be unimportant. Under these conditions it is likely that the $CH_3O_2^{\neq}$ or $RO_2^{\neq}$ will react either to abstract an H-atom in an early collision after formation or it will be thermallized by collisions before a suitable encounter with O_2 can occur. Once the CH_3O_2 or RO_2 radical has been thermallized, an activation energy greater than 25 kcal. would be required to form ozone by reactions 21 or 24; this is so large an energy as to make the reactions unimportant at room temperature. On the other hand the reverse of reactions 21 and 24, that is the reaction of ozone with an alkoxyl radical to form an alkylperoxyl radical and oxygen, is about 25 kcal. exothermic; if ozone is formed in the system by any path whatsoever, it should be rapidly removed, not only by reaction with alkyl free radidals (analogs to 22), but by reaction with alkoxyl radicals as well. Thus a very low stationary concentration of ozone would be quickly established.

There seems to be substantial evidence which supports the disproportionation reaction 5 in the photoöxidation of azomethane at room temperature.[2,3] The rather analogous disproportionation reaction 11 may also occur, and 11 may be followed by 13 and 23. Some evidence in this regard has been cited in the formic acid mechanism discussion above. The high exothermicity of these reactions suggests a low activation energy and their possible importance. Obviously some reliable estimates of the ozone concentrations in these systems under different conditions must be determined before a realistic evaluation of mechanisms can be made. A suitable method for such measurements has not yet been devised by these authors.

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The Quenching Effect of Naphthalene on the Photoreduction of Benzophenone

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Quantum yield determinations on the photoreduction of benzophenone have been used as a method of evaluating the efficiency of the triplet to triplet energy transfer between benzophenone and naphthalene. The ratio of the quenching rate constant to the reaction rate constant has been determined by two methods: benzhydrol concentration as a variable; naphthalene concentration as a variable. Naphthalene quenches photo-excited benzophenone as efficiently as oxygen and other paramagnetic molecules. The evidence indicates that the triplet to triplet energy transfer process must be diffusion controlled and gives additional support to the postulate that the triplet state is the chemically reactive state of benzophenone. A novel method of actinometry involving the limiting quantum yield of benzophenone is demonstrated.

The photochemistry of benzophenone in solution has been studied extensively.[1-3] Evidence has been accumulated to show that the triplet is the chemically reactive excited state[1] and that the limiting quantum yield for the disappearance of benzophenone is unity. Certain paramagnetic substances quench the triplet state of benzophenone and lower the quantum yield.[1] Oxygen and ferric dipivaloylmethide were found to be efficient quenchers, but aluminum dipivaloylmethide did not alter the photochemical activity. No appreciable quenching of the excited state by benzene, toluene, cumene, isopropanol or benzhydrol has been observed.[1,2]

Terenin and Ermolaev[4] demonstrated that benzophenone could photosensitize the phosphorescence of naphthalene in EPA glass at 77°K. The energy transfer process was such that the sensitized phosphorescence was more efficient than the normally induced phosphorescence. Simultaneously, the benzophenone phosphorescence was quenched. These workers suggested that a triplet to triplet energy transfer (with total spin conservation) was the mechanism for the process. The excited singlet state of naphthalene lies at a higher energy level than that of the excited singlet of benzophenone, but the triplet of naphthalene lies at a lower energy level than that of benzophenone. They postulated that energetically favorable triplet to triplet transfers might be of a general nature, and they illustrated several cases. Using biacetyl and benzil, which show phosphorescence under these conditions, Bäckström and Sandros[5] have found the same effect in solution at room temperature.

Recently, Farmer, Gardner and McDowell,[6] using electron spin resonance, demonstrated that the triplet state of naphthalene could be induced with photo-excited benzophenone. This work was done in EPA glass at 77°K. Porter[7] has mentioned studies involving flash photolysis techniques in which the triplet state of naphthalene was produced by benzophenone photosensitization.

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Experimental

Materials.—Reagent grade benzophenone, benzhydrol and naphthalene were used without purification since recrystallization showed no change in the melting point. Benzene (reagent grade, thiophene free) which imparted no color to concentrated sulfuric acid was distilled and used immediately to prepare solutions.

Apparatus.—An enclosed photochemical reactor was constructed which consisted of an 800- C SAH Westinghouse short arc mercury lamp at the focal length of a quartz lens (2.5 in. dia., 6 in. focal length). The collimated light beam was passed along a Cenco optical bench on which were mounted suitable filters and holders. The cell holder from a Beckman DU spectrophotometer was used to locate the tube in the light path. The cross-section of the collimated light beam was uniform to within 3% as determined by simultaneous photolysis of two identical solutions (see Table I). The solutions were cooled by a small fan, and the temperature rise in the vicinity of the solutions was approximately one degree per hour.

Filter System.—The filter system consisted of a saturated copper sulfate solution in a 2 cm. thick quartz cell and a Corning CS7-37 glass filter. This filter system isolated the mercury band at 3660 A. and passed very little light at other wave lengths. The efficiency of the filter system with the mercury arc was determined on an ARL two meter emission spectrograph.

Procedure.—The photolysis cells were 13 × 100 mm. Pyrex test tubes matched in pairs as to diameter and absorbance. Stock solutions of benzophenone, benzhydrol and naphthalene in benzene were prepared at concentrations of 0.5, 0.5 and 0.01 *M*, respectively, and all sample solutions were prepared from the stock solutions by dilution. Three milliliters of solution were placed in a test tube which had been fused to a ground glass joint. The tube was connected to a vacuum system, and the air removed during a minimum of three freeze-thaw cycles. The tube was sealed and stored in the dark until photolyzed. The photolyses were carried out to 20% benzophenone disappearance for the actinometer solutions, and where possible, over 10% for the sample. When long photolysis periods were required, several actinometer solutions were exposed consecutively throughout the time needed to irradiate one sample solution.

The solutions in which the concentration of benzophenone was 0.1 *M* were analyzed spectrophotometrically, after a 1 to 25 dilution, at five wave lengths: 330, 335, 340, 345 and 350 mμ. An unphotolyzed solution was used as standard and the absorbance ratios were averaged for the five readings.

Actinometry.—A novel method of actinometry was developed which eliminated errors due to light fluctuations and which may give inherently better quantum yield values than conventional techniques. Actinometer solutions, which contained 0.1 *M* benzophenone and a constant initial concentration of benzhydrol in benzene, were photolyzed *simultaneously* with sample solutions which contained 0.1 *M* benzophenone and varying initial concentrations of benzhydrol. No quantum yield value was assumed for the actinometer solution. Instead, the ratio of the concentrations of benzophenone photolyzed in the actinometer solution and the sample solution were used directly. The light absorbed and the time of photolysis was the same for both solutions, so the ratio of the concentrations of benzophenone photolyzed should be equivalent to the ratio of the quantum yields. If Φ_{act}/Φ_{sam} is plotted against the reciprocal of the benzhydrol concentration of the sample solution, the intercept of the linear relationship will give the quantum yield of the actinometer. It has been observed that *the limiting quantum yield for the photoreduction of benzophenone is unity.*[1] Once the quantum yield of the actinometer has been determined *independently* of an external standard, the quantum yield of the sample solutions can be calculated for any concentration of benzhydrol.

The method was tested on a standard solution 0.1 *M* benzophenone with 0.1 *M* benzhydrol in benzene and the data are given in Table I. The relationship is graphed in Fig. 1 where the intercept is 0.68, and the slope is 0.0308. The quantum yield for a solution of this concentration has been determined to be 0.69.[1] This method of actinometry will be tried on other solutions not containing benzophenone.

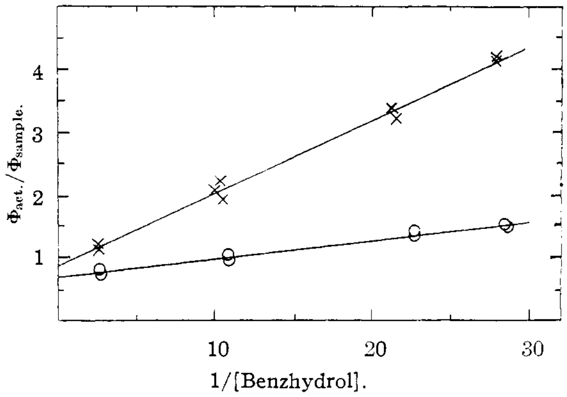

Fig. 1.—Photoreduction of 0.1 *M* benzophenone with benzhydrol in benzene solution: X—X, 2 × 10^{-4} *M* naphthalene (actinometer solution contained 0.375 *M* benzhydrol, no naphthalene), slope 0.116, intercept 0.88: O—O, no additive (actinometer solution contained 0.10 *M* benzhydrol), slope 0.0308, intercept 0.68.

TABLE I

PHOTOREDUCTION OF 0.1 *M* BENZOPHENONE[a] WITH BENZHYDROL IN BENZENE AT 3660 Å.

Molarity benzhydrol	% Conversion benzophenone	Φ act./Φ sample
0.375	20.8	0.745
Act.[b]	15.5	
0.375	20.1	0.788
Act.	15.9	
0.10	16.7[c]	1.00
Act.	16.7	
0.10	15.2[c]	1.02
Act.	14.9	
0.050	10.8	1.44
Act.	15.5	
0.050	10.5	1.33
Act.	14.0	
0.040	10.4	1.47
Act.	15.3	
0.040	10.0	1.56
Act.	15.6	
0.040	11.7	1.55
Act.	18.1	

[a] Absorbed light intensity was approximately 10^{16} quanta/sec. [b] Actinometer solution was 0.1 *M* benzophenone with 0.1 *M* benzhydrol in benzene. [c] Demonstrates beam uniformity.

Results and Discussion

The mechanism for the photoreduction of benzophenone, as proposed by Moore, Hammond and Foss,[1] is based on a simple competition for the excited state between chemical reaction, collisional deactivation and physical quenching. The rate law from such a mechanism is given in equation 1, where Φ is the quantum yield for benzophenone disappearance, k_d is the rate constant for collisional

$$\frac{1}{\Phi} = 1 + \frac{k_d + k_q\,(Q)}{k_r(BH_2)} \qquad (1)$$

deactivation, k_q is the quenching rate constant, k_r is the reaction rate constant, BH_2 is benzhydrol and Q is naphthalene. From equation 1 it is evident that there are two methods of determining the ratio, k_q/k_r, which is a measure of quenching efficiency: (1) quantum yield determinations at constant benzhydrol concentration and variable naphthalene concentration, (2) quantum yield determinations at constant naphthalene concentration and variable benzhydrol concentration.

The relationship between the ratio Φ_{act}/Φ_{quench} and the naphthalene concentration is shown in Fig. 2 and the data tabulated in Table II. The actinometer solution contained 0.1 M benzophenone and 0.1 M benzhydrol in benzene. The quenched solutions were identical to the actinometer solution in concentration of benzophenone and benzhydrol, but amounts of naphthalene varying from 2.5×10^{-4} to $2 \times 10^{-3} M$ were added. The intercept of the graph must necessarily be one

Table II

Photoreduction of 0.1 M Benzophenone[a] with 0.1 M Benzhydrol and Naphthalene in Benzene

Molarity naphthalene	% Conversion benzophenone	Φ_{act}/Φ_{quench}
2×10^{-3}	10.3	7.80
Act.[b]	80.4[c]	
2×10^{-3}	10.1	7.45
Act.	75.3[c]	
1×10^{-3}	9.9[d]	4.12
Act.	40.8	
1×10^{-3}	5.5	4.40
Act.	29.8	
5×10^{-4}	3.4	2.47
Act.	8.4	
5×10^{-4}	7.6	2.86
Act.	21.7	
5×10^{-4}	6.8	2.94
Act.	20.1	
2.5×10^{-4}	11.6	1.61
Act.	18.7	
2.5×10^{-4}	11.2	1.79
Act.	20.0	

[a] Absorbed light intensity was approximately 1×10^{16} quanta/sec. [b] Actinometer solution was 0.1 M benzophenone with 0.1 M benzhydrol in benzene. [c] Four actinometer solutions were used during the run. [d] Two actinometer solutions were used during the run.

$$\frac{\Phi\ \text{act}}{\Phi q} = 1 + \left\{\frac{k_q/k_r}{k_d/k_r + (\text{BH}_2)}\right\}(\text{Q}) \qquad (2)$$

The slope is equal to the naphthalene dependent term and the denominator of that term can be evaluated from data given for the unquenched series of runs depicted in Fig. 1. If the quenching term is neglected in equation 1, it becomes apparent that k_d/k_r is equal to the slope divided by the intercept, which is 0.0453. The slope of the line in Fig. 2 is 3350, which gives k_q/k_r a value of 453.

At a constant naphthalene concentration of $2 \times 10^{-4} M$, the benzhydrol concentration was varied from 0.375 M to 0.040 M, and the benzophenone concentration was 0.1 M. The results are shown in Fig. 1 and the data tabulated in Table III. The actinometer solution in this case was 0.1 M benzophenone with 0.375 M benzhydrol in benzene. The value of 0.88 for the intercept agrees with the quantum yield found for 0.1 M benzophenone with 0.375 M benzhydrol.[1] The slope was 0.116 as determined by the method of least squares. The slope divided by the intercept permits calculation of the ratio k_q/k_r, which was found to be 435.

Table III

Photoreduction of 0.1 M Benzophenone[a] with 2×10^{-4} M Naphthalene and Benzhydrol in Benzene

Molarity benzhydrol	% Conversion benzophenone	Φ act./Φ quench
0.375	16.9	1.17
Act.[b]	19.8	
0.375	18.5	1.11
Act.	20.6	
0.375	11.7	1.19
Act.	13.9	
0.375	10.9	1.23
Act.	13.4	
0.10	11.5	2.17
Act.	24.9	
0.10	12.9	1.92
Act.	24.9	
0.10	12.5	1.99
Act.	24.9	
0.10	6.6	1.91
Act.	12.6	
0.10	5.6	2.09
Act.	11.7	
0.10	5.4	2.12
Act.	11.6	
0.10	5.6	2.09
Act.	11.7	
0.050	7.3	3.23
Act.	23.6	
0.050	6.5	3.36
Act.	21.8	
0.050	6.7	3.38
Act.	22.7	
0.050	6.2	3.32
Act.	20.6	
0.040	8.6	4.13
Act.	35.5[c]	
0.040	8.2	4.20
Act.	34.4[c]	

[a] Absorbed light intensity was approximately 1×10^{16} quanta/sec. [b] Actinometer solution was 0.1 M benzophenone with 0.375 M benzhydrol in benzene. [c] Two actinometer solutions were used during the run.

The results verify previous work[1] and also confirm the simple mechanism by demonstrating the predicted dependence of the quantum yield on quencher concentration. Furthermore, since naphthalene quenches the photoreduction of benzophenone, this is additional proof that the triplet state, the phosphorescent state and the chemically reactive excited state are one and the same for benzophenone.

The value of k_q/k_r for oxygen quenching and ferric dipivaloylmethide quenching of benzophenone[1] is 230 and 400, respectively. Since paramagnetic quenching has been shown to be diffusion controlled,[8,9] naphthalene quenching must

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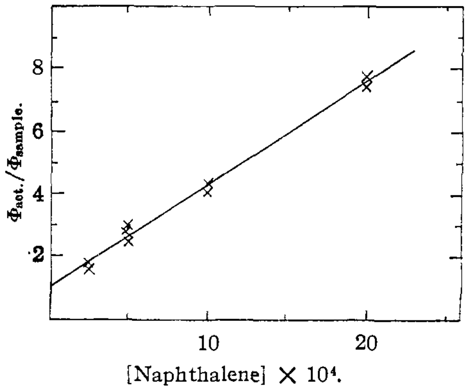

Fig. 2.—Photoreduction of 0.1 M benzophenone with naphthalene and 0.10 M benzhydrol in benzene solution (actinometer solution contained 0.10 M benzhydrol, no naphthalene), slope 3350., intercept 1.0.

also be diffusion controlled even though quenching occurs by a different energy dissipation mechanism. Oxygen and other paramagnetic substances are postulated to quench triplet states through the perturbation caused by the uncoupled spins. Evans,[10] in his study of singlet to triplet absorption spectra which are produced under the influence of high oxygen pressures, has vividly demonstrated paramagnetic perturbation on electronic transitions.

Molecules such as naphthalene, which are diamagnetic, must quench triplet states because of the favorable position of their lowest triplet state. Recently, two communications[11] have shown the practical application of predicted photosensitization with acceptors possessing triplet states of lower energy levels than benzophenone.

From the ratio k_q/k_r, it would appear that naphthalene is more efficient as a quencher than oxygen. This may be due to the fact that oxygen slowly reacts with the benzophenone–benzhydrol system while naphthalene is chemically inert.[1]

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CONTRIBUTION FROM NOYES CHEMICAL LABORATORY UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

The Infrared and Nuclear Magnetic Resonance Spectra of Ethyllithium

BY THEODORE L. BROWN, D. W. DICKERHOOF[1] AND D. A. BAFUS

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The infrared spectra for ethyllithium in hydrocarbon solvents, in a Nujol mull, and as a solidified melt are reported. Some bands previously associated with various associated and non-associated species of ethyllithium are shown to be due to lithium ethoxide. The proton and lithium n.m.r. spectra are reported. The spectral results, along with other experimental observations, suggest that ethyllithium exists as a single species in hydrocarbon solvent, probably as a hexamer. Models for both a hexamer and tetramer form of ethyllithium are presented and discussed in terms of the presently known properties of the compound.

Introduction

The structures and physical properties of lithium alkyls have been of considerable interest for many years. Recent infrared[2] and mass spectral[3] studies have shed new light on the properties of ethyllithium in both solution and the vapor phase.

It has become clear in the course of our work with lithium alkyls that decomposition has been an important factor in earlier incorrect interpretations of infrared spectral and other experimental results. In the work reported here we have identified the decomposition products which give rise to spurious absorptions in the spectra and have obtained data for material free from decomposition. Infrared and n.m.r. spectra for ethyllithium in hydrocarbon solvents are reported. Models for the structures of the compound in solution and in the vapor phase are proposed and discussed.

Experimental

Materials.—**Lithium.**—Lithium metal was obtained from Lithium Corp. of America or Maywood Chemical Works. Both bulk form or dispersions (the latter obtained from Lithium Corp. of America) were employed.

Ethyllithium.—Ethyllithium was prepared by methods previously described.[4] All results reported were obtained with samples which were recrystallized from an appropriate solvent (pentane, hexane, cyclohexane or benzene) in an inert atmosphere box.[5]

Solvents.—Reagent grade benzene was dried over sodium wire before use. Commercial grade cyclohexane, hexane and pentane were chromatographed through acid-washed alumina and stored over sodium wire. All solvents were thoroughly deaerated by flushing with argon before they were placed in the inert atmosphere box.

Lithium Ethoxide.—200 ml. of dry benzene was placed in a 500 ml. round-bottom flask under dry nitrogen. To this were added 3.5 g. (0.5 mole) of lithium metal and 29.2 ml. (0.5 mole) of absolute ethanol. The reaction was allowed to proceed to completion and benzene then removed by distillation at reduced pressure. Lithium ethoxide remains as a white amorphous solid.

Variations in the above procedure were also carried out. In one preparation a 50% excess of ethanol was employed. After removal of the solvent the white solid was heated for a time to remove the last trace of ethanol. On another occasion less than the stoichiometric quantity of ethanol was employed. The lithium ethoxide prepared in this instance was contaminated with lithium metal, but there was presumably no unreacted alcohol present.

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