been observed to produce singlet to triplet absorption transitions.\(^{(8)}\)

Deactivation by any other species will be specified by reaction (9).

\[
(9) \quad B^3 + K \rightarrow B + K \quad k_k
\]

In addition to physical quenching, oxygen is known to participate chemically in the benzophenone-benzhydrol system. In 1944, Bäckström\(^{(8)}\) studied the oxidation of alcohols initiated by the photoreduction of benzophenone. He found oxygen uptake to be constant for air saturated solutions, and that oxidation was not a chain process. Hydrogen peroxide and acetone were formed quantitatively in the oxidation of iso-


\(^{(38)}\) E. J. Bowen, Nature, 149, 528 (1942).

propanol. Reactions (10) and (11) account for the known facts, but other schemes are possible. The kinetic expression for (10) and (11) is cumbersome and does not affect the over-

(10) \[ BH^* + O_2 \longrightarrow BHO_2^* \]

(11) \[ BHO_2^* + BH_2 \longrightarrow BH^* + B + H_2O_2 \]

all rate law seriously. The role of oxidation will be discussed later, and is placed here for completeness of mechanism.

The rate of disappearance of benzophenone is given by the expression \( \phi_B I_a \), where \( \phi_B \) is the quantum yield for benzophenone. This rate is equal to the rate for radical formation.

(12) \[ \phi_B I_a = k_r(B^3)(BH_2) \]

A steady state treatment of the triplet state concentration and substitution into (12) yields equation (13). Inversion of equation (13) will give (14). A plot of \( 1/\phi_B \) versus

(13) \[ \phi_B = \frac{k_r(BH_2)}{k_r(BH_2) + k_h(BH_2) + k_d(M) + k_q(O_2) + k_k(K)} \]

\( 1/(BH_2) \) should give a linear function under all conditions employed. Figures 8 and 9 show this to be true.
Figure 8. Photoreduction of 0.1 M benzophenone by benzhydrol in benzene solution

- X-X \((C_6H_5)_2CHOH\)
- 0-0 \((C_6H_5)_2CDOH\)
Figure 9. Photoreduction of 0.1 M benzophenone by benzhydrol in benzene solution with additives present

X-X  No additive
0-0  $10^{-4}$M Fe(DPM)$_3$
0-0  Oxygen (approximately $10^{-3}$M)
It is significant that all the lines extrapolate to an intercept of 1.0, even though conditions employed were quite different. The results indicate that the quantum yield of the chemically reactive state is unity. It also indicates that the actinometry was sound. The ratio $k_\text{h}/k_\text{r}$ will be shown to be negligibly small. A quantum yield of less than one for either of the above processes would increase the value of the intercept (i.e., errors in both of these values would not be compensating). This result alone suggests the necessity for a long-lived state.

The slope is then equal to the sum of a combination of deactivation processes divided by the rate constant for radical formation. A summary of the values for the slope is given in Table 13.

A detailed examination of the values for the slope under

Table 13. Values for the slope from the plot $1/\Phi_B$ versus $1/(B\text{H}_2)$ for the photoreduction of 0.1 M benzophenone in benzene at 3660 Å.

<table>
<thead>
<tr>
<th>Hydrogen donor</th>
<th>Additive</th>
<th>Initial molarity of additive</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzhydrol</td>
<td>none</td>
<td>----</td>
<td>0.050</td>
</tr>
<tr>
<td>Benzhydrol</td>
<td>oxygen</td>
<td>$10^{-3}$</td>
<td>0.28</td>
</tr>
<tr>
<td>Benzhydrol</td>
<td>Fe(DPM)$_3$</td>
<td>$10^{-4}$</td>
<td>0.090</td>
</tr>
<tr>
<td>α-Deuterobenzhydrol</td>
<td>none</td>
<td>----</td>
<td>0.133</td>
</tr>
</tbody>
</table>
the various conditions employed should give some insight as
to the nature of the chemically reactive state. An argument
excluding the excited singlet state (except in steps 1 and 2) from the chemical reaction will be presented, followed by
a rationalization of the lifetimes involved.

In the absence of oxygen and other additives, the slope
becomes;

\begin{equation}
0.050 = \frac{k_d}{k_r},
\end{equation}

which indicates that deactivation processes are much slower
than the chemical reaction. The fastest rate possible for
the hydrogen abstraction step would be a diffusion-controlled
rate. Schultz\textsuperscript{40} has formulated the equations and calculated
the bimolecular rate constants for organic molecules of this
size participating in diffusion-controlled processes. Using
a diffusion coefficient of $10^{-5}$ cm.\(^2\) per sec., and a molecular
size of 5 A., a rate constant of $10^9$ liter mole\(^{-1}\) sec.\(^{-1}\) was
calculated. Substitution of this value into equation (15)
gives $k_d$ a maximum value of $5 \times 10^7$ sec.\(^{-1}\). The mean life-
time of the excited singlet was calculated\textsuperscript{41} to be $4 \times 10^{-6}$

\textsuperscript{40}G. V. Schultz, Z. physik. Chem., 8, 284 (1956).

\textsuperscript{41}The integrated intensity of the 0-0 absorption band of
the $\pi \rightarrow \pi^*$ transition was calculated, which is inversely pro-
portional to the mean lifetime of the excited state\textsuperscript{42}.

\begin{equation}
\tau = \frac{\varepsilon_u}{g_1 \cdot n^2 \cdot c \cdot 8\pi \cdot \nu_m^2 \int_0^\infty \mathcal{E}(\nu) \, d\nu}
\end{equation}

79 sec., if the energy were only dissipated by radiation. Fluorescence might thus be expected to compete with other deactivation processes, even though calculations have been made to yield maximum values for the deactivation constant and the mean lifetime of the singlet state (if the singlet were actually the species participating in the hydrogen transfer reaction).

The results from the investigation of α-deuterobenzhydrol indicate that radical formation is much slower than diffusion-controlled. A slope of 0.133 was obtained from the plot in Figure 8. Since deactivation processes are the same for the α-deuterobenzhydrol system as for the benzhydrol system, a ratio of $k_r(H)/k_r(D)$ is given by a ratio of the slopes, and is equal to 2.7. This isotope effect demonstrates that radical formation is the rate controlling step and cannot be diffusion-controlled.

Upon reflection, it must be conceded that deactivation processes are too slow to quench the excited singlet state, and therefore the excited molecule must be the triplet state. It should be remembered that fluorescence of benzophenone in benzene solution has not been observed.

Now, an attempt will be made to evaluate the rate constants involved in this mechanism. Equation (15) can be substituted into equation (14) for the benzophenone-benzhydrol system studied in air, since $k_r$ and $k_d$ have not changed.
This gives a minimum value for the ratio $k_q/k_r$, if the concentration of dissolved oxygen is assumed to be $10^{-3}$ M.

$$\frac{k_q}{k_r} = \frac{0.28 - 0.05}{10^{-3}} = 230$$

Oxygen is consumed during the reaction, and the concentration must fall to some lower level. From Table 5 a trend can be noticed for the photolysis of $1.0$ M. solutions of benzhydrol in air. The quantum yield increases with increased conversion of benzophenone. This indicates that oxidation proceeds slowly, but, as the oxygen concentration is reduced, the quantum yield approaches that for degassed solutions. Also, since oxidation of benzhydrol produces benzophenone, the apparent quantum yield for low conversion was less than predicted by the rate law. It was only at high concentrations of benzhydrol that reaction (10) and (11) became appreciable and distorted the kinetics.

Backström and Sandros\textsuperscript{44} found that the rate constant for the quenching of biacetyl phosphorescence by oxygen was $5 \times 10^9$ liter mole\textsuperscript{-1} sec\textsuperscript{-1}. Also, Livingston and Tanner\textsuperscript{45} have reported a rate constant of $2.0 \times 10^9$ liter mole\textsuperscript{-1} sec\textsuperscript{-1} for the quenching of triplet anthracene by oxygen.


Substitution of $5 \times 10^9$ for $k_q$ into equation (16) gave a value of $2 \times 10^7$ liter mole$^{-1}$ sec.$^{-1}$ for $k_r$. All rate constants related to $k_r$ can now be evaluated. The deactivation rate constant $k_d$ is $1 \times 10^6$ sec.$^{-1}$, and $k_r(D)$ is $7.5 \times 10^6$ liter mole$^{-1}$ sec.$^{-1}$.

Also, through the use of the results from the ferric dipivaloylmethide investigation, the rate constant $k_r$ can be evaluated. From the plot in Figure 9 a slope of 0.090 was obtained for the benzophenone-benzhydrol system in the presence of ferric dipivaloylmethide. If equation (14) is solved for the case where $K$ is Fe(DPM)$_3$, equation (17) gives

$$(17) \quad \frac{k_k}{k_r} = \frac{0.090 - 0.050}{10^{-14}} = 400$$

the ratio of $k_k$ to $k_r$. Although the ratio of $k_k$ to $k_q$ is calculated to be 1.7, it will be assumed that it is 1.0 since there is some uncertainty in the value for the concentration of oxygen. Therefore, a value of $5 \times 10^9$ will be used for $k_k$.

Turning to the benzophenone-toluene system, several runs have been made using various concentration of Fe(DPM)$_3$ in degassed solutions. The results were presented in Table 9. A similar mechanism to the one illustrated for the benzenophenone-benzhydrol system in equations (1) through (9) can be formulated, and the resulting rate law is shown in equation (18), where $k_t$ is the rate constant for the deactivation
process involving toluene, \( k'_{t} \) is the rate constant for radical formation involving toluene, and \( (T) \) is the concentration of toluene. A plot of \( 1/\vartheta_{B} \) against \( (K) \) should result in a linear function. The data given in Table 14 suggest a straight line with a slope of \( 6.9 \times 10^{3} \).

Table 14. Values for \( 1/\vartheta_{B} \) and molarity of ferric dipivaloylmethide for the benzophenone-toluene system

<table>
<thead>
<tr>
<th>Molarity of Fe(DPM)(^3)</th>
<th>( \vartheta_{B} )</th>
<th>( 1/\vartheta_{B} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.35</td>
<td>2.86</td>
</tr>
<tr>
<td>( 4 \times 10^{-5} )</td>
<td>0.27</td>
<td>3.7</td>
</tr>
<tr>
<td>( 8 \times 10^{-5} )</td>
<td>0.27</td>
<td>3.7</td>
</tr>
<tr>
<td>( 1 \times 10^{-3} )</td>
<td>0.07</td>
<td>14.</td>
</tr>
<tr>
<td>( 2 \times 10^{-3} )</td>
<td>0.08</td>
<td>12.</td>
</tr>
</tbody>
</table>

The experimental difficulties are great in this type of study. Fe(DPM)\(^3\) has an annoying absorption band at 3550 A. which interferes with benzophenone absorption if large concentrations of Fe(DPM)\(^3\) are employed. Decomposition of the chelate necessitates its complete removal before a spectral analysis can be made for benzophenone. Since the quantum yields in toluene are intrinsically small, conversion of sufficient amounts of benzophenone becomes a problem. How-
ever, the trend is evident, and the consistency of the argument lends support to the validity of the interpretation.

Now $k_1'$ can be calculated from the slope which is $k_1/k_1'(T)$. Baker\textsuperscript{12} showed that $k_s/k_1'$ was 1.85 from the investigation of the benzophenone-toluene system in benzene. From the value for $k_1'$ calculated in equation (19), $k_s$ is found to be $1.3 \times 10^5 \text{ liter mole}^{-1} \text{ sec}^{-1}$. Equation (15) can be modified to separate the deactivation processes. Baker found that the quantum yield of benzophenone was insensitive to varying concentration of benzophenone, so $k_b$

\begin{equation}
(19) \quad k_1' = \frac{(5 \times 10^9)}{(6.9 \times 10^3)(10)} = 7.3 \times 10^4
\end{equation}

can be neglected, since it would have to be 100$k_s$ to be significant. Using the value for $k_s$ and substituting into equation (20), $k_\tau$ is calculated to be $2 \times 10^7 \text{ liter mole}^{-1} \text{ sec}^{-1}$. This is in good agreement with the value of $k_\tau$

\begin{equation}
(20) \quad 0.050 = \frac{k_s(C_6H_6) + k_b(B)}{k_\tau}
\end{equation}

found from the oxygen investigation. The internal consistency of the theory has been verified, and the quenching constant for oxygen was the only non-photochemical result employed. The rate constants evaluated are collected in Table 15.

Benzophenone in cumene, the original system intended for investigation, helps to complete the picture. The
Table 15. Rate constants for the photoreduction of benzophenone

<table>
<thead>
<tr>
<th>Reaction process</th>
<th>Second order rate constant liter mole$^{-1}$ sec.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen abstraction in benzhydrol</td>
<td>$k_r = 2 \times 10^7$</td>
</tr>
<tr>
<td>Hydrogen abstraction in toluene</td>
<td>$k'_r = 7.3 \times 10^4$</td>
</tr>
<tr>
<td>Hydrogen abstraction in cumene</td>
<td>$k''_r = 3 \times 10^5$</td>
</tr>
<tr>
<td>Hydrogen abstraction in isopropanol</td>
<td>$k'''_r \geq 10^6$</td>
</tr>
<tr>
<td>Deactivation by benzene</td>
<td>$k_s = 1.3 \times 10^5$</td>
</tr>
<tr>
<td>Quenching by oxygen</td>
<td>$k_q = 5 \times 10^9$</td>
</tr>
<tr>
<td>Quenching by Fe(DPM)$_3$</td>
<td>$k_k = 5 \times 10^9$</td>
</tr>
</tbody>
</table>

mechanism for that system is the same as for the benzophenonetoluene system, as indicated by product analysis. If the deactivation rate constant for cumene is approximately the same as the rate constant for benzene, a rate constant of $3 \times 10^5$ liter mole$^{-1}$ sec.$^{-1}$ is calculated for the hydrogen abstraction step using the same rate law already derived, and a quantum yield of 0.70 in pure solvent. Ferric dipivaloylmethide reduced the quantum yield of benzophenone in cumene from 0.70 to 0.61 as shown in Table 10. Taking these data and performing a calculation similar to the one described, a quenching constant of $6 \times 10^9$ liter mole$^{-1}$ sec.$^{-1}$ was approximated for Fe(DPM)$_3$, which is in agreement with the value suggested.
Ferric dipivaloylmethide did not alter the quantum yield for the benzophenone-isopropanol system. Although there is no way to evaluate the rate constant for the hydrogen abstraction step of this system with the present data, it must be $10^6$ or greater to not be influenced by the chelate. The rate constant may be of the order of that for benzhydrol.

These maximum rate constants offer the best evidence that intersystem crossing is very efficient and that the triplet state is the chemically reactive state. The mean lifetime of the triplet state is 0.01 sec. at $77^\circ K^{10}$, which would allow competitive processes to deactivate the triplet completely without phosphorescence occurring.

The entire argument could be rendered ineffective if an association between benzophenone and benzhydrol were shown to exist. Alcohols are known to form hydrogen bonds to ketones and this complex can be observed by a shift in the carbonyl stretching frequency and the $\pi \rightarrow \pi^*$ absorption transition.$^{46}$

In benzene solutions of benzophenone and benzhydrol, the association was found to be small, and did not influence the mechanism cited. This statement is based on: (1) cryoscopic measurements, (2) shifts in the absorption spectra, and (3) quantum yield determinations in other solvents.

Although a depression of the freezing point of the benzophenone-benzhydrol system was observed, it was mostly attributed to dimerization of benzhydrol.

Becker found a blue shift of 940 cm$^{-1}$ for the $\pi \rightarrow \pi^*$ absorption transition of benzophenone in ethanol. A shift of approximately 800 cm$^{-1}$ was observed for benzophenone in t-butyl alcohol. Assuming that benzophenone was completely complexed by t-butyl alcohol, the spectra of benzophenone (0.01 M) in benzene, t-butyl alcohol, and 1 M benzhydrol in benzene were compared, and an association constant of 0.8 was calculated. This means that the maximum association in 1 M benzhydrol is 45%, which was the highest benzhydrol concentration employed in this investigation. To decide the effect of any association, the quantum yield of the benzophenone-benzhydrol system was determined in other solvents. Acetonitrile and t-butyl alcohol were chosen since they would inhibit any benzophenone-benzhydrol complexing. Acetonitrile would form hydrogen bonds with benzhydrol leaving benzophenone free, and t-butyl alcohol would form hydrogen bonds with benzophenone leaving benzhydrol free. The benzophenone-t-butyl alcohol complex was observed in the absorption spectra mentioned previously. Benzophenone was found to be unreactive in either t-butyl alcohol or acetonitrile containing no added hydrogen donor. No change in the quantum yield of the benzophenone-benzhydrol system was observed in either
acetonitrile or t-butyl alcohol as shown in Table 7. A decrease in the quantum yield might have been expected if association played an important role in the hydrogen abstraction reaction.

The benzophenone-benzhydrol complex would necessarily bring the molecules in line; carbonyl oxygen to hydroxyl oxygen (-C=0 -- HOC-). For the hydrogen abstraction reaction to occur, the molecules must line up; carbonyl oxygen to the carbon on which the hydroxyl group is attached (-C=0 -- H-COH).

The efficient quenching of the excited state by paramagnetic molecules is extremely interesting, and has much potential for the elucidation of reaction mechanisms. The observation that ferric dipivaloylmethide was as effective as oxygen in quenching the excited state was very satisfying, and verified its predicted behavior.

The singlet to triplet absorption transition is observed for aromatic compounds in the presence of oxygen or ferric acetylacetonate. Aluminum acetylacetonate had no effect on the absorption spectra. Yuster and Weissman found that paramagnetic ions decreased the lifetimes of

\[ ^{48} \text{P. Yuster and S. I. Weissman, J. Chem. Phys., 17, 1183 (1949).} \]
phosphorescence of metallic dibenzoylmethanes. This was accompanied by a decrease in the ratio of the quantum yield of fluorescence to the quantum yield of phosphorescence. Studies by Kasha and Becker on porphyrin-like molecules indicated that those containing diamagnetic ions showed fluorescence, but that those containing paramagnetic ions showed phosphorescence but no fluorescence.

These results show that the conservation-of-spin rule is altered by the presence, either internally or externally, of a paramagnetic substance. Kasha attributes the breakdown of the spin barrier to increased spin-orbital coupling within the molecule.

The effect of paramagnetic substances on excited molecules has again been exhibited in the present investigation. Since both singlet and triplet excited states are potentially reactive, differences in the lifetimes should determine their roles in chemical reactions. If the singlet state has a moderate lifetime ($10^{-6}$ sec.), paramagnetic molecules should easily deactivate both the singlet and the triplet, resulting in an increase in the number of molecules populating the triplet state, as observed by Yuster and Weissman. Under these conditions, the quantum yield might be expected to

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increase. If as postulated for the systems presently studied, intersystem crossing is already very efficient, then the triplet state would be the only state deactivated by paramagnetic substances, and a decrease in the quantum yield would be observed. Assuming *a priori* that both the excited singlet and the triplet states are chemically reactive, the results again indicate that the excited state observed in the photoreduction of benzophenone is the triplet state.
SUMMARY

Employing conventional photochemical techniques, a correlation between the spectroscopic states and the chemical reactivity of electronically excited benzophenone has been achieved. The triplet state, which causes the phosphorescence of benzophenone at low temperatures, has been identified as the chemically reactive species.

Methods for the examination of excited states in photochemical reactions by means of paramagnetic substances have been suggested and applied to the investigation. Oxygen and ferric dipivaloylmethide were used as the paramagnetic probes in this work.

The photoreduction of benzophenone has been studied with toluene, cumene, and benzhydrol as hydrogen donors. A rate law has been formulated which gives a linear relationship between the inverse of the quantum yield for the disappearance of benzophenone and the inverse of the concentration of hydrogen donor. This relationship indicates a simple competition between deactivation of the chemically reactive state and its reaction with hydrogen donor. With benzhydrol as the hydrogen donor, a plot of the data gave an intercept for the inverse of the quantum yield of 1.0 under all conditions employed. The slope gave the ratio of the rate constant of deactivation to the rate constant for hydrogen abstraction. Assuming a diffusion-controlled rate for the hydrogen ab-
Abstraction process, a maximum rate constant for deactivation was obtained which was too slow to completely quench fluorescence. Fluorescence has not been observed in solutions of benzophenone. The limiting quantum yield of 1.0 indicates that all excited molecules pass through the chemically reactive state. This evidence necessitates a long-lived state as the chemically reactive species.

The photoreduction of benzophenone with \( \alpha \)-deuterobenzhydrol gave a substantial isotope effect, demonstrating that the hydrogen abstraction step could not be diffusion-controlled. Efficient quenching of the chemically reactive state by small amounts of paramagnetic substances supported the case for a long-lived state. Also, the use of oxygen as a quencher (the rate constant for oxygen quenching of phosphorescence is known) permitted the evaluation of all the important rate constants involved.

A simple mechanism can be postulated that explains the observed results. The \( \pi \rightarrow \pi^* \) transition of benzophenone is produced by light of 3660 A. and the molecule is excited to a higher singlet state. Intersystem crossing to the triplet state is very efficient and occurs before the singlet can be deactivated. The triplet is then deactivated by; chemical reaction with a hydrogen donor, collisional deactivation by solvent molecules, and quenching by paramagnetic molecules.
ACKNOWLEDGMENTS

The author wishes to acknowledge the following persons who have influenced and aided him: Dr. George S. Hammond, Patricia Moore, Dr. William P. Baker, Jr., Dr. Richard Keys, and Dr. Ernest Wenkert.

This work was carried out in part at the California Institute of Technology, and supported by grants from the Film Department of the DuPont Company and from the National Science Foundation.