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Photochemical Studies in an Alkali Halide Matrix. I. An *o*-Nitrobenzaldehyde Actinometer and Its Application to a Kinetic Study of the Photoreduction of Benzophenone by Benzhydrol in a Pressed Potassium Bromide Disk

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The feasibility of quantitative photochemical studies in a solid KBr "pellet" of the type customarily used for infrared studies has been explored. Irradiation was by filtered ultraviolet light at an angle to the "analyzing" infrared beam from the infrared spectrophotometer. An actinometer consisting of *o*-nitrobenzaldehyde dispersed in the KBr disk was developed to measure light intensities and was used to obtain room temperature quantum yields in the system benzophenone–benzhydrol similarly dispersed in KBr. Infrared spectroscopy was used to identify products and determine reaction rates by repetitive scanning *in situ*. In the photoreduction of benzophenone by benzhydrol at 3340 Å., the value of Φ for benzophenone disappearance was a function of benzhydrol concentration and approached unity at high concentrations. Benzhydrol disappeared by an apparent first-order law. Assuming a simple mechanism, the ratio of the rate constants for the deactivation *vs.* the reduction of excited benzophenone to form ketyl radicals, k_2/k_3, was 0.0125 mole/l. of KBr. Addition of naphthalene to the "pellet" reduced the Φ of benzophenone disappearance. The ratio of the rate constants k_5/k_3 for naphthalene "quenching" *vs.* reduction of benzophenone by benzhydrol was estimated at about 50. These experimental findings indicate that photoreduction in the KBr matrix proceeds *via* triplet benzophenone, as in liquid solutions. "Blending" benzophenone and benzhydrol with KBr and forming disks at a pressure of 4800 p.s.i. by the usual pelletizing technique seems to result in a uniformly dispersed "solid solution." Diffusion processes seem to occur at rates comparable to "true" liquid systems. The utility of the technique in general photochemical studies is briefly discussed.

Introduction

The pellet technique employing KBr as a solid matrix has been well developed for studies of infrared spectra of solids.[1-3] Bent and Crawford[4] have applied this method in a study of the thermal decomposition of peroxides and nitrate esters in a potassium halide pressed disk, while Patai, Cross, and Albeck[5] have studied the kinetics of oxidation of solid organic substrates pressed in a $KClO_4$ pellet at high temperatures. In qualitative studies, at low temperatures, Chilton and Porter[6] photolyzed some organic compounds dispersed in potassium halide matrices and analyzed the trapped intermediates by ultraviolet or infrared spectroscopy. Indeed, most of the recent photochemical studies of organic compounds in rigid inert media are at low temperatures.

Recently, we pointed out the possibility of quantitative photochemical studies in pressed KBr pellets[7] at ordinary temperatures. Such quantitative kinetic and mechanistic studies of photochemical systems in an "inert" solid matrix at room temperature can yield information on the nature of energy transfer, the quantum yield of over-all reactions, and the mobility and reactivity of photoexcited molecules and labile species. Application of the pellet technique also can eliminate the difficulty of finding suitable inert liquid solvents for photochemical studies of a number of complex organic molecules. Finally, this technique enables one to study photochemical processes using a very small sample.

Although such a pellet technique would seem convenient for studies of unimolecular reactions, the general concepts of "cage" and "diffusion" in a "solid" KBr matrix might render doubtful the possibilities of this method when applied to investigations of bimolecular reactions. Thus, one aim of the present research was to study quantitatively several well-known intermolecular as well as intramolecular processes in order to test the utility and generality of this technique. The benzophenone–benzhydrol system was chosen because of its simplicity since the bimolecular reaction gives virtually a quantitative yield of pure benzopinacol and only one type of radical intermediate is involved. Furthermore, detailed studies of this system in liquid solutions have been carried out in several laboratories.[8-12]

Experimental

Materials.—Infrared spectroscopic grade potassium bromide powder was supplied by Harshaw Chemical Co. Benzophenone, benzhydrol, and naphthalene were obtained from Matheson Coleman and Bell; *o*-nitrobenzaldehyde was supplied by Aldrich Chemical Co. They were used without further purification as their infrared spectra were identical with the published ones.

Potassium ferrioxalate was prepared[13] by mixing three volumes of 1.5 *M* potassium oxalate with one volume of 1.5 *M* ferric chloride with vigorous stirring. The ferrioxalate was then recrystallized three times from warm water and was dried in a current of air at 45°.

Preparation of Pellets.—A few milligrams of the organic substrates were well ground and thoroughly mixed with 500 mg. KBr powder in a vibrator, and the mixture was pressed under vacuum into pellets of 14.5-mm. diameter and 1.1-mm. thickness under a pressure of 4800 p.s.i. The pellets were usually optically transparent in the visible region. The amount of KBr in each pellet was precisely controlled so as to give maximum reproducibility in optical characteristics such as scattering, etc. Since the amount of organic substrates added was usually less than 1% of the KBr in weight, it is assumed that the optical characteristics of the matrix other than absorption by the solute remain unchanged. Over the region of 3600–3100 Å., a 20% transmission was observed in a pure KBr pellet. Quantities of substrates introduced were chosen to give complete absorption of the re-

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(1) M. M. Stimson and M. J. O'Donnel, *J. Am. Chem. Soc.*, **74**, 1805 (1952).

(2) U. Schiedt and H. Z. Rheinween, *Naturforsch.*, **76**, 270 (1952).

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(9) W. R. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

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(11) V. Franzen, *Ann.*, **633**, 1 (1960).

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(13) The preparation was carried out by Dr. J. H. Sharp, to whom we are indebted.

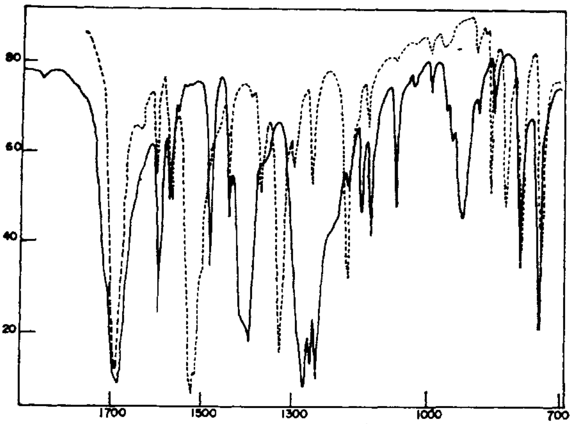

Fig. 1.—Spectra of *o*-nitrobenzaldehyde and photoisomerized product in KBr; dashed lines and solid lines correspond to *before* and *after* irradiation, respectively.

maining fraction of the monochromatic ultraviolet light while leaving sufficient transmission for infrared study. The concentrations of organic substrates in the KBr matrix were determined from the infrared spectra with individually calibrated extinction coefficients of selected absorption bands.

The range of concentrations of compound examined was of the order of 3-4 mmoles of reactant/mole of KBr. However, in the interpretation of kinetic data, the concentrations of compounds in the KBr pellet were calculated and expressed as moles per liter *of compressed KBr*. For 0.5 g. of KBr, this compressed volume was 0.182 cc. as calculated either from KBr density values or the measured diameter and thickness of the KBr disk.

Apparatus.—Photochemical reactions were carried out at room temperature with the pellet suspended in the light path of a Perkin-Elmer 221 infrared spectrophotometer. The ultraviolet source was 40 cm. from the pellet and set at an angle to permit ultraviolet irradiation of the pellet and simultaneous scanning of its infrared spectrum. The nature and the rates of the reactions were followed by recording the spectra as a function of time. The light source was a high pressure mercury arc (Bausch and Lomb SP200) equipped with a Pyrex water filter cell and an interference filter system (Jenaer Glaswerk Schott and Gen.) with a maximum transmission of 41% at 3290 Å. and a half-width of 80 Å.

Quantum Yield Determination.—The photoisomerization of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid was chosen as an actinometer in a KBr pellet because the reaction has been studied carefully[14,15] and the quantum yield of the rearrangement in the region 4300–3100 Å. is 0.50 in a solid, solution, or gaseous system.[14]

Thus, while the physical state of photolytes in the pressed KBr disk has not yet been well defined, it seems reasonable to assume a Φ of 0.50 in the pellet.

To calibrate the intensity of the monochromatic source, various amounts of *o*-nitrobenzaldehyde were pressed into pellets each with 500 mg. of KBr. In all cases complete absorption of the 3340 Å. monochromatic light was indicated. Since a pure KBr pellet transmitted only 20% at 3340 Å., the initial fraction of light absorbed by the *o*-nitrobenzaldehyde was 0.20. During irradiation, the infrared spectra of the pellets were continuously recorded as a function of time and the nitro peak at 1530 cm.$^{-1}$ was used to follow the disappearance of *o*-nitrobenzaldehyde. The absorbed light intensity was then calculated at various times and extrapolated to zero irradiation time, thus correcting absorption due to "internal filtering" by the product.

The determination of molecules per second of benzophenone reacting on irradiation was carried out in essentially the same manner as the actinometry. The carbonyl absorption band at 1650 cm.$^{-1}$ was used to follow the disappearance of benzophenone and the band at 730 cm.$^{-1}$ for the disappearance of benzhydrol. Since the reaction product, benzopinacol, does not absorb at the exciting wave length, no correction for "internal filtering" was necessary. Within the concentration range of benzophenone used, a constant fraction of light absorbed by the molecules was observed during the first 30% of the reaction.

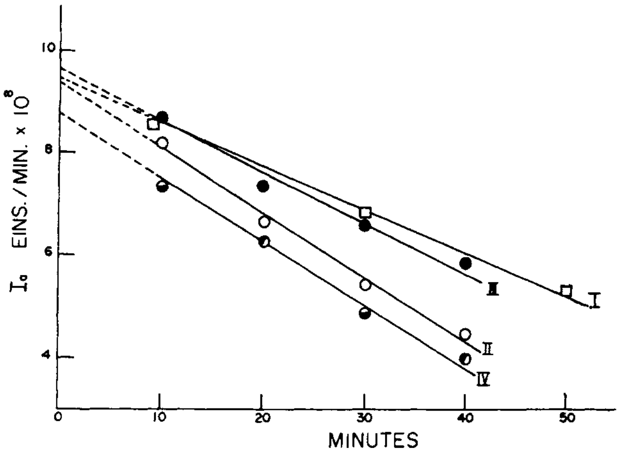

Fig. 2.—Relationship between the absorbed light intensities and the time of exposure; I–IV refer to runs 12–16 in Table I.

Results and Discussion

Actinometry.—The molecular rearrangement of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid accounts fairly well for the changes in the infrared spectra when the mixture of *o*-nitrobenzaldehyde and KBr pressed into a pellet was exposed to ultraviolet irradiation. A portion of the spectra showing the major changes when the reaction was allowed to go to completion is reproduced in Fig. 1. The diminution of the band at 1530 cm.$^{-1}$ is attributed to the gradual disappearance of the nitro group.

Four experiments carried out to determine the average intensity of the light source at 3340 Å. are reported in Table I. The effect of "internal filtering" by the reaction product and the method of its correction is shown in Fig. 2. The average initial intensity was 9.2 × 10^{-8} einstein/min. (9.2 × 10^{14} quanta/sec.). Its reproducibility in four separate runs was, on the whole, reasonably satisfactory.

TABLE I

DETERMINATION OF LIGHT INTENSITY AT 3340 Å. BY THE *o*-NITROBENZALDEHYDE–KBr PELLET ACTINOMETER

Run	*o*-Nitrobenzaldehyde, mole/l. of KBr	I_a, einstein/min., × 10^8
12	0.044	9.2
14	0.0327	9.4
15	0.0358	9.6
16	0.0328	8.8

The intensity obtained by this method was checked by the internal photooxidation–reduction reaction of potassium ferrioxalate, generally employed as a liquid solution actinometer.[16]

A KBr pellet, 0.0135 mole/l. in potassium ferrioxalate, was irradiated at 3340 Å. The infrared spectrum observed during irradiation showed the growth of a new band at 2350 cm.$^{-1}$. This is attributed to the formation of CO_2 *in situ*. A similar phenomenon was also observed by Bent and Crawford[4] during the thermal decomposition of nitrate esters in pressed KBr disks. Trapping of CO_2 in the KBr matrix was further checked by mixing Dry Ice and KBr powder to form a standard pellet which gave an identical absorp-

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[14] P. Leighton and F. A. Lucy, *J. Chem. Phys.*, **2**, 756 (1934).

[15] E. J. Bowen, H. Harley, W. D. Scott, and H. G. Watts, *J. Chem. Soc.*, **125**, 1218 (1924).

[16] C. A. Parker and C. G. Hatchard, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); **A235**, 518 (1956).

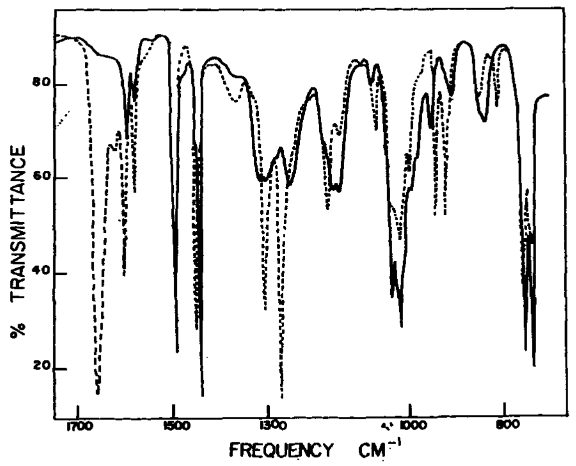

Fig. 3.—Spectra of the photoreduction of benzophenone by benzhydrol in a KBr pellet; dashed lines and solid lines correspond to *before* and *after* irradiation, respectively.

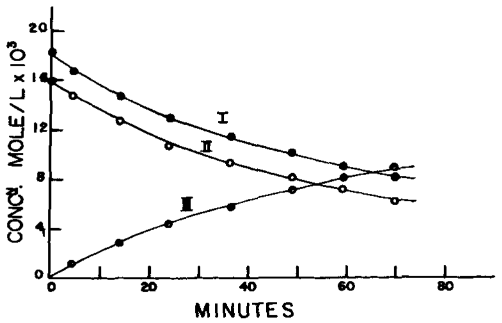

Fig. 4.—Rate of photoreduction of benzophenone by benzhydrol in KBr: I, disappearance of benzophenone; II, disappearance of benzhydrol; III, formation of benzopinacol.

tion band. After irradiation, the potassium ferrioxalate pellet was dissolved in water and the ferrous ion concentration determined colorimetrically.[17] Assuming an intensity of 9.2 × 10^{-8} einstein/min., $\Phi_{Fe^{2+}}$ was found to be 1.3, in reasonable agreement with the value of 1.2 in solution reported by Parker and Hatchard.[16] Thus, it appears that this "pellet" actinometer containing *o*-nitrobenzaldehyde could be useful for general photochemical studies in the region of 4300–3100 Å. The simplicity in experimental procedures, the convenience in sample handling, and the stability of the pellet system enhance the potential value of this actinometer.

Kinetic and Quantum Yield Studies.—When a KBr pellet containing benzophenone and benzhydrol is exposed to 3340 Å. irradiation, the only product is benzopinacol. In a typical pellet with an equimolar mixture of benzophenone and benzhydrol, the infrared spectrum, observed during irradiation, gradually changed to one identical with benzopinacol, as shown in Fig. 3. This simplifies product analysis and the rates of reaction can be followed easily by infrared spectroscopy.

In a series of experiments, the results of which are in Table II, the concentrations of benzophenone and benzhydrol in the KBr pellets were varied. Different light intensities were also used. A typical rate curve for the photoreduction is shown in Fig. 4. In order to keep the absorbed light intensity constant, the reactions were followed only in the first 60 min.

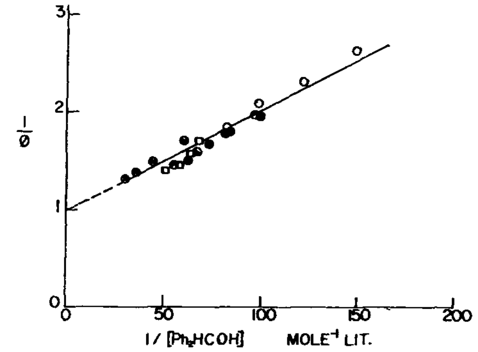

Fig. 5.—Plot of 1/Φ for the photoreduction of benzophenone in KBr against the reciprocal benzhydrol concentration; different marks represent different sets of experiments.

The quantum yield of the photoreduction in each experiment was determined at various times. It was found that the Φ decreased with time; this dependence is not surprising since the concentration in benzhydrol in the pellet decreased as a function of time. In other words, at constant absorbed light intensities, the Φ of the reaction varies as a function of benzhydrol concentration. The initial Φ was thus obtained by extrapolating to zero time or simply by obtaining the initial reaction rate from the experimental curves. The results thus obtained are presented in Table II.

TABLE II

QUANTUM YIELD OF BENZOPHENONE DISAPPEARANCE AT 3340 Å. IN THE PHOTOREDUCTION OF BENZOPHENONE BY BENZHYDROL IN A KBr MATRIX

Run	I_a, einstein/min., × 10^8	[Ph$_2$CO], mole/l. of KBr	[Ph$_2$HCOH], mole/l. of KBr	Φ
2	9.2	0.0228	0.0122	0.53
3	5.6	0.0112	0.0194	0.73
4	9.2	0.0221	0.0178	0.70
5	9.2	0.0182	0.0159	0.68
6	3.9	0.0248	0.0330	0.78

A simplified mechanism which accounts for the observed results is

$$\mathrm{Ph_2CO} + h\nu \longrightarrow \mathrm{Ph_2CO^*} \longrightarrow \mathrm{Ph_2CO^{**}} \quad I_a \quad (1)$$

$$\mathrm{Ph_2CO^{**}} \longrightarrow \mathrm{Ph_2CO} + \text{"energy"} \quad k_2 \quad (2)$$

$$\mathrm{Ph_2CO^{**}} + \mathrm{Ph_2HCOH} \longrightarrow 2\mathrm{Ph_2\dot{C}OH} \quad k_3 \quad (3)$$

$$2\mathrm{Ph_2\dot{C}OH} \longrightarrow (\mathrm{Ph_2COH})_2 \quad k_4 \quad (4)$$

where reaction 2 includes all possible deactivation processes. A steady-state treatment yields the following expression

$$1/\Phi = 1 + (k_2/k_3)(1/[\mathrm{Ph_2HCOH}])$$

In applying the experimental data to fit the derived expression, it is assumed that the product formed *in situ* has little inhibiting influence on the nature of the reaction. However, the benzopinacol might form a barrier to diffusion.

Figure 5 shows the plot of 1/Φ against the reciprocal benzhydrol concentration. The experimental points in Fig. 5 which were obtained from five different pellets prepared from different amounts of reactants fit a single straight line reasonably well. The slope of the straight line, k_2/k_3, is 0.0125 mole/l. of KBr. The extrapolated intercept suggests that at high benzhydrol concentration, Φ approaches unity. These findings are comparable with those of Moore, Hammond, and Foss,[9]

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(17) We are grateful to Mr. E. Baum, who performed the measurement.

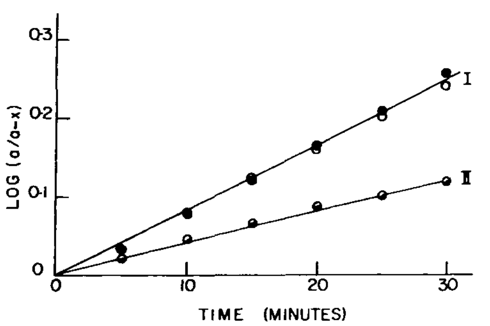

Fig. 6.—The photoreduction of benzophenone by benzhydrol in KBr, plotted according to the integrated first-order rate law; I refers to runs 4 and 5, II refers to run 3 in Table II.

who studied extensively the same reaction in liquid systems and reported a value of 0.045 for k_2/k_3 and a limiting Φ of 1.

If reaction 3 is rate determining, then the equation

$$\text{rate} = k_3[\mathrm{Ph_2CO^{**}}][\mathrm{Ph_2HCOH}]$$

should dominate the experimentally observed kinetics. At constant intensity of light absorbed the steady-state concentration of $\mathrm{Ph_2CO^{**}}$ is assumed constant, therefore, the rate of reaction becomes

$$\text{rate} = k'[\mathrm{Ph_2HCOH}]$$

which is first order.

This is shown in Fig. 6 in which the integrated equation was used in the form

$$kt = \log\,[a/(a - x)]$$

where a is the initial concentration of $\mathrm{Ph_2HCOH}$ and $a - x$ is the concentration of $\mathrm{Ph_2HCOH}$ at time t. Dependence of the slopes of these plots on light intensity is also apparent in Fig. 6.

The quantum yield of the photoreduction which is shown in Fig. 5 to approach unity at high benzhydrol concentration suggests that physical quenching of the excited molecules by KBr must be negligible. It further suggests that the compressed pellets were free of oxygen and were not permeable for atmospheric oxygen during irradiation, otherwise, the presence of traces of oxygen would reduce the Φ of $\mathrm{Ph_2CO}$ disappearance and lead to products other than benzopinacol.[9,18]

Addition of Naphthalene.—When naphthalene was introduced into the pellets containing a mixture of KBr, benzophenone, and benzhydrol, the photoreduction proceeded with slower rates and Φ was reduced in proportion to the amount of naphthalene added. The results are shown in Fig. 7. The initial concentrations of benzophenone and benzhydrol in this series of experiments were both equal to 0.025 mole/l. of KBr.

The decrease in Φ indicates that an energy transfer process is involved, presumably the same as in liquid solution.

$$\mathrm{Ph_2CO^{**} + C_{10}H_8 \longrightarrow Ph_2CO + C_{10}H_8^{**}} \quad k_5 \qquad (5)$$

$$\mathrm{C_{10}H_8^{**} \longrightarrow C_{10}H_8} + h\nu'' \qquad (6)$$

$$\mathrm{C_{10}H_8^{**} \longrightarrow C_{10}H_8} + \text{energy} \qquad (7)$$

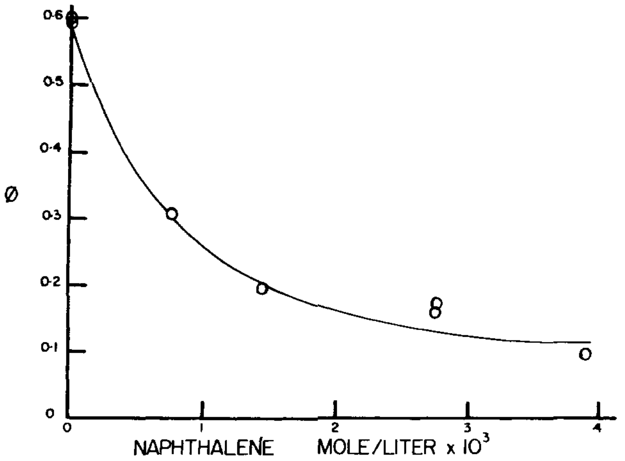

Fig. 7.—Effect of addition of naphthalene on Φ for the photoreduction of benzophenone by benzhydrol in KBr.

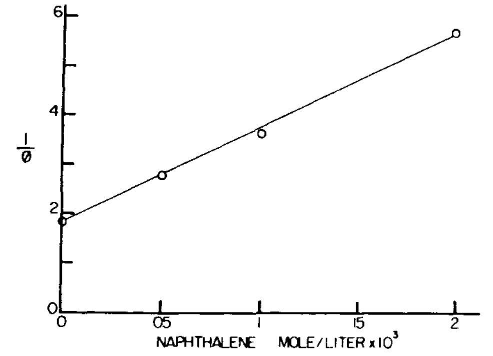

Fig. 8.—Plot of $1/\Phi$ for the photoreduction of benzophenone by benzhydrol in KBr against the naphthalene concentration; initial concentrations of benzhydrol and benzophenone = 0.025 mole/l.

Thus, the chemically active species in reaction 2, $\mathrm{Ph_2CO^{**}}$, would seem to be the triplet state of benzophenone since energy transfer from triplet benzophenone to naphthalene is known to be highly efficient in both liquid and solid phase.[10,11,19,20] From Fig. 7 it was shown that the value of naphthalene concentrations which reduced the original Φ by one-half was 8.0×10^{-4} mole/l. of KBr. At this naphthalene concentration

$$k_5[\mathrm{C_{10}H_8}] = k_2 + k_3[\mathrm{Ph_2HCOH}]$$

Using the values of 0.0125 for k_2/k_3 and 0.025 for $[\mathrm{Ph_2HCOH}]$, the relative constant k_5/k_3 was found to be 47. Alternatively, the value of k_5/k_3 can be obtained from the steady-state treatment of the mechanism which leads to

$$1/\Phi = (1 + (k_2/k_3)[\mathrm{Ph_2HCOH}]) + ((k_5/k_3)[\mathrm{Ph_2HCOH}])[\mathrm{C_{10}H_8}]$$

Plotting $1/\Phi$ against the concentration of naphthalene added gives a straight line as shown in Fig. 8, and the value of k_5/k_3 can be calculated from the slope, which is equal to $(k_5/k_3)[\mathrm{Ph_2HCOH}]$. This gives 49 for k_5/k_3 and the average value from two methods would then be 48.

If the triplet benzophenone in the KBr pellet does not phosphoresce and does not react with the matrix, as suggested by the Φ approaching unity, we may assume, *with caution*, that the lifetime of the triplet benzophenone τ_t may be close to the value of 1.6×10^{-6} sec. which was reported by Backstrom and Sandros[21]

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(18) J. N. Pitts, Jr., R. L. Setsinger, R. P. Taylor, J. M. Patterson, G. Recktewald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

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

(20) R. M. Hochstrasser, *J. Chem. Phys.*, **39**, 3153 (1963).

(21) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

in a benzene solution. There is presently not sufficient evidence for the justification of this assumption; however, it is made for the sole purpose of comparison with solution kinetics. The rate constant k_5 can then be calculated from the expression

$$\tau_t = 1/k_5[C_{10}H_8]$$

where τ_t is the lifetime of the triplet benzophenone in the KBr matrix and $[C_{10}H_8]$ the concentration which reduces Φ by one-half. Knowing k_5 and the relative rate constants k_5/k_3 and k_2/k_3, the values of k_2 and k_3 can be calculated. However, it is to be emphasized that the rate constants so obtained are not to be taken as absolute values. A precise method for obtaining the absolute rate constants is not yet available. The rate constants together with the published values are given in Table III.

TABLE III

THE CALCULATED RATE CONSTANTS FOR THE PHOTOREDUCTION OF BENZOPHENONE BY BENZHYDROL

	k_2, sec. $^{-1}$	k_3, l. mole $^{-1}$ sec. $^{-1}$	k_5, l. mole $^{-1}$ sec. $^{-1}$
This work (KBr matrix)	2.0×10^5	1.6×10^7	7.8×10^8
Porter and Wilkinson[a]	...	...	1.2×10^9
Moore, Hammond, and Foss[b]	2.6×10^5	5.0×10^6	...
Moore and Ketchum[c]	...	-...	2.2×10^9

[a] Ref. 12. [b] Ref. 9. [c] Ref. 10.

In Table III, the value of k_5 taken from Moore and Ketchum[10] was calculated from taking k_5/k_3 as 453 and k_3 being the same as reported by Moore, Hammond, and Foss.[9] Moore, Hammond, and Foss[9] have shown that in a liquid system reaction 3 is not diffusion-controlled. If reaction 5 is diffusion-controlled as suggested by Moore and Ketchum[10] and Porter and Wilkinson,[12] it would follow that reaction 5 would proceed slower in a solid matrix than in a liquid medium. Hence, k_5/k_3 in a KBr matrix would be smaller. However, this reasoning would also lead to the suggestion that k_3 is greater in the solid matrix. This is not entirely unreasonable as reaction 3 is expected to be exothermic and the solid matrix would serve to remove efficiently all the excess energy.

Diffusion in Solid KBr Matrix.—The activation energy of diffusion is generally quite high in solids. Although the true physical state of the reactants in a pressed KBr pellet is not well defined, a bimolecular mechanism involving reactions 3 and 5 requires at least partial diffusion of one of the reactants. Nevertheless, the possible formation of a complex between benzophenone and benzhydrol when pressed with KBr into a pellet warrants some consideration since by such a complex-forming mechanism diffusion is not necessary to bring about reduction.

Figure 3 indicates that when benzophenone and benzhydrol were mixed with KBr to form a pellet, the resulting infrared spectrum is a superimposition of the two-component spectra. This suggests that the components are probably not complexed. The experimental finding showing that reduction is inhibited by naphthalene further precludes the complex formation. In liquid solutions, Moore, Hammond, and Foss[9] have shown that complex formation between benzophenone and benzhydrol is negligible.

The electronic energy acquired by benzophenone molecules through photoexcitation may be greater than the activation energy required for diffusion. Thus, the photoexcitation of organic molecules held in a solid KBr matrix may cause sufficient "localized melting" of the cage to allow diffusion of the excited molecules comparable to a liquid system. In addition, presence of excited organic molecules in close proximity may also lower the activation energy for diffusion of other unexcited reactants. We are currently using several techniques to obtain deeper insight into the diffusion kinetics of this interesting reaction system. Also being explored are NaCl and other matrices.

Evaluation of the KBr Pellet Technique.—It is seen that a KBr matrix is inert and suitable for general photochemical studies; however, in an attempt to evaluate the method the following factors must be considered.

The greatest disadvantage of this pellet system lies in the fact that the state of aggregation of the mixture has not been established; this is usually the case in most solid state reactions. We have observed that when mixtures of Ph_2CO and Ph_2HCOH are ground together in the vibrator, the result is a liquid phase. This is also true when the Ph_2CO and Ph_2HCOH are mixed with 80% KBr. It appeared that the KBr was dissolved in the resulting liquid phase. In fact, it has not been possible to obtain other than a liquid phase unless the Ph_2CO and Ph_2HCOH are present at less than 5% by weight in KBr. At the present stage of this work we are reluctant to speculate on this matter although we are inclined to believe that the reactants were suspended in a KBr solid solution.

Another aspect of this technique is the proper choice of substrates. It is logical to assume that the technique would be difficult to apply to substrates of gases or volatile liquids. Since the method employs infrared spectroscopy to follow the photochemical changes, complicated systems leading to complex products would also be difficult to study. Neverthless, there are many photochemical systems including photoisomerization, photosensitized reactions, photodimerization, and unimolecular photodecompositions which could be studied by this method with ease. Bowen[22] has pointed out that study of the photochemistry of aromatic hydrocarbons is often limited by solubility consideration, thus the KBr pellet technique would help to solve this difficulty. Investigations now in progress in this laboratory include studies of the photodimerization of anthracene and the Ph_2CO-photosensitized isomerization of maleic acid to fumaric acid.

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