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[CONTRIBUTION NO. 2637 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

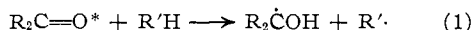
### Mechanisms of Photoreactions in Solutions. I. Reduction of Benzophenone by Benzhydrol

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The photochemical reduction of benzophenone by benzhydrol has been studied in detail. The reduction reaction produces only benzpinacol. At high concentrations of the alcohol the quantum yield approaches unity. The variation in the quantum yield with benzhydrol concentration follows a law indicative of simple competition between thermal deactivation and hydrogen transfer from the alcohol to an excited state of the ketone. Analysis of the data indicates that even if the hydrogen-transfer reaction is diffusion controlled, the lifetime of the chemically active excited state must be so long as to preclude the possibility that it is a singlet state of benzophenone. Identification of the triplet state as the reactive intermediate is consistent with the action of paramagnetic quenchers.

The photochemical reaction of ketones with alcohols is a familiar method for the preparation of pinacols.<sup>1</sup> Until recently relatively little effort has been directed toward the study of the mechanisms of such reactions. Pitts, *et al.*,<sup>2</sup> have reported an extensive study of the benzophenone-isopropyl alcohol system, and Weizmann, Bergmann and Hirshberg<sup>3</sup> have given a mechanistic interpretation of the reaction of acetophenone with *n*-butyl alcohol. Emphasis in all of these discussions has centered on the "chemical" mechanisms; that is, the description of the radical-producing reactions and the subsequent behavior of the radicals. It is generally agreed that an excited state of the ketones extracts a hydrogen atom from the hydrogen donor and that the ultimate reaction products are formed by coupling and disproportionation reactions of the radicals thus formed. Franzen<sup>4</sup> recently has shown that hydrogen exchange between benzophenone and diphenylhydroxymethyl radicals occurs.



Bäckstrom and his co-workers have been attacking the problems of identification of the excited state responsible for the hydrogen-transfer reaction

- (1) A. Schönberg and A. Mustafa, *Chem. Revs.*, **40**, 181 (1947).
- (2) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).
- (3) C. Weizmann, E. Bergmann and Y. Hirshberg, *ibid.*, **60**, 1530 (1938).
- (4) V. Franzen, *Ann.*, **633**, 1 (1960).

and have very recently provided virtually compelling evidence for identification of the reactive state as a triplet.<sup>5</sup> Their results were derived from a study of the energy transfer from the excited state of benzophenone to biacetyl, with the concomitant formation of the phosphorescent triplet state of the latter. Their conclusions, which agree qualitatively with our own,<sup>6,7</sup> will be shown in this paper also to agree quantitatively. It should also be pointed out that Bäckstrom has been suggesting for some years that many photoreactions of carbonyl compounds involve "biradical" states.<sup>8</sup> Although the term has not always been understood to be equivalent to triplet states, Bäckstrom has made it very clear that such was his intention.<sup>9</sup>

On the other hand, Bridge and Porter<sup>10</sup> have studied the reduction of duroquinone by paraffin hydrocarbons using the technique of flash photolysis. Both the semiquinone radical and the lowest triplet state of the quinone were characterized spectroscopically; it was found that the radical is not produced from the triplet state.

- (5) H. L. J. Bäckstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).
- (6) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959).
- (7) W. M. Moore, G. S. Hammond and R. P. Foss, *J. Chem. Phys.*, **32**, 1594 (1960).
- (8) H. L. J. Bäckstrom, *Z. physik. Chem.*, **B25**, 99 (1934).
- (9) H. L. J. Bäckstrom and K. Sandros, *J. Chem. Phys.*, **23**, 2197 (1955).
- (10) N. K. Bridge and G. Porter, *Proc. Roy. Soc. (London)*, **A244**, 259, 276 (1958).

### Experimental

**Materials.**—Benzophenone (Matheson, Coleman and Bell, Reagent Grade) was used without further purification. Benzhydrol (Matheson, Coleman and Bell, Reagent Grade) was recrystallized from hot ligroin (b.p. 60–70°). The product melted at 65–66°.  $\alpha$ -Deuteriobenzhydrol<sup>11</sup> was prepared by reduction of benzophenone with lithium aluminum deuteride (Metal Hydrides Corp., 96.6% pure) in anhydrous ether. The use of the stoichiometric amounts of the reactants gave a yield of 85%. The product was recrystallized twice from ligroin (b.p. 60–70°) to give white needles, m.p. 69–70°. Comparison of the infrared spectra of benzhydrol and  $\alpha$ -deuteriobenzhydrol showed them to be identical, except that the C–H stretching frequency found at 2850 cm.<sup>-1</sup> was shifted to 2110 cm.<sup>-1</sup> in the deuterio compound. Deuterium analyses gave values of 0.85, 1.00 and 1.00 deuterium atoms per molecule.

**Ferric dipivaloylmethide** was prepared by dissolving ferric chloride and excess sodium acetate in 50% ethanol-water and then adding dipivaloylmethane (2,2,6,6-tetramethyl-3,5-pentanedione). A red precipitate formed immediately, was separated by filtration and dissolved in ligroin. Evaporation of the ligroin extract left red crystals that were recrystallized from dimethylformamide, m.p. 161–162°.

*Anal.* Calcd. for C<sub>24</sub>H<sub>32</sub>O<sub>6</sub>Fe: C, 65.5; H, 9.4; ash, 13.2. Found: C, 65.5; H, 9.42; ash, 13.28.

The electronic spectrum of the compound had maxima at 2730 Å. ( $\epsilon$  30,000), at 3540 Å. ( $\epsilon$  4,400) and at 4230 Å. ( $\epsilon$  3,300).

**Lead tetraacetate** (Matheson, Coleman and Bell, Reagent Grade) was dissolved in hot glacial acetic acid and lead oxide was removed by filtration. White needles of lead tetraacetate were deposited on cooling the solution. The crystals were removed by filtration, immediately dissolved in glacial acetic acid and diluted to the concentration desired for analytical purposes.

**Benzene** (Baker and Adamson, Reagent Grade, thiophene free) was stored over sodium and used without further purification. *t*-Butyl alcohol (Matheson, Coleman and Bell, Reagent Grade) was allowed to stand in contact with anhydrous magnesium sulfate for several hours. The mixture then was filtered and the alcohol was distilled. A fraction, b.p. 82° and m.p. 24.8°, was used in the photochemical experiments. Acetonitrile (Matheson, Coleman and Bell) was used without further purification.

**Apparatus.**—An optical system was designed using mirrors to provide a collimated beam. The light source was a Westinghouse (SAH 800-c) 800-watt short arc, medium pressure, mercury lamp. An aluminized spherical mirror, 2.5-inch in diameter, and having a focal length of 1.5 inches, was placed three inches behind the lamp. The collimating mirror was placed in front of the arc in a position such that the arc was at the focal point of the mirror. The collimated beam was passed down the optical bench through filters and reaction cells to a collecting mirror, which focused the beam on the thermopile. The collimating and collecting mirrors were both aluminized, off-axis, parabolic reflectors, four inches in diameter, having focal lengths of five inches and an off-axis angle of 34°. The thermopile (Eppley Laboratories) was a single-junction, constantan-manganin element with a circular receiver one-eighth inch in diameter. The thermopile case was water cooled. Output from the thermopile was measured with a Rubicon portable potentiometer having a range of 161 mv.

Accessory equipment for the lamp included an inductive ballast (Nothelfer Winding Laboratories, No. 1301) and a voltage regulator (Superior Electric Co., Model IE 205). The lamp was run at close to optimum operating conditions (70 volts at 11.8 amperes). A tesla coil was used to start the lamp with an open-circuit potential of 150 volts.

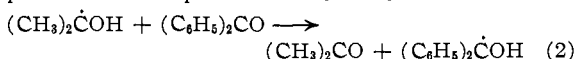
All components of the reactor were mounted on a lathe-bed type, optical bench consisting of steel rails welded together by cross bars and mounted on concrete pillars. Mirrors, filters and reaction cells were held in holders that could be positioned by means of three way screw adjustments.

**Cells.**—Two types of fused quartz cells were constructed. One cell was 10 cm. in diameter and 2-cm. thick. Two outlet tubes were provided separated by an angle of 90°. Cells of this type were used for water (to absorb infrared

radiation) and for filter solutions. They could also be used as reaction cells when degassing was not necessary. The second type of cell was designed to allow degassing of reaction mixtures before photolysis. The cell was 64 mm. in diameter and 25 mm. thick. It was attached by means of two outlet tubes to a manifold tube. The manifold was approximately one inch from the cells and the two ends were terminated in quartz-to-Pyrex seals: one end was connected to a degassing tube made of Pyrex, the other served as an outlet.

**Filter System.**—The filter system in this work consisted of a 2.0-cm. solution of copper sulfate pentahydrate (400 g. per liter) and Corning filter 7-51 (5970). The band passed had a maximum at 3660 Å. and was 500 Å. wide at the half height; this completely excludes the 3130 Å. line from the mercury arc.

**Actinometry.**—Throughout this study the rate of reduction of benzophenone by isopropyl alcohol was used to monitor light intensity. As is shown by the data in the accompanying paper,<sup>12</sup> the quantum yield for disappearance of benzophenone is very close to one under our reaction conditions. Pitts, *et al.*,<sup>2</sup> found that the quantum yield could exceed one and attributed the higher rate of disappearance of benzophenone to occurrence of reaction 2



This reaction probably disappears under our reaction conditions. The light intensities in our experiments were of the order of  $2.8 \times 10^{19}$  quanta per minute, much higher than those used in Professor Pitts' laboratory, and the concentrations of benzophenone also were higher in our experiments. Both factors contrive to make the steady-state concentrations of radicals higher in our experiments so that radical-radical reactions should compete much more effectively with reaction 2. As is shown in Table I, all of the data obtained for the rate of the reaction showed con-

TABLE I  
PHOTOREDUCTION OF BENZOPHENONE IN ISOPROPYL ALCOHOL

Run no.	Cell	% conversion	Rate of benzophenone disappearance (mole l. <sup>-1</sup> min. <sup>-1</sup> × 10 <sup>9</sup> )	$\frac{\Delta[\text{Benzpinacol}]^a}{-\Delta[\text{benzophenone}]}$
1	2	19.7	655	...
2	2	21.6	617	...
3	2	20.4	600	...
4	1	20.5	640	...
5	1	20.0	645	...
6	2	20.0	640	...
7	2	35.4	553	...
8	1 <sup>b</sup>	47.6	535	0.35
9	1 <sup>b</sup>	39.9	713	.39
10	1 <sup>b</sup>	20.0	633	.31
11	3 <sup>b</sup>	23.1	762	...
12	4 <sup>b</sup>	22.6	754	.32
13	1 <sup>b</sup>	36.6	585	.39
14	4 <sup>b</sup>	33.6	620	.39

<sup>a</sup> Benzpinacol determined gravimetrically. <sup>b</sup> Degassed solutions.

siderable dispersion. It will be noted that some variation is associated with variations in optical properties of the cells. In addition, there is a tendency for rates to fall off at high conversion. This cannot be due to depletion of the benzophenone since virtually all of the light was absorbed in all experiments; it probably is due to the build-up of a minor by-product that absorbs competitively on the short wave length side of the exciting band. The average of all rates is  $629 \times 10^{-6}$  mole l.<sup>-1</sup> min.<sup>-1</sup>; however, a large number of runs, carried to about 20% conversion, gave results grouped closely about  $640 \times 10^{-6}$  mole l.<sup>-1</sup> min.<sup>-1</sup>. The latter figure was taken as the standard for actinometry. Since the volume of solution irradiated was 67 ml., this rate corresponds to a light intensity of  $2.85 \times 10^{19}$  quanta per minute if the quantum yield is unity.

(11) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

(12) G. S. Hammond, W. P. Baker and W. M. Moore, *ibid.*, **85**, 2795 (1961).

**Determination of Benzophenone.**—Residual benzophenone was determined spectrophotometrically using as a reference a sample withdrawn from the original mixture before photolysis. Both solutions were diluted 25-fold and their absorbancies were measured at 3800, 3900 and 4000 Å. with a Beckman DU spectrophotometer. On occasion both solutions were again diluted 10-fold and the absorbancies were measured at 3500, 3600 and 3700 Å. In most cases the ratios of the absorbancies of the two solutions were independent of wave length. This was not true of isopropyl alcohol solutions, which were degassed before photolysis and examined without exposure to air; such solutions contain an unstable, colored intermediate as was reported by Pitts, *et al.*<sup>2</sup> We have studied the decay of this substance in the presence and in the absence of oxygen and have confirmed the observations of the earlier workers in every detail. Such solutions were exposed to oxygen before the analysis for benzophenone was carried out.

**Titrimetric Determination of Pinacol.**—Pinacol oxidation by lead tetraacetate was carried out by Criegee's method.<sup>13</sup> Erratic values were obtained with reaction mixtures produced by irradiation of isopropyl alcohol solutions of benzophenone in the presence of air. The values indicated that more than one mole of pinacol was produced for each mole of ketone reduced. This result is attributed tentatively to reaction of lead tetraacetate with hydrogen peroxide.

Titration of reaction mixtures from irradiation of degassed solutions gave consistent results, indicating that 0.56 mole of pinacol was obtained for every mole of benzophenone reduced. However, gravimetric determination of benzpinacol (Table I) showed that 0.39 mole of that product was formed from each mole of benzophenone. This result is consistent with the view that pinacols are formed by coupling reaction of 2-hydroxy-2-propyl radicals under our experimental conditions.

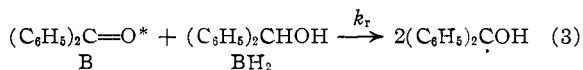
**Gravimetric Determination of Benzpinacol.**—Most of the solvent was removed from the reaction mixtures by careful distillation under reduced pressure. The residue was mixed with ligroin (b.p. 60–70°) and allowed to stand overnight. The residual crystalline solid was removed by filtration through a fritted glass crucible, dried and weighed. The product thus obtained was identified as benzpinacol by its decomposition point (186°) and infrared spectrum.

**Association of Benzophenone with Benzhydrol.**—Cryoscopic measurements were made with benzene solutions of the two compounds. A solution of benzophenone (0.116 molal) and benzhydrol (0.116 molal) in benzene gave a freezing-point depression of 1.115°. Assuming that the cryoscopic constant of benzene is 5.7°, this gives an apparent average molecular weight of 217. A solution of benzophenone (0.218 molal) gave a depression of 1.10°; apparent molecular weight, 206. A solution of benzhydrol (0.216 molal) gave a depression of 0.98°, apparent molecular weight, 232. It is apparent that there is limited molecular association in all solutions. Since benzhydrol is obviously more prone to associate with itself than with benzophenone, no attempt was made to evaluate an association constant for the alcohol and ketone.

The ultraviolet spectra of benzophenone show maxima at 3430 Å. in benzene, at 3340 Å. in *t*-butyl alcohol and at 3410 Å. in benzene containing 1 *M* benzhydrol. Addition of 1.0 *M* benzhydrol to the solution in *t*-butyl alcohol produced no further spectral shift; it was assumed that benzophenone is entirely hydrogen bonded in *t*-butyl alcohol and that the spectra of the ketone is the same when the molecule is complexed by the two alcohols. This permits an estimate of the amount of ketone complexed in 1.0 *M* benzhydrol in benzene as 45%. A complete absorption curve then was calculated, assuming 45% complex, which matched the experimental for the solution in mixed solvent with a precision of ± 1% at ten wave lengths from 3200 to 3700 Å.

## Results and Discussion

The reaction of benzophenone with benzhydrol has an inviting symmetry since hydrogen transfer produces only a single kind of radical



(13) R. Criegee, *Ber.*, **64B**, 264 (1931).

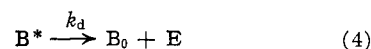
Subsequent hydrogen-transfer reactions, such as observed by Franzen,<sup>4</sup> would produce no net change in the system; but dimerization should produce benzpinacol in quantitative yield unless some disproportionation to regenerate benzophenone and benzhydrol were to occur. Comparison of the rates of disappearance of benzophenone and appearance of benzpinacol showed that the two were equal. The reaction was studied in benzene solution, and the quantum yield for disappearance of benzophenone was measured in a series of experiments in which the ketone concentration was maintained constant and the concentration of alcohol varied. The results are presented in Table II.

TABLE II  
PHOTOREDUCTION OF 0.1 *M* BENZOPHENONE WITH  
BENZHYDROL IN BENZENE<sup>a</sup> AND OTHER SOLVENTS<sup>b</sup>

Run no.	Benzhydrol	% conversion of benzophenone	Quantum yield of benzophenone <sup>c</sup>	$-\frac{\Delta[\text{Benzpinacol}]^d}{\Delta[\text{benzophenone}]}$
1	1.0	11.0	0.57 <sup>e</sup>	...
2	0.96	18.1	.58 <sup>e</sup>	...
3	.96	42.9	.73 <sup>e</sup>	...
4	.48	36.6	.64 <sup>f</sup>	...
5	.50	44.3	.72 <sup>e</sup>	1.08
6	.29	16.3	.53 <sup>f</sup>	...
7	.10	18.5	.26 <sup>f</sup>	...
8	.045	6.4	.12 <sup>e</sup>	...
9	.029	9.6	.075 <sup>f</sup>	...
10	1.0 <sup>g</sup>	56.1	.97 <sup>e</sup>	0.93
11	0.20 <sup>g</sup>	34.9	.78 <sup>e</sup>	1.00
12	.070 <sup>g</sup>	20.5	.52 <sup>e</sup>	1.11
13	.050 <sup>g</sup>	18.1	.45 <sup>e</sup>	0.96
14	.040 <sup>g</sup>	16.6	.4 <sup>e</sup>	0.99
15	.030 <sup>g</sup>	10.4	.29 <sup>e</sup>	1.16
16	1.0 <sup>h</sup>	15.0	.49 <sup>f</sup>	...
17	1.0 <sup>i</sup>	25.0	.61 <sup>f</sup>	...
18	0.10 <sup>j</sup>	28.0	.54 <sup>e</sup>	...
19	.050 <sup>j</sup>	18.8	.29 <sup>e</sup>	...
20	.030 <sup>j</sup>	9.6	.21 <sup>e</sup>	...

<sup>a</sup> Maximum intensity of irradiation at 3660 Å. <sup>b</sup> Benzene solution unless otherwise noted. <sup>c</sup> Calculated assuming quantum yield for disappearance of benzophenone in isopropyl alcohol is unity. <sup>d</sup> Benzpinacol determined by lead tetraacetate assay. <sup>e</sup> Light intensity =  $2.58 \times 10^{19}$  quanta min.<sup>-1</sup>. <sup>f</sup> Light intensity =  $1.98 \times 10^{19}$  quanta min.<sup>-1</sup>. <sup>g</sup> Degassed solution. <sup>h</sup> *t*-Butyl alcohol solution. Acetonitrile solution. <sup>i</sup> Degassed; contained  $10^{-4}$  *M* ferric dipivaloylmethide.

The simplest mechanism that can be devised to account for the decrease in quantum yield with decreasing concentration of the hydrogen donor involves deactivation of the chemically active excited state by a first-order mechanism.



Treatment of B\* as an unstable intermediate yields the rate law

$$\frac{1}{\Phi_B} = \frac{1}{a} + \frac{k_d}{ak_r[\text{BH}_2]} \quad a = \text{yield of the chemically active state.} \quad (5)$$

Figure 1 shows a plot of data obtained with degassed solutions. The fit to the linear law is good and the intercept at  $[\text{BH}_2] = \infty$  is one, indicating that *a*, the yield of the chemically reactive state, is unity. The good fit to linearity also indicates that specific, non-chemical quenching action by

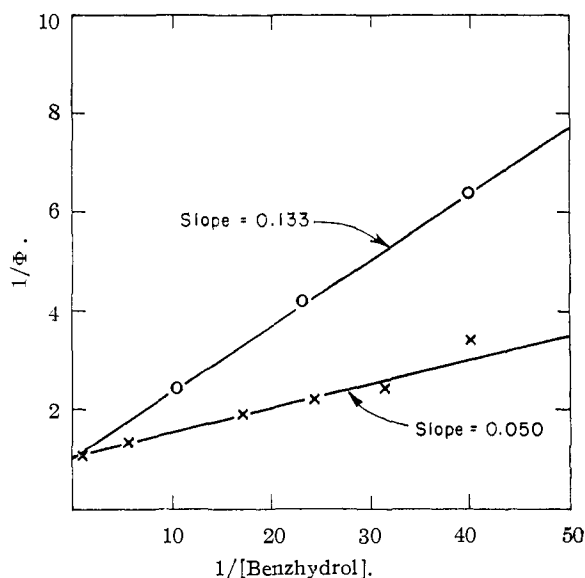


Fig. 1.—Photoreduction of 0.1 *M* benzophenone by benzhydrol in benzene solution: X-X, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CHOH; O-O, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CDOH.

benzhydrol is negligible. The data are striking in that reaction is appreciable even with concentrations of benzhydrol as low as 0.1 *M*. Qualitative reasoning indicates that this demands the excited state be rather long-lived. Quantitative analysis of the data confirms this conclusion.

The slope of the line in Fig. 1 shows that the value of  $k_d/k_r$  is 0.05. The fastest rate that can be easily conceived of for reaction 3 is the diffusion controlled rate. The rate constant for collision of benzhydrol with benzophenone was calculated using Schultz's formulation,<sup>14</sup> eq. 6, of the Smoluchowski equation<sup>15</sup>

$$k_{\text{Dif}} = 8 \times 10^{-8} \pi r_{12} D \quad (6)$$

The diffusion constant for benzophenone in benzene was calculated by means of the empirical equation of Chang and Wilke.<sup>16</sup> The molar volume at the boiling point was estimated using the atomic increments listed by Partington.<sup>17</sup> The calculated diffusion constant,  $1.90 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>, was used for both benzophenone triplet and benzhydrol. The value of  $r_{12}$  was taken at 10 Å. The calculated value of  $k_{\text{Dif}}$  is  $2 \times 10^9$  liter mole<sup>-1</sup> sec.<sup>-1</sup>. This implies an upper limit for  $k_d$

$$k_r \leq 2 \times 10^9 \text{ l. mole}^{-1} \text{ sec.}^{-1}; \quad k_d \leq 1.0 \times 10^8 \text{ sec.}^{-1}$$

However, it was possible to show that reaction 3 is not diffusion controlled. When  $\alpha$ -deuterio-benzhydrol was used as the reductant, a new linear relationship between  $1/\Phi_B$  and  $1/[\text{BHD}]$  was obtained (see Table III and Fig. 1); the limiting quantum yield is still 1.0, but the slope of the line is now 0.133. This indicates that  $k_{r(\text{H})}/k_{r(\text{D})} = 2.7$ . While the result is difficult to interpret exactly, it indicates that reaction does not occur on every encounter. If 2.7 is a "normal" isotope effect for this type of hydrogen-transfer reaction, the

result would indicate that the diffusion rate is at least ten times  $k_{r(\text{H})}$ ; however, if the "true" isotope effect is larger, as is true in many reactions,<sup>18</sup> the difference between  $k_{\text{Dif}}$  and  $k_{r(\text{H})}$  will become smaller. Perhaps a safe estimate, considering the conservative nature of the estimate of the diffusion rate and the possible isotope effect, is  $k_r \leq 2 \times 10^8$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, i.e., smaller than the diffusion controlled rate by at least a factor of five.

TABLE III  
PHOTOREDUCTION OF 0.1 *M* BENZOPHENONE WITH  $\alpha$ -DEUTERIOBENZHYDROL IN BENZENE

Run no.	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> -CDOH	% conversion of benzophenone	Quantum yield <sup>a</sup> of benzophenone	$-\frac{\Delta[\text{Benzpinacol}]^b}{\Delta[\text{benzophenone}]}$
1	0.10 <sup>c</sup>	25.5	0.41 <sup>d</sup>	1.00
2	.050 <sup>c</sup>	12.9	.24 <sup>d</sup>	1.12
3	.030 <sup>c</sup>	10.0	.16 <sup>d</sup>	...

<sup>a</sup> Quantum yield calculated assuming quantum yield for disappearance of benzophenone in isopropyl alcohol is unity. <sup>b</sup> Benzpinacol determined by lead tetraacetate assay. <sup>c</sup> Degassed solution. <sup>d</sup> Light intensity =  $2.58 \times 10^{19}$  quanta min.<sup>-1</sup>.

Now let us consider the value to be expected for  $k_d$  if B\* is the lowest excited singlet state of benzophenone. Although benzophenone fluorescence never has been observed, we can estimate the rate at which fluorescence would be expected to occur if there were no competing deactivation processes. The solution spectrum of benzophenone, measured with a Cary spectrophotometer, shows clear resolution of the O → O band with a maximum at 3750 Å. Assuming that the band is symmetrical, we estimate the integrated intensity of the total band as  $\int \epsilon \, d\bar{\nu} = 2.5 \times 10^8$ ; this estimation leads to a calculated mean lifetime value of the excited state of  $2 \times 10^{-7}$  sec.<sup>19</sup> However, since fluorescence is observable when the quantum yields are 0.01 or less,<sup>21</sup> we can assume that the mean lifetime is actually less than  $2 \times 10^{-9}$  sec. In fact, Kasha<sup>22</sup> has estimated that more than 99.9% of the excited singlets produced by  $n \rightarrow \pi^*$  transitions are converted to triplets in rigid media. This leads to a value of  $2 \times 10^{-10}$  as the *minimum* lifetime of benzophenone singlets and gives a value of  $k_{d(\text{S})}$ , the expected rate constant of deactivation of the lowest excited singlet, of  $5 \times 10^9$  sec.<sup>-1</sup> or greater. Since conservative estimates have been used at every stage, we can conclude safely that

$$k_{d(\text{S})} > k_{d(\text{B}^*)}$$

These data compel the conclusion that the excited state responsible for reaction 1 must be longer lived than the lowest singlet state of benzophenone. The only attractive hypothesis left is the assumption that, even in solution at room temperature, the excited state produced by the  $n \rightarrow \pi$  transition of benzophenone undergoes quantitative intersystem crossing with the production of a long-lived triplet. The latter is, therefore, the chemically reactive species in the photoreduction reaction.

(18) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(19) The formula<sup>20</sup> used was  $\tau = g_u/g_v n^2 \bar{\nu}^2 \int \epsilon \, d\bar{\nu}$ .

(20) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **67**, 994 (1945).

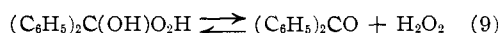
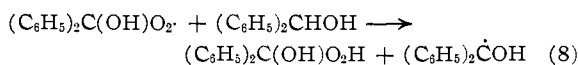
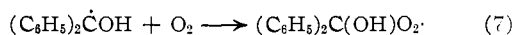
(21) See, for example, M. Fust, H. Kallmann and E. H. Brown, *J. Chem. Phys.*, **26**, 1321 (1957).

(22) M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950).

(14) G. V. Schultz, *Z. physik. Chem.*, **8**, 284 (1956).  
 (15) M. v. Smoluchowski, *ibid.*, **92**, 129 (1918).  
 (16) P. Chang and C. R. Wilke, *J. Phys. Chem.*, **59**, 592 (1955).  
 (17) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. II, Longmans, Green and Co., New York, N. Y., 1951, p. 24.

We were plagued by the thought that the interpretation outlined above might be bedeviled by complex formation between benzhydrol and benzophenone. It is clear that quite a different interpretation would have to be rendered if it should turn out that absorption only resulted in reaction if the absorbing ketone molecule were bound by hydrogen bonding to a molecule of alcohol. Two types of measurements allayed our concern on this score: First, a brief study of solutions of benzophenone and benzhydrol in benzene showed evidence for only a small amount of association; second, irradiation of solutions of the ketone and benzhydrol in acetonitrile and *t*-butyl alcohol gave quantum yields as high as parallel experiments in benzene solution. Since the polar solvents are capable of complexing solute molecules by hydrogen bonding, complexing between the reactants should be minimized. This assumption was borne out by study of the ultraviolet spectrum of benzophenone in *t*-butyl alcohol. In benzene the maximum absorption occurred at 3430 Å.; in *t*-butyl alcohol the maximum was shifted to 3340 Å. This blue shift, which usually accompanies increasing solvent polarity, is considered characteristic of  $n \rightarrow \pi$  transitions.<sup>23</sup> No further change in the spectrum occurred upon addition of 1.0 *M* benzhydrol.

Further revealing information is provided by the effects of paramagnetic solutes on the quantum yields. When the reaction solutions were not degassed, the quantum yields were lower with the effect being especially large in solutions containing low concentrations of benzhydrol; relevant data are contained in Table II. This effect is attributed to the presence of oxygen in the solutions. Furthermore, it is not conceivable that this effect is due primarily to irreversible reactions of diphenylhydroxymethyl radicals with oxygen. Such reactions should not lead to reduction in the rate of disappearance of benzophenone since reactions 7-9 regenerate  $(C_6H_5)_2\dot{C}OH$  while producing hydrogen peroxide from benzhydrol. Assumption that oxygen concentration falls very slowly is consistent with the report by Bäckstrom that the photosensitized oxidation of benzhydrol is very slow.<sup>24</sup>



If it is assumed that the concentration of oxygen in solution remains steady at about its saturation solubility at room temperature ( $\sim 10^{-3}$  mole per liter),<sup>25</sup> the ratio of the rate constant  $k_Q$  for oxygen quenching to the rate constant for hydrogen transfer  $k_r$  can be estimated. The slope of the line through the points determined in the presence of oxygen (Fig. 2) is 0.28. Equation 10 gives the appropriate expression for the quantum yield in the

(23) R. S. Becker, *J. Mol. Spectroscopy*, **3**, 1 (1959).

(24) H. L. J. Bäckstrom, "The Svedberg Memorial Volume," Almquist and Wiksells Boktryckeri, Upsala, 1944, p. 45.

(25) M. Reznikovskii, Z. Tarasaova and B. Dogadkin, *Zhur. Obshchei Khim.*, **20**, 63 (1950); *C. A.*, **44**, 4754 (1950).

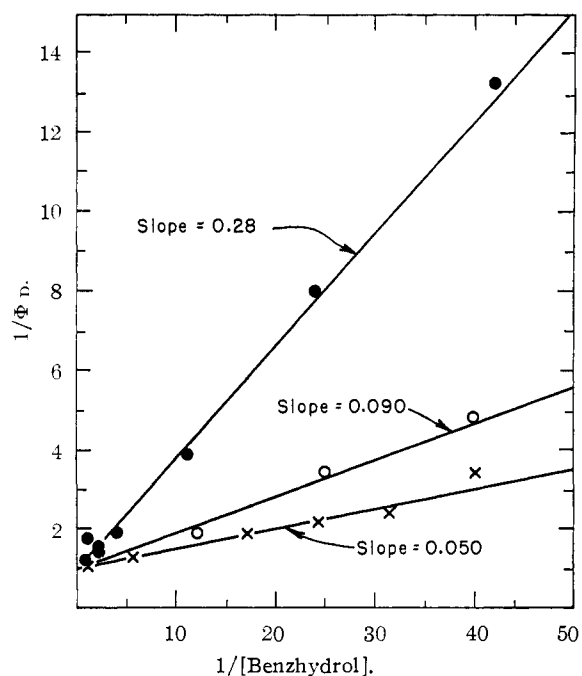


Fig. 2.—Photoreduction of 0.1 *M* benzophenone by benzhydrol in benzene solution: X-X, no additive; ○-○,  $10^{-4}$  *M* Fe(DPM)<sub>3</sub>; ●-●, oxygen ( $\sim 10^{-3}$  *M*).

presence of a quencher

$$\frac{1}{\Phi} = \frac{1}{a} + \frac{k_d + k_Q[Q]}{ak_r[BH_2]} \quad (10)$$

Assuming again that  $a = 1$ , combination of eq. 5 and 10 gives the desired relationship.

$$\frac{k_Q[Q]}{k_r} = \frac{k_d + k_Q[Q]}{k_r} - \frac{k_d}{k_r} = (0.28 - 0.05) \text{ l./mole}^{-1} \\ k_Q/k_r = 230 \text{ mole liter}^{-1}$$

The same treatment has been applied to data for the quantum yields in the presence of  $10^{-4}$  moles per liter of ferric dipivaloylmethide. The slope of the line drawn through the experimental points in Fig. 2 is 0.090, which indicates that  $k_Q/k_r$  is approximately 400. Granted that neither figure is very precise, it is striking that the rate constants for quenching by oxygen and by the iron chelate compound are so similar. In a related study of the quenching of anthracene triplets, Porter and Wright<sup>26</sup> found that oxygen was much more efficient than iron salts. We interpret the similarity of quenching efficiencies in our work as indicating that both quenching reactions are either diffusion controlled or close to it. Bäckstrom and Sandros<sup>9</sup> found that the rate constant for quenching of biacetyl triplets by oxygen in benzene solution was  $5 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, and Livingston and Tanner<sup>27</sup> found a value of  $2.0 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup> for oxygen quenching of anthracene triplets in bromobenzene. Although we suspect that the latter reaction at least involves a chemical change (photo-oxide formation), we are again impressed that the rate constants look like those for diffusion-con-

(26) G. Porter and M. R. Wright, *J. chim. phys.*, **55**, 705 (1958).

(27) R. Livingston and D. W. Tanner, *Trans. Faraday Soc.*, **54**, 765 (1958).

trolled processes. Bäckstrom has adduced that the quenching of benzophenone triplets by  $\text{NO}^{28}$  is very fast, probably diffusion controlled, and has based his recent estimate of the lifetime of the triplet on the assumption that energy transfer to biacetyl is also diffusion controlled.<sup>5</sup>

If we assume that quenching by ferric dipivaloylmethide is diffusion controlled, we can tentatively evaluate rate constants involved in this and related studies.<sup>12</sup> Table IV contains a summary of all of the rate constants for all reactions in the benzhydrol system based on the assumption that  $k_Q$  for the ferric chelate is  $2 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. This is considered to be a better basis than can be obtained from the oxygen data since the oxygen concentration is not accurately known.

TABLE IV

APPROXIMATE VALUES OF RATE CONSTANTS INVOLVED IN THE REACTION OF BENZOPHENONE WITH BENZHYDROL

Constant	Value
$k_Q$ for ferric dipivaloylmethide	$2 \times 10^9$ l. mole <sup>-1</sup> sec. <sup>-1</sup>
$k_Q$ for oxygen	$1 \times 10^9$ l. mole <sup>-1</sup> sec. <sup>-1</sup>
$k_{r(B)}$	$5.0 \times 10^6$ l. mole <sup>-1</sup> sec. <sup>-1</sup>
$k_{r(D)}$	$1.8 \times 10^6$ l. mole <sup>-1</sup> sec. <sup>-1</sup>
$k_d$	$2.6 \times 10^8$ sec. <sup>-1</sup>

Obviously, the value of  $k_r$  comes out much below the value estimated for the diffusion-controlled process. This conclusion is mandatory, independent of any assignment of absolute values, since quenching and hydrogen transfer are both bimolecular processes; it is evident that tiny amounts of quenchers provide very efficient competition for relatively large amounts of benzhydrol. Since the quenching reactions cannot be faster than diffusion controlled, it is obvious that the hydrogen-transfer rate must fall far short of that rate.

Our results may be compared directly with those of Bäckstrom and Sandros.<sup>5</sup> They estimated the average lifetime ( $\tau = 1/k_d$ ) for the triplet as  $1.9 \times 10^{-6}$  sec.<sup>-1</sup>. This gives a value of  $5.3 \times 10^5$  l. mole<sup>-1</sup> sec.<sup>-1</sup> for the rate constant for deactivation in benzene at 20°. In view of the assumptions involved in the methods of estimation, the agreement is remarkably good; in fact the choice of a method for estimation of the collision rates in solution appears to be a greater source of uncertainty than any of the measurements made in either study. For example, Bäckstrom and Sandros used the value  $10^{10}$  for the rate constant for collision between biacetyl and the triplets. This is larger than we would have estimated by our procedure. The use of a value of  $2 \times 10^9$  would reduce their estimated value of  $k_d$  to  $10^5$ . Since accurate data for linear diffusion rates in solution are reasonably available,

(28) H. L. J. Bäckstrom, A. Steneryr and P. Perlmann, *Acta Chem. Scand.*, **12**, 8 (1958).

the greatest uncertainty in the estimation of absolute rate constants by studying reactions in competition with diffusion-controlled processes arises from uncertainty in the assignment of collision diameters to non-spherical molecules.

The lifetime of the triplet state is shorter by 3–4 orders of magnitude than values reported<sup>29,30</sup> for phosphorescence lifetimes. This is to be expected since no phosphorescence is observed in benzene solutions at room temperature.

The indication from this study that quenching by the ferric chelate is diffusion controlled adds new food for thought concerning quenching by paramagnetic solutes. Many reports of fluorescence quenching by nitric oxide, oxygen and metallic compounds are found in the literature. Theory on the subject has been propounded by Karyakin, Terenin and Kalenichenko,<sup>31</sup> who decided that paramagnetic materials could catalyze intersystem crossing only if the two states were close together in energy. This conclusion led Bäckstrom<sup>28</sup> to suggest that covalent bond formation is involved in the quenching of benzophenone triplets by oxygen and nitric oxide since the triplet energy is high above that of the ground state. We believe it is unlikely that such a process can be responsible for quenching by the iron chelate. It is true that the ferric compound is partly reduced to a ferrous compound during the reaction<sup>32</sup> but because the ligand of the chelate is highly sterically hindered and the chelate is generally rather inert, we believe that there is little prospect that any bond-forming reaction of the compound will be diffusion controlled. It seems most probable to us that a mechanism for paramagnetic catalysis similar to that proposed by McConnell<sup>33</sup> to account for catalysis of thermal isomerization of olefin by way of triplet transition state probably is involved in quenching. The weak electronic interactions required to obtain spin correlation between the triplet and the catalyst probably could be accomplished by formation of a charge-transfer complex between the two. If much or all of the energy lost by the triplet in deactivation is transferred to the quencher, this would account for the slow destruction of the latter that is observed.

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(29) D. S. McClure and P. L. Hanst, *J. Chem. Phys.*, **23**, 1776 (1955).

(30) A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956).

(31) A. W. Karyakin, A. N. Terenin and Y. I. Kalenichenko, *Doklady Akad. Nauk SSSR*, **67**, 305 (1949).

(32) Unpublished observations by W. M. Moore and K. Kopecky; details will be published elsewhere.

(33) H. M. McConnell, *J. Chem. Phys.*, **20**, 1043 (1952); **23**, 2440 (1955).