

acid which had been three times recrystallized from water was used.

Sodium methoxide was prepared from reagent grade sodium and pure methanol. The sodium pellets were first freed of surface impurities by one washing with ether and several washings with pure methanol. The final solution was standardized by potentiometric titration, using constant boiling hydrochloric acid as primary acidimetric standard.²⁸

Preparation of Solutions.—The buffered solutions were prepared from fresh solutions of benzoic acid and sodium methoxide in methanol. The synthetic titers were confirmed by potentiometric titration in anhydrous methanol. Satisfactory end-points could be obtained in the titration of sodium benzoate with hydrochloric acid even in solutions of concentration as low as $2 \times 10^{-4} M$ and acid/base ratios as high as 2700. At the latter acid/base ratio the benzoate concentration, as calculated from the amounts of benzoic acid and sodium methoxide used in the solution preparation, was 6% less than the analytical value. This gives an estimate of 0.002 mole per cent for the benzoate impurity in the sample of benzoic acid obtained from the National Bureau of Standards. In a few cases, a very high acid/base ratio was checked by measuring the pH of the solutions with glass and calomel electrodes. The pH meter was calibrated in methanol with a benzoic acid–sodium benzoate solution of known, somewhat higher, pH.

All of the reaction mixtures were analyzed for water by Karl Fischer titration after the completion of the experiment. The water titers were usually below 0.01 molar, and always below 0.02 molar. The kinetic effect of water in buffered solutions is

(28) C. W. Foulk and M. Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923).

quite small; the deliberate addition of 1 *M* water to one of the solutions caused a doubling of R_M .

In experiments involving acid/base ratios greater than 1000 the glassware was pretreated with solutions of the same nominal concentration, as described in a previous paper.¹¹

Most of our experiments were done in air-saturated solutions. However, we did a few experiments in outgassed samples. Outgassing did not significantly affect the coefficient m in eq. 9 and 10, nor did it have a significant effect on the rate, as illustrated in Table VI.

The air-saturated samples were sealed with corks lined with Saran, and were further sealed against the possible seepage of atmospheric moisture by a strip of Parafilm (paraffin-coated polyethylene). The procedure gave satisfactory seals, and eliminated the danger of changes of composition which is always present when sample tubes are sealed with a torch.

Instrumental.—All measurements were made at a frequency of 60 Mc. per second. Details concerning the instrument and measuring techniques have been reported in a previous paper.¹¹ Great care was always exercised in obtaining the highest possible homogeneity and stability. Measurements were rejected if $(1/T_2)_{ref}$ changed by more than 20% during a measurement.

Temperature control was within $\pm 0.25^\circ$ at -81.6° and within $\pm 0.05^\circ$ at 24.8° .

Conductance Measurements.—The conductance of KCl in methanol was measured by standard techniques at -78.8° to a precision of $\pm 0.25\%$. Temperature control was obtained by immersing the cell in a Dry Ice–acetone bath. The cell constant was determined at 25° with KCl in methanol.²⁹

(29) J. P. Butler, H. I. Schiff and A. P. Gordon, *J. Chem. Phys.*, **19**, 752 (1951).

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Decay Kinetics of the 1-Naphthaldehyde and Benzophenone Triplet States in Benzene^{1a}

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Flash excitation studies have been made on the metastable (triplet) states of 1-naphthaldehyde and benzophenone in benzene solution with added hydrogen donors and heavy metal chelates. This technique permits direct measurement of the rate constants for triplet decay, k_d , hydrogen abstraction, k_r , and triplet quenching, k_q . The ratios k_d/k_r and k_q/k_r calculated from the direct measurements agree well with previous values for the ratios obtained from photochemical data. The effect of impurities is discussed and found to play a major role in the decay of triplet states in solution. The short lifetime of benzophenone triplet in benzene solution seems to be anomalous.

The excited state involved in the photochemical formation of pinacols from aromatic carbonyl compounds has been identified as the lowest triplet state of the carbonyl.^{1b-3} Recent work on this reaction has been directed toward the measurement of the relevant rate constants for processes involving the excited state, such as energy degradation or hydrogen abstraction.² The ratios of these rate constants are readily obtained by standard photochemical kinetic methods, but the absolute values are, of course, more difficult to establish. In the case of the reaction between benzophenone and various donors, Hammond, *et al.*,² have measured the effect of various quenching species on the quantum yield of benzophenone disappearance. Making the assumption that the quenching process is diffusion controlled, the quenching rate constant was estimated and the other kinetic constants evaluated. For benzophenone, absolute lifetimes were obtained which were in good agreement with those deduced by Bäckström and Sandros³ from a study of the benzophenone sensitized phosphorescence of biacetyl. Here again, how-

ever, it was necessary to assume a diffusion controlled rate for the energy transfer process.

Previous attempts to observe directly the triplet state of benzophenone in photochemically active fluid solvents were unsuccessful, due essentially to the short lifetime of the triplet and the overlap of its absorption with that of the ketyl radical.^{4,5} Using flash excitation equipment with short time resolution, we have now been able to distinguish the short-lived triplet from the ketyl radical and to measure directly the rate constants for hydrogen abstraction and energy degradation.

1-Naphthaldehyde was found not to form pinacols when irradiated in alcohols or benzene.⁶ This lack of reactivity readily permits the study of energy degradation and quenching processes of the naphthaldehyde triplet by flash techniques. The naphthaldehyde triplet decay and quenching data, besides being of intrinsic interest, may be germane to the benzophenone case as can be judged by the over-all consistency of the results.

Experimental

Materials.—1-Naphthaldehyde was E. K. White Label which was twice vacuum distilled with the middle third being taken each time. The product boiled at 101° at about 1 mm. The infrared spectrum of the purified naphthaldehyde was identical

(1) (a) This work was supported by a grant from the U. S. Atomic Energy Commission to Brandeis University (No. AT(30-1)-2003). (b) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *J. Am. Chem. Soc.*, **80**, 1068 (1959); J. N. Pitts, H. W. Johnson and T. Kuwana, Symposium on Reversible Photochemical Processes, Durham, No. Carolina, April, 1962.

(2) (a) W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); (b) G. S. Hammond, W. P. Baker and W. M. Moore, *ibid.*, **83**, 2795 (1961).

(3) H. I. J. Bäckström and K. Sandros, *Acta. Chem. Scand.*, **14**, 48 (1960).

(4) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

(5) D. McClure and P. Hanst, *J. Chem. Phys.*, **23**, 1772 (1955).

(6) G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

with that given in the Sadtler catalog. Ultraviolet absorption spectra were taken in a number of solvents. The solvents, wave length maxima in Ångströms (and molar decadic extinction coefficients where obtained) are: water 3200 (7770), 2425 (16,890), 2120 (46,490); ethanol 3270, 3130, 2430, 2120; benzene 3290 (7090), 3150 (7910); cyclohexane 3290 (7300), 3120 (7900), 2490 (21,700), 2440 (20,000), 2120 (37,100).

Benzophenone (Fisher Certified Reagent Grade) was recrystallized from alcohol. Benzhydrol (E. K. White Label) was shown by gas chromatography to be free from benzophenone and benzpinacol and was used directly from the bottle.

Benzene for some runs was Fisher Certified Reagent Grade (thiophene-free) taken directly from a freshly opened bottle. Such benzene is referred to below as "unpurified." For the rest of the experiments the benzene was especially purified by the following procedure.⁷ It was shaken with successive portions of concentrated sulfuric acid until the acid layer remained colorless. The wet benzene was shaken with aqueous sodium bicarbonate to deacidify it, dried over P_2O_5 , and decanted onto liquid sodium-potassium alloy. The mixture was refluxed for a day and then distilled through a 91-cm. column, packed with glass helices, into a flask containing clean potassium. Whenever benzene was needed it was refluxed for a few hours over this potassium (molten) and distilled through the above column. All stock solutions were prepared and all experiments with quenchers were done with this benzene as solvent.

Ferric acetylacetonate, $Fe(AA)_3$, was prepared by adding 2,4-pentanedione and NaOH to an aqueous solution of ferric chloride, extracting the product in benzene, evaporating the solvent, vacuum drying the product, and twice recrystallizing it from alcohol. The melting point of the deep red product was $180 \pm 3^\circ$, the large error being due to a tendency to decompose (perhaps to iron oxide) when heated. The spectrum in benzene has maxima (and molar decadic extinction coefficients) at 4360 Å. (3410) and 3530 Å. (3390). The sample of ferric dipivaloyl-methide, $Fe(DPM)_3$, was kindly supplied by Professor George Hammond. Its spectrum in benzene had maxima (and extinction coefficients) at 4360 Å. (3980) and 3570 Å. (4040).

Experimental Technique.—The flash photolysis apparatus has been described previously.⁸ Some of the present experiments were done with an oxygen-filled quartz flash lamp,⁹ operated at 8 kv. and 2 μ f., instead of the lamps previously used. Samples were prepared by diluting appropriate volumes of stock solutions of the carbonyl compound and quencher or reactant in benzene to the desired concentrations and degassing and sealing off the Pyrex flash cell assemblies under "stick vacuum." The degassing procedure involved the usual freezing, pumping and thawing cycles, augmented by vigorous agitation of the solution under vacuum. Since some of the solvent was always lost by the freezing and pumping procedure, the concentrations in the flash cells were determined spectrophotometrically.

The data were treated, as in earlier work in this laboratory,^{8,10} by employing the rate law

$$-dT/dt = k_1T + k_2T^2 + k_3TS + \sum_i k_{4i}TQ_i \quad (1)$$

Here T , S and Q_i are the triplet, ground state, and quencher concentrations, respectively. By substituting the observed change in optical density at an arbitrary time zero after the flash, ΔD_0 , and the optical density change at some later time, ΔD , in equation 1, one may derive

$$d \ln (\Delta D_0/\Delta D)/dt = A + B_\lambda \Delta D \quad (2)$$

In equation 2, $A = k_1 + k_3C_0 + \sum_i k_{4i}Q_i$, C_0 being the initial concentration of carbonyl compound. B_λ is a wave length-dependent combination of rate constants and extinction coefficients. The intercept of a plot of the left hand side of equation 2 versus ΔD gives A , and the variation of A with C_0 or Q_i gives the corresponding rate constant.

Results

1-Naphthaldehyde.—The naphthaldehyde triplet shows a broad absorption with a maximum at 4950 Å. All naphthaldehyde rate data were obtained at this monitoring wave length.

The effect on A of changing the initial concentration of naphthaldehyde in unpurified benzene is shown in Fig. 1. The studies in unpurified benzene were made to establish contact between this work and the photochemical studies of Hammond, *et al.*⁶ The two sets of points in Fig. 1 indicate the effect of repeated flashing.

(7) We are grateful to Mr. J. Fajer for performing this purification.

(8) H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, **80**, 4826 (1958).

(9) S. Claesson and L. Lindquist, *Arkiv Kemi*, **11**, 535 (1957).

(10) H. Linschitz and L. Pekkarinen, *J. Am. Chem. Soc.*, **82**, 2411 (1960).

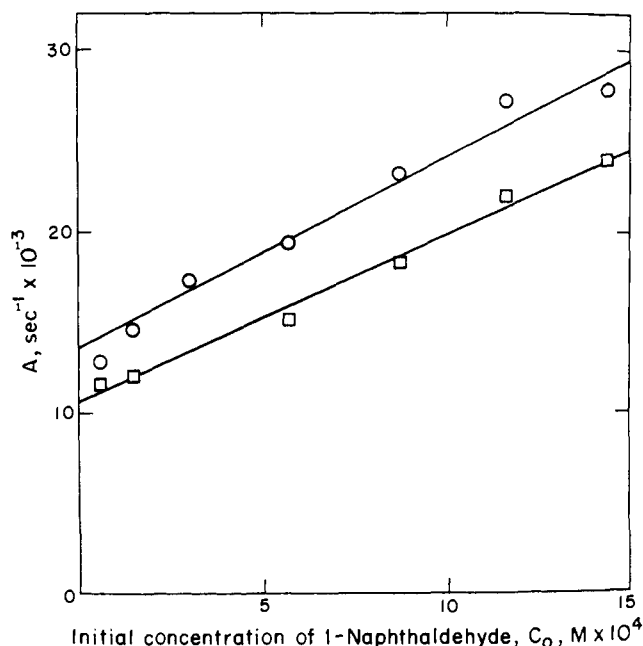


Fig. 1.—Dependence of A , for 1-naphthaldehyde, on the initial concentration of solute: O, average of A values from first three flashes, □ average of A values from the fifth through seventh flashes. Solvent is unpurified benzene.

The rate constant, k_3 , obtained from the upper set of points, is $1.1 \times 10^7 M^{-1} \text{sec}^{-1}$ and the intercept, $k_1 + \sum_i k_{4i}Q_i$, is $13.7 \times 10^3 \text{sec}^{-1}$. The decrease in A with

repeated flashing cannot be explained by destruction of the naphthaldehyde, resulting in a change in A due to the k_3 term, as only slight irreversibility of the reaction (less than 5%) was observed after twenty flashes. The drop is probably due to reactions between the excited naphthaldehyde and traces of quenching impurities (oxygen, peroxides) which destroy the impurities and, perhaps, a small amount of the naphthaldehyde. This sort of "cleanup" action has been noted by other workers.¹¹ The effect did not continue indefinitely at the same rate as values only a bit lower than the lower set of points in Fig. 1 were reached after about twenty flashes. Attempts to obtain a similar plot in purified benzene gave values for A which were lower but somewhat erratic. The scatter probably is due to unavoidable irreproducible trace contamination of the samples.

Figure 2 shows the variation of A with the concentration of added quenchers $Fe(AA)_3$ and $Fe(DPM)_3$. The slopes of the lines give $k_4 = 2.7 \times 10^9$ and $0.9 \times 10^9 M^{-1} \text{sec}^{-1}$, respectively. The extrapolation of these plots to zero added quencher gives $7 \times 10^3 \text{sec}^{-1}$ as an upper limit for the first order decay constant in benzene purified by our procedure. The concentration of $Fe(DPM)_3$ decreased as a consequence of the flash experiments. Four or five flashes caused a nearly constant amount of about $1.3 \times 10^{-6} M$ to disappear in each sample. This amount is insufficient to account for the observed quenching by stoichiometric chemical reactions.

Benzophenone.—Flash excitation of benzophenone in benzene solution resulted in two new absorbing species in the spectral region 5000–5600 Å., easily distinguishable by their decay times (Fig. 3). The long-lived product decays strictly by second order reactions (Fig. 4) and is formed in increasingly higher yields as hydrogen donors such as benzhydrol or ethanol are added. We therefore assign this absorption to

(11) M. Hoffinan and G. Porter, *Proc. Roy. Soc. (London)*, **A268**, 46 (1962).

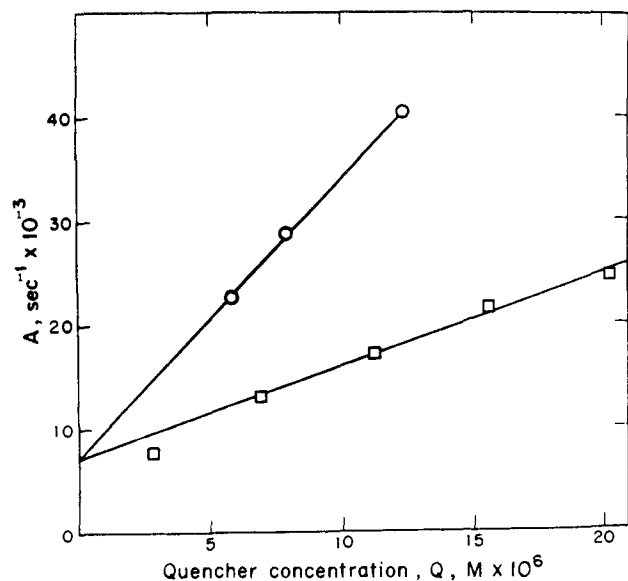


Fig. 2.—Dependence of A , for 1-naphthaldehyde, on the concentration of added quenchers: \circ $\text{Fe}(\text{AA})_3$, \square $\text{Fe}(\text{DPM})_3$. Concentration of 1-naphthaldehyde is $6.6 \pm 0.3 \times 10^{-4} M$. Solvent is purified benzene.

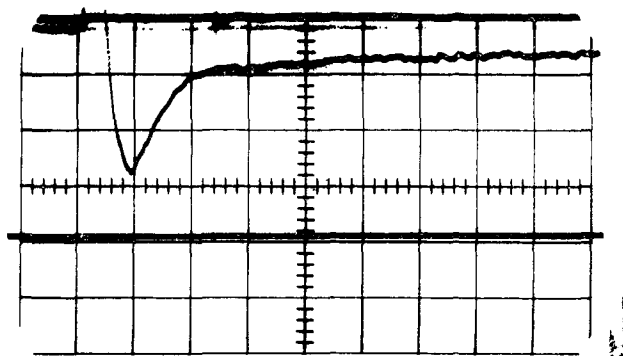


Fig. 3.—An oscillogram showing the short- and long-lived species produced by flash excitation of $2.3 \pm 0.2 \times 10^{-3} M$ benzophenone in purified benzene. The oxygen lamp was used in this experiment: $\lambda = 5250 \text{ \AA}$.; slit width = 35 \AA .; sweep = $100 \mu\text{sec}$. full scale, lower trace, base line; upper trace, initial transmission, 0.10 v./cm .; central trace, effect of the flash, 0.05 v./cm .

the ketyl radical. The spectrum (Fig. 5) and assignment agree with those of Porter and Wilkinson.⁴

The new short-lived product identified here is assumed to be the triplet on the basis of its lifetime and specific quenching reaction with heavy metal chelates. The decay of benzophenone triplet was first order, within the limits of error of the measurements, with a rate constant $k_1 = 1 \times 10^5 (\pm 50\%) \text{ sec}^{-1}$. This is very high compared with the first order decay of unsubstituted aromatic hydrocarbons.^{12,13} The upper line in Fig. 6 is a plot of the variation of A with the concentration of added $\text{Fe}(\text{DPM})_3$. The slope yields a bimolecular rate constant, $k_4 = 0.9 \times 10^9 M^{-1} \text{ sec}^{-1}$, identical within experimental error with that for naphthaldehyde. This is an indication, though not proof, that the quenching is diffusion controlled. The lower line in Fig. 6 is the variation in A with the concentration of benzhydrol and gives a rate constant for hydrogen abstraction from benzhydrol, $k_r = 2 \times 10^6 (\pm 50\%) M^{-1} \text{ sec}^{-1}$. The relatively large uncertainty in k_1 and k_r arises from the extremely short lifetime and from the base line corrections due to radical formation. As was the case with naphthaldehyde, a small portion

(12) H. Linschitz, C. Steel and J. A. Bell, *J. Phys. Chem.*, **66**, 2574 (1962).

(13) G. Jackson and R. Livingston, *J. Chem. Phys.*, **35**, 2182 (1961).

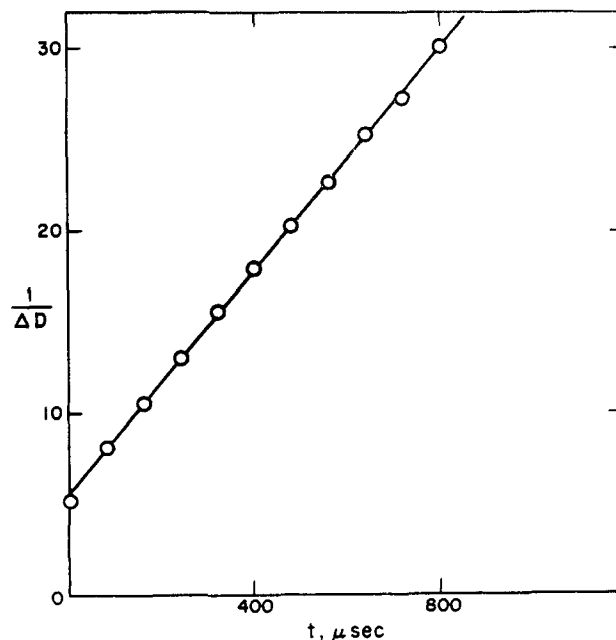


Fig. 4.—A second order plot for the decay of the ketyl radical: benzophenone, $2.3 \pm 0.2 \times 10^{-3} M$; benzhydrol, $1.5 \pm 0.2 \times 10^{-2} M$; $\lambda = 5450 \text{ \AA}$. Solvent is purified benzene.

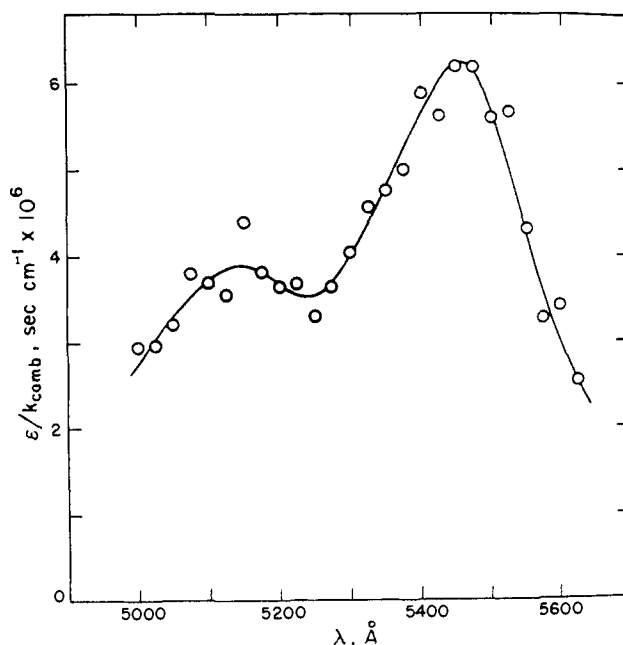


Fig. 5.—Absorption spectrum of the ketyl radical formed by flash excitation of benzophenone in benzene with $3 \times 10^{-3} M$ benzhydrol added. The rate constant, k_{comb} , refers to the second order reaction by which ketyl radicals disappear.

of the quencher disappeared as a consequence of flashing.

The photochemical formation of a substance in degassed solutions of benzophenone which has an optical absorption at slightly longer wave lengths than benzophenone itself^{1b,2a} was confirmed in this work for solutions of benzophenone in benzene, hexane and benzene plus benzhydrol.

Discussion

1. Reaction of Benzophenone Triplet and Benzene.

—The flash data clearly indicate the formation of ketyl radical in benzene without any added hydrogen donors (Fig. 3). This ketyl is presumably formed by hydrogen abstraction from the solvent itself. We will now consider the kinetics of this reaction.

The amount of ketyl formed in pure benzene is about one-eighth of that formed in benzene containing the same concentration of benzophenone with $3 \times 10^{-2} M$ benzhydrol added. Since two ketyl radicals are formed for each triplet that reacts with benzhydrol, about four times as many triplets react in the solutions with added benzhydrol as in pure benzene, assuming the same initial yield of triplets in the two cases. The quantum yield for disappearance of benzophenone under the above conditions with added benzhydrol is between 0.3 and 0.4.^{2a} Hence, we estimate that about one tenth of the benzophenone triplets react in pure benzene to give ketyl radicals. The quantum yield for the disappearance of benzophenone in pure benzene would be, therefore, about 0.1, assuming no back reaction.

Although the ketyl radical apparently disappears by a second order process, we cannot exclude the possibility that this is a back reaction between ketyl radicals and phenyl radicals, which would also give second order kinetics. The disappearance of the ketyl radical appears to be about 1.5 times as rapid in pure benzene as in benzene with added benzhydrol. In the latter case little hydrogen abstraction from benzene occurs, so the predominant radical species is ketyl radical. In the former case both phenyl radicals and ketyl radicals are formed. If the radical reactions are diffusion controlled, then the reaction of phenyl radicals with ketyl radicals should be faster than ketyl radical combination, as the smaller phenyl radical diffuses more rapidly. This could be the explanation for the faster rate of disappearance of ketyl radicals formed in pure benzene. Whether or not the hydrogen abstraction from benzene is reversible does not affect the succeeding argument concerning the rate of the forward reaction.¹⁴

Estimating that one tenth of the benzophenone triplet reacts in pure benzene to yield ketyl radicals, the rate constant for this process may be calculated. One tenth of the decay constant, about 10^4 sec^{-1} , will be due to this reaction. The concentration of benzene is $11.3 M$. The rate constant for reaction of benzophenone triplet abstracting hydrogen atom from benzene is, therefore, about $9 \times 10^2 M^{-1} \text{ sec}^{-1}$.

It is possible, also, to estimate the extinction coefficient for both the ketyl radical and the triplet. If we assume that the second order rate constant for ketyl radical combination, k_{comb} , is about $2 \times 10^9 M^{-1} \text{ sec}^{-1}$, then from Fig. 5 we find that the molar decadic extinction coefficient for the ketyl radical at the 5450 \AA . maximum is about 1.2×10^4 .¹⁵

By this same argument the extinction coefficient of the radical at the 5250 \AA . minimum is about 7×10^3 . A combination of this value with the observed changes in optical density (see Fig. 3 for example) due to the triplet and the ketyl radical and with the estimate that one-tenth of the initially formed triplet is converted to ketyl in the benzene solution gives $6 \pm 3 \times 10^3$ as the extinction coefficient for the benzophenone triplet at 5250 \AA .

(14) The final products of the reaction are, of course, very much dependent on the possible reversibility of the hydrogen abstraction. We have carried out a few low intensity steady state photolyses of $7 \times 10^{-2} M$ benzophenone solutions in degassed benzene. Analyses were done spectrophotometrically after aerating the solutions. After two hours of irradiation, 17% of the benzophenone, in a solution with $1 M$ benzhydrol added, had reacted. There appeared to be little decrease in the concentration of benzophenone in pure benzene after irradiation for almost forty hours. However, some product(s) of the reaction absorbs in the region $3000\text{--}4000 \text{ \AA}$, and makes it impossible to be certain whether or not any benzophenone has disappeared. A very small amount of biphenyl was the only product which could tentatively be identified by gas chromatography, but this cannot be responsible for the new absorption.

(15) This is within the experimental error the same value (1.2×10^4 (40%)) obtained by Garst for the ketyl radical anion with sodium: J. Garst, private communication.

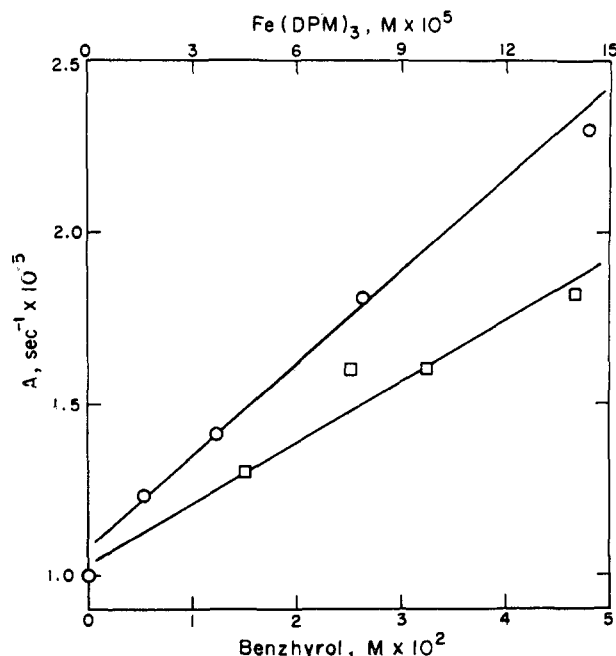
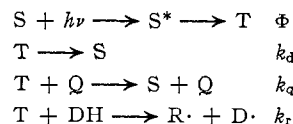
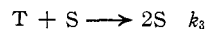


Fig. 6.—Dependence of A , for benzophenone, on the concentration of $\text{Fe}(\text{DPM})_3$, \circ , and benzhydrol, \square ; benzophenone, $2.3 \pm 0.2 \times 10^{-2} M$. Solvent is purified benzene.

2. Kinetics of Energy Degradation and Hydrogen Abstraction.—The following reaction scheme describes the formation and disappearance of the triplet state. For comparison with our results, it is convenient to use the rate constant notation of Hammond, *et al.*,^{2,6}



This sequence predicts no variation of the lifetime of the triplet with changing concentration of S , in contradiction with Fig. 1. The dependence of A on the initial concentration observed in our work with naphthaldehyde may be due to a quenching impurity in the naphthaldehyde or to quenching of the triplet by a singlet. In the absence of information about impurities we write the reaction



This reaction, as well as quenching by adventitious quenchers, is first order in triplet concentration. At given concentrations of naphthaldehyde and adventitious quenchers, the two "first order" terms, A obtained in this work in the unpurified benzene and k_d determined by Hammond, *et al.*,⁶ who used tributyltin as a competing hydrogen donor, should be identical. Extrapolation of the upper line in Fig. 1 to the concentration of naphthaldehyde, $5 \times 10^{-2} M$, used by Hammond, *et al.*, gives $A = 5.7 \times 10^5 \text{ sec}^{-1}$. (The upper line is used in the extrapolation because the "cleanup" noted in the flash experiments probably does not occur under steady illumination where the triplet concentration is many orders of magnitude lower.) The value of k_d (see below) determined from the data of Hammond, *et al.*, is $3.3 \times 10^5 \text{ sec}^{-1}$. The agreement is very good considering the error of about $\pm 50\%$ in each value. It must be reiterated that k_d and A include *pseudo* first order decay constants as well as the "true" first order decay for the naphthaldehyde triplet in this medium. Indeed, the intercept of Fig. 2 (in purified benzene), which is an upper limit to the intrinsic first order decay constant, is $7 \times 10^3 \text{ sec}^{-1}$, about a factor of fifty less than k_d .

The measured rate constant for 1-naphthaldehyde and benzophenone triplet quenching by $\text{Fe}(\text{DPM})_3$, k_4 , is equal to $k_q = 0.9 \times 10^9 M^{-1} \text{sec.}^{-1}$. The constant for $\text{Fe}(\text{AA})_3$ with naphthaldehyde is $2.7 \times 10^9 M^{-1} \text{sec.}^{-1}$. The fact that the $\text{Fe}(\text{DPM})_3$ quenching rate constant is the same for the two carbonyls, which are quite similar in size, does not prove that the quenching is diffusion controlled. Indeed, for aromatic hydrocarbons, we have measured rate constants which are quite similar from one hydrocarbon to another for the same quencher, but are much too slow to be diffusion controlled. The quenching constant obtained here for $\text{Fe}(\text{AA})_3$ with naphthaldehyde is about 100 times greater than the corresponding constant for the anthracene or phenanthrene triplets. Further comments on these phenomena will be given elsewhere.¹⁶

The $\text{Fe}(\text{DPM})_3$ constant measured here is about half the value assumed by Hammond, *et al.*^{2,6} Using this experimental value of k_q , the other rate constants in the reaction sequence are obtained from the photochemical data for 1-naphthaldehyde, 2-acetophenone, and benzophenone and gathered in Table I. Also given in Table I are the rate constants for benzophenone reactions measured in this work. The agreement is excellent.

TABLE I

RATE CONSTANTS FOR PHOTOREDUCTION REACTIONS OF SOME AROMATIC CARBONYLS

	1-Naphthaldehyde	2-Acetophenone	Benzophenone
	$k_q, M^{-1} \text{sec.}^{-1}$		
$\text{Fe}(\text{DPM})_3$	0.9×10^{10a}	0.9×10^{10b}	0.9×10^{10a}
$\text{Fe}(\text{AA})_3$	2.7×10^{10a}		
	$k_d, \text{sec.}^{-1}$		
	3.3×10^{10c}	1.5×10^{10c}	1.2×10^{10c}
	$\leq 7 \times 10^{10a}$		1×10^{10d}
	$k_r, M^{-1} \text{sec.}^{-1}$		
Tributyltin	5.5×10^{10e}	9.0×10^{10e}	
Benzhydrol (H)			2.3×10^{10e}
			2×10^{10e}
Benzhydrol (D)			0.8×10^{10e}
Benzene			9×10^{10d}
Toluene			9×10^{10d}
Cumene			3×10^{10d}

^a Experimental value, this work. ^b Assumed on basis of this work. ^c Calculated from the data of Hammond, *et al.*,^{2,6} using the measured value of k_q from this work. ^d Based on assumed kinetics ($k_{\text{comb}} = 2 \times 10^9$) for ketyl radical combination.

A direct comparison between the experimental results obtained in this work and in the photochemical studies using benzophenone is best made by considering the ratios k_d/k_r and k_q/k_r . In our work these are 0.05 M and 450, respectively. The results of Hammond, *et al.*, are 0.05 M and 400.²

The rate constant we calculate for hydrogen abstraction from benzene, $9 \times 10^2 M^{-1} \text{sec.}^{-1}$, is reasonable compared with the values for toluene and cumene (Table I). The rate constants for the reaction increase with the ease of hydrogen abstraction.

The purification of the solvent benzene reduced the upper limit for the first order decay constant of naphthaldehyde from 13.7×10^3 to $7 \times 10^3 \text{sec.}^{-1}$. The latter value is almost certainly still very much too large as shown by the much longer radiative lifetime observed in rigid solvents.¹⁷ In this connection we have

recently found that the first order decay constant for anthracene triplet in a chemically purified fluid solvent is the same as that found in rigid glasses or very viscous solvents.¹² The apparent increase in the first order decay constant noted in the past in going to fluid solvents is an artifact due to the presence of quenching impurities.^{18,19} The term involving k_3 was also shown to play no role in the triplet decay for a highly purified sample of anthracene in this solvent. This lends credence to the suspicion that this rather odd term is actually due to impurities introduced with the solute. The rate constant for phosphorescence decay of 1-naphthaldehyde in rigid media is of the order of unity.¹⁷ Therefore it appears that the high values of k_q and A observed might be due primarily to impurities in the solvents or solutes, although effects similar to those discussed below for benzophenone cannot be excluded. (The impurities have little effect on quenching rate constants, $k_4 = k_q$, which are determined by difference.)

In the case of benzophenone, a very short triplet lifetime ($1 \times 10^{-5} \text{sec.}$) is found, together with a relatively low chemical reactivity toward the solvent and a low quantum yield for benzophenone disappearance. The radiative lifetime, measured in rigid solvents at low temperatures, is $6 \times 10^{-8} \text{sec.}$ ^{5,20} Thus, the short triplet lifetime in benzene solution must be ascribed to rapid radiationless transitions to the ground state, competing effectively with slow radical formation. As in the naphthaldehyde case, it cannot be excluded that quenching impurities in solvent or solute may be responsible for the rapid decay, particularly in view of the observed high sensitivity of the aromatic ketone triplets toward added quenchers (such as $\text{Fe}(\text{AA})_3$) compared with unsubstituted aromatic hydrocarbons.¹⁶ However, the value of k_d for benzophenone triplet in purified benzene is so extremely high that other mechanisms for the decay must also be considered. Direct radiationless transition from the triplet to the ground state would evidently be the simplest such process. The marked inhibition of this transition in rigid media at low temperatures would then imply an appreciable activation energy for the process, perhaps combined with an unusually large viscosity dependence. The latter effect would be reasonable if torsional vibrations were involved in the transition state. Moreover, the enhanced spin-orbit coupling in $n-\pi^*$ levels²¹ which contributes to the high triplet yield in benzophenone, would also increase the rate of radiationless transition out of the $n-\pi^*$ triplet back to the ground state for molecules of this class. Nevertheless, in view of the recent indications of very slow rates of uncatalyzed radiationless transitions from the lowest excited states to the ground state,^{12,18} we are reluctant to account for the short benzophenone triplet lifetime in this way. Alternatively, we suggest that specific interactions between the triplet and the aromatic solvent may occur. These may lead directly to quenching, *via* weak (charge-transfer) complex formation between the triplet and benzene,¹⁰ or indirectly, *via* resonative energy transfer, made possible in this case by energy level shifts accompanying complex formation. Further work to test these various possibilities is in progress.

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