Table I: Solubility of Gases in $(C_4F_9)_3N$, $i\text{-}C_8H_{18}$, and $CCl_2F \cdot CClF_2$[a]

							$\bar{s}_2 - s_2^g$, cal. mole^{-1} deg.$^{-1}$
SF_6 in $(C_4F_9)_3N$		4.91	14.91	24.96	35.20	25.0	
		1085	888	728	607.9	731	−11.3
CH_4 in $i\text{-}C_8H_{18}$		4.36	14.97	24.77	35.07		
		62.36	(56.88)	53.51	49.89	54.0	−4.2
CO_2 in $i\text{-}C_8H_{18}$		4.48	15.12	24.97	35.05		
		183.8	157.5	138.5	122.8	139	−7.7
CO_2 in $CCl_2F \cdot CClF_2$		2.90	13.03	24.92	35.35		
		251.4	231.7	182.3	156.0	181	−8.15
CH_4 in $CCl_2F \cdot CClF_2$		4.00	14.90	25.09	35.00		
		56.51	52.78	49.78	48.72	49.8	−3.35
N_2 in $CCl_2F \cdot CClF_2$		4.00	15.00	24.98	35.00		
		19.33	19.46	19.31	19.88	19.3	0.00
Ar in $CCl_2F \cdot CClF_2$	0.10	4.21	14.90	20.02	24.91		
	33.4	32.8	31.85	31.40	30.95	30.9	−1.85
SF_6 in $CCl_2F \cdot CClF_2$		4.05	14.97	24.98	34.98		
		416.6	341.9	294.1	261.3	294.0	−9.5

[a] Upper row, t, °C., lower row, 10^4x_2 at 1 atm. partial pressure; values at 25° interpolated.

would be if soluble gases involved only the entropy of dilution. This re-emphasizes an important point already made,[8] that in addition to the entropy of dilution there is a large contribution resulting from increased freedom of motion of solvent molecules adjacent to a solute molecule in progressing to gases with weaker and weaker attractive potentials.

(c) Archer and Hildebrand[5] had found $10^4x_2 = 279$ for SF_6 in $CCl_2F \cdot CClF_2$, larger than the figure reported by Kobatake and Hildebrand for SF_6 in C_7F_{16}, 224, an incredible discrepancy. Therefore, we redetermined the former, finding the value in Table I, 294, and the same entropy. Our supply of C_7H_{16} is exhausted, so we substituted $(C_4F_9)_3N$, which has nearly the same solvent power, obtaining the value 731, in Table I. Evidently, the value reported by Kobatake contains a gross error that we have been unable to locate.

(d) The order and spacing of the points for the different gases are very different in the several solvents; the positions of the points for CF_4 and SF_6 are especially irregular. These facts express again the conclusion stressed by Archer and Hildebrand,[5] and again by Hildebrand,[9] that the energies of interaction between molecules of different types do not all conform to the usually assumed geometric mean "law."

(e) These rather comprehensive systematic values for entropy of solution afford material for carrying out the suggestion made by Hildebrand and Scott[5] in "Regular Solutions" that we are now in a position to calculate energies of solution and study their relation to solubility parameters of solvents and "force constants" of gases. This relation is now being examined.

Acknowledgment. We express our gratitude to the Atomic Energy Commission for the support of this work.

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(8) J. E. Jolley and J. H. Hildebrand, *J. Am. Chem. Soc.*, **80**, 1050 (1958).

(9) J. H. Hildebrand, *J. chim. phys.*, in press.

The Limiting Quantum Yield for the Photoreduction of Benzophenone with Isopropyl Alcohol

by William M. Moore and Marshall D. Ketchum

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(Received August 29, 1963)

The photoreduction of benzophenone with isopropyl alcohol is a well known photoreaction that has been used for the synthesis of benzpinacol.[1] As a result of several recent investigations,[2,3] the general mechanism for the photoreduction of benzophenone is fairly well

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(1) W. E. Bachman "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 71.

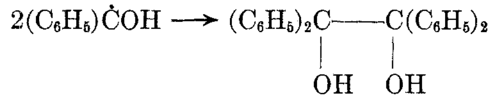
understood. Under the influence of absorbed light; photoexcited benzophenone molecules convert to the long-lived triplet state by a highly efficient intersystem crossing. These triplet state molecules abstract hydrogen atoms from suitable hydrogen donors in the rate-determining step forming two free radical species. The properties of the resulting radicals then determine the course of the subsequent reactions.

In at least one case, the benzophenone–isopropyl alcohol system, the subsequent free radical reactions have complicated the basic kinetic measurements. Pitts, *et al.*,[4] have obtained a quantum yield greater than one for the photoreduction of benzophenone with isopropyl alcohol (the limiting quantum yield of the primary hydrogen abstraction process is one[2,5]). A mechanism that would account for the products, acetone and benzpinacol, and the high quantum yield, 1.06 ± 0.2, was given by Pitts, *et al.*[4] All of the steps except (3) are general reactions that have been postulated for photoreductions of benzophenone.[2] Step 3 would have a great effect on the apparent quantum yield for the disappearance of benzophenone, and if it predominated over other processes in the competition for dimethylhydroxymethyl radicals, the limiting quantum yield should be two. Pitts[4] predicted that this should be the case, since the quantum yield of acetone and benzpinacol was much higher than the corresponding quantum yield for benzophenone. Stoichiometrically, step 3 would predict that: $\Phi_{(\text{acetone})} = \Phi_{(\text{benzpinacol})} = {}^1/_2\,\Phi_{(\text{benzophenone})}$ in the limiting case, and a quantum yield of 0.92 was found for acetone and benzpinacol at 3660 Å.[4]

$$(C_6H_5)_2CO + h\nu \longrightarrow (C_6H_5)_2CO^* \qquad (1)$$

$$(C_6H_5)_2CO^* + (CH_3)_2CHOH \longrightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2\dot{C}OH \qquad (2)$$

$$(CH_3)_2\dot{C}OH + (C_6H_5)_2CO \longrightarrow (CH_3)_2CO + (C_6H_5)_2\dot{C}OH \qquad (3)$$



$$2(C_6H_5)\dot{C}OH \longrightarrow \underset{\displaystyle OH}{(C_6H_5)_2C}-\underset{\displaystyle OH}{C(C_6H_5)_2} \qquad (4)$$

The actinometer system, based on the limiting quantum yield of benzophenone,[5] was well suited to the benzophenone–isopropyl alcohol system, and since the photolysis of benzophenone has become the condensed phase analog of the gas phase classic, the photolysis of acetone, a reinvestigation of the problem seemed in order.

Experimental

Materials. Benzophenone (reagent grade) was recrystallized twice from ethyl alcohol and water. The resulting white crystals had a melting range of 47–47.5° (uncor.).

Benzhydrol (reagent grade) was recrystallized once from hot ligroin and then twice from ethyl alcohol and water. The resulting white crystals had a melting range of 66–67° (uncor.).

Isopropyl alcohol (reagent grade) was purified by a method similar to that used by Pitts, *et al.*[4] It was distilled into anhydrous potassium carbonate and then dried over calcium in a nitrogen atmosphere. It was redistilled and the fraction boiling at 79–79.9° (647.6 mm.) was used for the preparation of solutions.

Triphenylmethane (reagent grade) was recrystallized twice from alcohol and water; the resulting white crystals melted in the range 92–92.5° (uncor.).

2-Propanol-2-*d* was prepared by reducing acetone with lithium aluminum deuteride (Metal Hydrides Corp., 96.6% pure) in anhydrous ether. The infrared spectrum of the compound was identical with that of isopropyl alcohol except for a shift in the C–H stretching frequency from 2855 to 2150 cm.$^{-1}$. The 2-propanol-2-*d* was purified on an Aerograph vapor phase chromatograph by repeated 0.1-ml. injections. A vapor phase chromatogram taken at high sensitivity showed the alcohol to be uncontaminated by water or other impurities.

Deuterium isopropoxide was prepared by treating sodium metal with excess isopropyl alcohol on an oil bath at 50° overnight. The resulting wet mixture of sodium isopropoxide and sodium hydroxide was dried under vacuum, immediately hydrolyzed with a slight excess of deuterium oxide (99.6% pure), and distilled. The result was a deuterium isopropoxide–isopropyl alcohol azeotrope. The azeotrope was purified on the v.p.c., but complete separation was not possible and further effort was not warranted. The deuterium isoproxide content of the final mixture was estimated at 83% from infrared analysis.

Procedure. Details of the apparatus, filter system, and general procedure have been given previously.[5] A collimated light beam from a Westinghouse 800-C SAH mercury arc lamp was filtered to isolate the mercury band centered at 3660 Å. The Beckman DU cell holder was used to locate the photolysis cells in the light beam. Actinometer and sample solutions were photo-

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(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) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

(4) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).

(5) W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962).

lyzed simultaneously. All solutions were irradiated *in vacuo.*

Results and Discussion

The method of actinometry developed by Moore and Ketchum[5] has been applied to the photoreduction of benzophenone with isopropyl alcohol in two ways: (1) the quantum yield for the photoreduction in pure isopropyl alcohol has been determined by the limiting quantum yield of the benzophenone–benzhydrol system in benzene; and (2) the limiting quantum yield of the benzophenone–isopropyl alcohol system in benzene has been determined by comparison with a benzophenone–benzhydrol solution of known quantum yield.

The first method gave erratic results similar to those reported by Pitts, *et al.*,[4] except that quantum yields as high as 1.8 were obtained. A 0.1 *M* solution of benzophenone in isopropyl alcohol was photolyzed simultaneously with a 0.1 *M* solution of benzophenone and varying concentrations of benzhydrol. The quantum yield was fairly insensitive to moderate changes in the light intensity and the concentration of benzophenone. Increasing the purity of the reagents did not reduce the erratic nature of the results. The average of five intercept determinations (four concentrations of benzhydrol were used for every determination) gave a quantum yield of 1.4 ± 0.4. Several other determinations were made which would not give any sort of a linear relationship. Several years of operating with the benzophenone–benzhydrol system and the present type light source have shown that both are stable and reproducible. For some unknown reason, the precision that is possible with other benzophenone photoreductions is not achieved in 100% isopropyl alcohol.[6]

By contrast, the second method gave very reproducible and consistent results. The isopropyl alcohol concentration was varied from 1 to 0.025 *M* while a constant benzophenone concentration of 0.10 *M* was maintained. The actinometer standard was 0.10 *M* benzophenone and 0.375 *M* benzhydrol in benzene. The results are shown in Fig. 1 and they obey the standard rate law for photoreduction of benzophenone. The intercept and slope, as determined by the method of least squares, were 0.45_5 and 0.042_1, respectively. The intercept represents the limiting value for the ratio of the quantum yield of the actinometer standard to the quantum yield of the sample. Using a quantum yield of 0.89 for the standard,[2,5] a limiting quantum yield of 1.9_6 is obtained for the benzophenone–isopropyl alcohol system.

The experiment was repeated with 2-propanol-2-*d* and the results are also shown on Fig. 1. The intercept and slope, as determined by the method of least squares, were 0.47_5 and 0.11_6, respectively. A kinetic isotope effect of 2.7_8 was calculated from the slopes, which is in good agremeent with an isotope effect of 2.7 found for the same photoreduction with benzhydrol.[2] The intercept represents a limiting quantum yield of 1.88 for the benzophenone–2-propanol-2-*d* system, which is in good agreement with the undeuterated system.

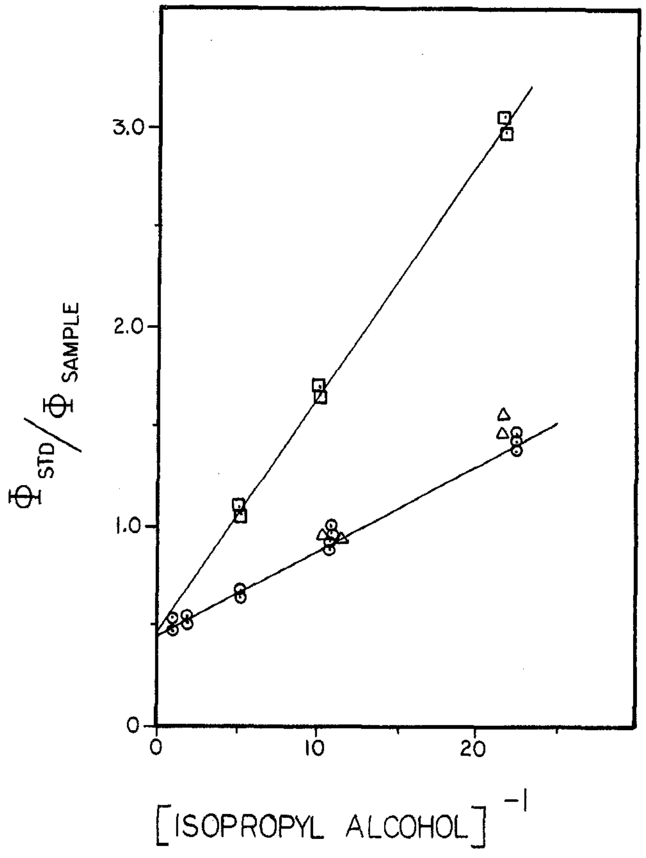

Figure 1. Photoreduction of 0.1 *M* benzophenone with isopropyl alcohol in benzene solution (standard solution contained 0.1 *M* benzophenone with 0.375 *M* benzhydrol in benzene): ○, isopropyl alcohol, intercept 0.455, slope 0.0421; △, deuterium isopropoxide; □, 2-propanol-2-*d*, intercept 0.475, slope 0.1166.

Several runs were made with deuterium isopropoxide and the results are again shown in Fig. 1. No pronounced deviation from the undeuterated system was observed, as might be expected.

One other somewhat disconcerting but useful observation of this system has been made. Triphenylmethane *is not a hydrogen donor* for photoexcited benzophenone. It is not a quencher since its presence does not seem to affect the photoreduction of benzophenone

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(6) Some small impurity in the isopropyl alcohol which is not removed by purification and not detected by the v.p.c. would be the most likely candidate. Also, the yellow intermediate, which has only been observed in the photolysis of benzophenone in isopropyl alcohol,[4] could possibly quench the photoreaction.

with benzhydrol. However, the quantum yield for the photoreduction of benzophenone with isopropyl alcohol is reduced in a benzene solution saturated with triphenylmethane. Although the products have not been determined and more work needs to be done, a limiting quantum yield of 1.07 was obtained for this system.

These results, in conjunction with the study of Pitts, *et al.*,[4] confirm the validity of the Pitts mechanism. It has also been demonstrated that the photoreduction of benzophenone with isopropyl alcohol is a special case of the more general mechanism for photochemical hydrogen abstraction reactions.

Step 3, the hydrogen exchange reaction between benzophenone and dimethylhydroxymethyl radical, predominates over other possible secondary reactions involving this radical even when the hydroxyl hydrogen is replaced by deuterium. Pitts observed that oxygen scavenges the dimethylhydroxymethyl radical and lowers the ratio of benzpinacol to acetone.[4] We have also observed this in the reduced limiting quantum yield for benzophenone. Triphenylmethane can also disrupt step 3, presumably by acting as a hydrogen donor for dimethylhydroxymethyl radical.

The ratio of the slope to the intercept in Fig. 1 will give the ratio k_d/k_r, where k_d is the rate constant for the deactivation of photoexcited benzophenone in solution, and K_r is the rate constant for the hydrogen abstraction reaction. This ratio is 0.0926, which compares with a value of 0.045 for benzhydrol.[5] In both cases the solvent is principally benzene, so if k_d is assumed to be constant, then K_r (benzhydrol) = $2K_r$ (isopropyl alcohol).

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Surface Area of Active Carbon and Carbon Black by the B.E.T. Method Using Argon, Carbon Dioxide, Methanol, Krypton, and Xenon

by K. A. Kini[1]

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Attention recently has been drawn[2] to the widely varying values of the B.E.T. surface area obtained by Freeman and Kolb[3] for a solid with an area of the order of several hundred square meters per gram, from adsorption measurements with a homologous series of gases. Freeman and Kolb consider the variation to be a consequence of the assumption of a substantially uniform heat of adsorption in the B.E.T. theory. They have suggested instead a two-energy surface theory, which they consider allows calculation of unambiguous values for surface area.

In this connection it may be of interest to record the results of measurements of the B.E.T. surface areas of two carbonaceous solids, using argon at −195.8°, carbon dioxide at −78°, krypton at −78°, xenon at 0°, and methanol at 30°. These results lend support to the B.E.T. theory in its original form.

Experimental

The samples investigated were "Neospectra" carbon black and an active charcoal (B.D.H.) as supplied for gas adsorption. Adsorption of krypton and of xenon was studied under pressure in a metal adsorption apparatus.[4,5] Adsorption of argon and of carbon dioxide was measured in a conventional volumetric apparatus, and that of methanol with a McBain sorption balance. The samples were degassed *in vacuo* (10^{-6} cm.) at 150° overnight before the adsorption measurements were made. Adsorption of the rare gases occurred rapidly, equilibrium being reached within a few minutes except in the case of argon on "Neospectra" carbon black at −195.8°, where a small creep was noticed. Methanol, however, was slow to equilibrate. The readings were continued until no further uptake of gas or vapor occurred overnight at each relative vapor pressure studied.

Results and Discussion

As shown in Table I, approximately equal surface area values were obtained for "Neospectra" carbon black with argon, carbon dioxide, and krypton, but the value with xenon was distinctly smaller. Again, for active charcoal, the surface areas obtained with argon and carbon dioxide were almost the same, but xenon and krypton gave a (constant) lower value. It is reasonable to attribute the differences in the areas observed with the various materials to a size effect (*i.e.*, molecular sieve action) of the adsorbed molecule rather than to failure of the B.E.T. theory. The existence of pores of cross-sectional area smaller than 24.9 and 21.0

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(1) Department of Fuel Technology, Pennsylvania State University, University Park, Pa.

(2) *Chem. Eng. News*, **40**, No. 38, 66 (1962).

(3) M. P. Freeman and K. Kolb, *J. Phys. Chem.*, **67**, 217 (1963).

(4) K. A. Kini, paper to Sixth Biennial Conference on Carbon, University of Pittsburgh, Pittsburgh, Pa., June, 1963.

(5) K. A. Kini, *Fuel*, **42**, 103 (1963).