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Experimental Measurement of the Effect of a Solvent on the Rate of a Very Fast Bimolecular Reaction

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RECEIVED FEBRUARY 5, 1952

A comparison has been made of the rate of quenching of the fluorescence of β-naphthylamine by carbon tetrachloride in the gas phase with the rate in solutions in isoöctane and cyclohexane. In order to calculate the bimolecular rate constants from the quenching constants it is necessary to know the lifetime of the excited state. It is estimated that the lifetimes in the gas phase and in solution must lie between 1.2×10^{-8} and 1.2×10^{-7} sec. On the basis of a lifetime of 1.2×10^{-8} sec. for the gas phase and 2.0×10^{-8} sec. for the solutions the bimolecular constants are calculated to be 5.9×10^{10}, $2.0 \times 10^{11} e^{-1600/RT}$ and $4.5 \times 10^{11} e^{-2470/RT}$ for the gas phase, isoöctane solutions, and cyclohexane solutions, respectively. These results are discussed in terms of various theories which have been proposed for rate processes of this kind.

Few bimolecular reactions have been studied both in the gas phase and in solution. A survey by Bell[1] lists eleven but points out that eight of these either are predominantly wall reactions or do not follow the same mechanisms in both phases. The remaining three are the decomposition of ethylene diiodide, the dimerization of cyclopentadiene, and the conversion of parahydrogen to orthohydrogen by paramagnetic molecules. All three are relatively slow reactions and in no case do the rate constants differ much in the two phases. Recently Miller and Willard[2] have reported that the constants for the exchange reaction between bromine and bromotrichloromethane are about the same in the gas phase and in solution. No studies have been made of the effect of the transition from the gas phase to solution on the rates of fast reactions. In this paper we wish to present the results of such a study.

Fluorescence quenching is a type of fast reaction which may be expected to follow the same mechanism in the gas phase and in solution and, therefore, is particularly well suited for studying the effect of an inert solvent on a reaction rate. An exploratory survey showed that the following quenching reactions may be used for such a study: fluorene by carbon tetrachloride; carbazole, α- and β-naphthylamine by benzonitrile, pyridine and carbon tetrachloride; anthracene by aniline. From this list the quenching of β-naphthylamine by carbon tetrachloride was selected for detailed study since it was found that the gas phase and solution reactions could be studied in overlapping temperature ranges. Furthermore, partition experiments such as were carried out by Rollefson and Stoughton[3] showed that there was no complex formation between the reactants prior to photoexcitation.

It has been shown in a previous paper[4] that in the presence of inert gases the rate of quenching in the gas phase becomes independent of the frequency of the exciting light used just as it is in solution. Under these conditions it is possible to compare the quenching rate for the lowest vibrational level of the excited state in the two phases.

Materials and Apparatus.—The materials used were the same as described in the previous paper. The measurements on the gas phase have been fully described in that paper. The measurements in the liquid phase were made with essentially the same electrical apparatus as was used for the gas phase studies except that the 931 A phototube was replaced by a Weston "Photronic" barrier-layer cell. This change was made, because it was found necessary to compare readings taken several hours apart, a period somewhat too long to count on the stability of a 931 A tube. During the experiments the cells were cooled by a stream of compressed air.

The solutions to be studied were made up in 25 mm. o.d. Pyrex tubes. These tubes were mounted inside a $3^1/_4$ inch o.d. quartz dewar flask which had gaps in the silvering to permit the passage of light. The tubes were heated by passing a carefully controlled stream of air through a small muffle furnace and into the dewar through a tube which extended nearly to the bottom with an exit tube near the top. It was assumed that thermal equilibrium had been established when a thermocouple inside the insulation on the entry tube and two thermometers inside the dewar, one near the top and the other near the bottom, all read the same temperature within one degree.

Experimental Procedures and Results.—The solutions were prepared at room temperature. In order to eliminate oxygen, which has a quenching action, nitrogen was bubbled through the solution in a tube which was then attached to a vacuum system; the solution was frozen at liquid nitrogen temperature, the system evacuated and sealed off. Some solutions were deoxygenized by refluxing them in a vacuum between room temperature and that of a Dry Ice–acetone mixture. This method was found to give the same intensity readings as the nitrogen bubbling, the removal of oxygen is believed to have been essentially complete in both cases.

Five solutions were used in each run. One tube contained pure solvent and was used to measure reflection, another contained an amine solution, the others contained the same amount of amine plus various amounts of carbon tetrachloride. Concentrations at the working temperatures were calculated from the values at room temperature and the densities observed by Evans.[5]

Tests showed that there was no significant dependence of the quenching constant on the frequency of the light used to excite the fluorescence so most of the measurements were made with the mercury lines at 3130 Å. as the exciting source. This light was isolated from the radiation of a quartz mercury vapor arc by Pyrex, two Corning 9863 filters and a 2-cm. cell containing solutions of 500 g./l. nickel sulfate hexahydrate and 35 g./l. chrome alum. The exciting light was blocked from the cell used to measure the fluorescence intensity by a Corning 7380 filter. For the runs above room temperature the tubes were preheated in an oven before being put in the fluorescence apparatus. In these cases approximately an hour was allowed for the establishment of thermal equilibrium. Under these conditions there was some drift in the photocell reading which resulted in a different "I_0" reading for each reading on a solution containing quencher. This drift could be represented reasonably well by a linear equation so I_0 is represented as a linear function of time in the tabulated data.

Results and Discussion.—Typical data under a variety of experimental conditions are presented in

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[1] R. P. Bell, *Ann. Rep. Chem. Soc.*, **36**, 82 (1939).

[2] A. A. Miller and J. E. Willard, *J. Chem. Phys.*, **17**, 168 (1949).

[3] G. K. Rollefson and R. W. Stoughton, THIS JOURNAL, **63**, 1517 (1941).

[4] H. G. Curme and G. K. Rollefson, *ibid.*, **74**, 28 (1952).

[5] E. B. Evans, *J. Inst. Petroleum Tech.*, **24**, 321 (1938).

TABLE I

QUENCHING OF FLUORESCENCE BY CARBON TETRACHLORIDE IN SOLUTIONS. EXCITING λ = 3130 Å. EXCEPT AS NOTED

Temp., °C.	K_Q	
		Isoöctane solutions
20	267	Exciting λ = 2537-2650
20	247	Concn. naphthylamine 4.45 × 10^{-4} *M*
20	243	Concn. naphthylamine 0.59 × 10^{-4} *M*
60	329	
90	403	
120	497	
		Cyclohexane solutions
20	142	
60	241	
90	322	
120	408	

Table I. A survey of these observations show that the quenching constant is not significantly affected by the wave length of the exciting light nor is it affected by the concentration of the fluorescer over nearly an eightfold variation of the latter. Quenching constants have been calculated for every point listed instead of drawing a smooth curve through the points of a given series and calculating an average constant from the slope of the line thus obtained. Although this procedure tends to exaggerate the errors in measurement, it also emphasizes the fact that these errors were not large. Since in a large percentage of the experiments the value of I_0/I was less than two, it follows that an error of more than 1% in the value of either intensity would cause an error of more than 2% in the value of the quenching constant. The data indicate that in spite of the drifts in the sensitivity of the photocells and the drift caused by a photochemical reaction (discussed in the previous paper) the results are consistent with the assumption that the intensity readings are good to about 1%.

The quenching constants in solution are dependent on the temperature and can be expressed by means of the Arrhenius equation. Thus, k_Q (isoöctane) = $3960\ e^{-1600/RT}$ and k_Q (cyclohexane) = $8980\ e^{-2470/RT}$. On the other hand, in the gas phase the quenching constant was found to be independent of the temperature and to have the limiting value 950 when there was sufficient inert gas present to eliminate the dependence on the nature of the exciting light. The quenching constants in this form are the products of the bimolecular rate constants for the quenching process and the lifetime of the excited state. Since we are primarily interested in the bimolecular rate constants, we can calculate these quantities with the aid of Neporent's value for the lifetime.[6] He has given 1.6 × 10^{-8} sec. as the value for the gas phase and reports that the fluorescence yield in the gas phase is 0.8 of that in the liquid. Neporent calculated his value from data on the quenching of the fluorescence by oxygen assuming every collision to be effective. His value is, therefore, a lower limit rather than an actual determination. Another estimate may be obtained by integrating the first absorption band of the naphthylamine which is reasonably well defined. This process yields a value of 1.2 × 10^{-7} if we assume that deactivation occurs solely by a radiation process. Actually other modes of deactivation decrease the fluorescence yield and correspondingly shorten the lifetime so that the limit calculated from the absorption spectrum is an upper one. The solvents we used have little effect on the absorption of light by the naphthylamine, hence the probability of a radiation transfer between the upper and lower electronic states is not affected significantly by the solvent. (Our estimate of the lifetime given above was based on the absorption of a solution in isoöctane.) The higher fluorescent yield observed by Neporent in the liquid phase must be due to diminution of the other deactivation processes in the liquid state thus increasing the lifetime and permitting more fluorescence. On this basis we obtain 2 × 10^{-8} sec. as the lifetime in the liquid according to Neporent's measurements. In order to calculate bimolecular rate constants from our measurements we have used the lifetimes based on Neporent's work and obtained 5.9 × 10^{10}, 2.0 × $10^{11}\ e^{-1600/RT}$ and 4.5 × $10^{11}\ e^{-2470/RT}$ liters mole^{-1} sec.$^{-1}$ for the gas phase, isoöctane solutions and cyclohexane solutions, respectively. If we used the lifetime calculated from the absorption measurements these constants would be increased by a factor of about six. We are inclined to favor the values as given but if the higher values should ultimately prove to be correct it would make little difference to the discussion which follows.

The bimolecular rate constants just given make no assumptions concerning the detailed mechanism of the bimolecular process. The value for the gas phase corresponds to reaction at 0.4 of the collisions calculated on the basis of diameters deduced from models of the molecules involved. In solution the frequency factor is somewhat larger than the gas collision number which may be due to less space being available for the solute molecules. The activation energies may be those for the diffusion of the solute molecules (the diffusion coefficients are not known); they are roughly proportional to, but definitely less than, the activation energies for viscosity (2110 for isoöctane and 2975 for cyclohexane) which can be calculated from the data of Evans[5] and of Geist and Cannon.[7]

From the point of view of the absolute rate theory the magnitudes of the frequency factors are determined by changes in entropy associated with the formation of the activated complex. In the gaseous state, since it is observed experimentally that there is no activation energy, the rate constant is simply $(kT/h)e^{\Delta S^*/R}$. At 120°, the lowest temperature at which the rate was measured, the experimental value leads to −10.0 cal./mole deg. The translational change, calculated from the Sackur-Tetrode equation, for the addition of two molecules such as these at 120° is −32.6. This indicates that the restriction introduced in forming the activated complex corresponds to freezing out only one degree of freedom with respect to translation, *i.e.*, it is only necessary for the two molecules to come within some more or less fixed distance of

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(6) B. Neporent, *J. Phys. Chem.* (*U.S.S.R.*), **21**, 1111 (1947).

(7) J. M. Geist and M. R. Cannon, *Ind. Eng. Chem., Anal. Ed.*, **18**, 611 (1946).

each other to form an activated complex. If it is assumed that the same fraction of the translational entropy is eliminated at all temperatures, it may be calculated that the value at 20° is -9.7. The rates in solution were measured at 20° and if we calculate the corresponding values for the entropy of activation, we find -8.78 for the isoöctane solution and -7.17 for the cyclohexane. It is apparent that the values are essentially the same in all three environments.

On the basis of the absolute rate theory, it should be possible to calculate exactly the effect of a solvent on the entropy of activation if we could determine the entropies of solvation of the reactants and the activated complex. Such treatment assumes that the activated complex is the same in both phases. Although there may be little doubt about the validity of this assumption in reactions with relatively large energies of activation, it may be argued that for a reaction with little or no activation energy the activated complex in solution may correspond to the passing over a potential barrier as the molecule forces its way between solvent molecules rather than the approach of the two reactants within some specified distance of each other. However, it has been found[8] by a study of the effect of temperature on the constants for the diffusional quenching and for the formation of reactant pairs[9] in the same solvent cage that the entropy changes are the same within rather narrow limits of error. Therefore, it seems justifiable to assume that in the case under discussion the essential feature for the formation of the activated complex is to bring the two reactants into the same small element of volume regardless of whether the reaction is occurring in the gas phase or in solution. It is possible to obtain reasonable estimates of the solvation entropies of the reactants if, for example, we assume that they conform to Hildebrand's conditions for regular solutions and use data from the literature. No data can be obtained for the activated complex. If it is assumed that the complex is similar in behavior to one of the component molecules, then the net effect of transferring the reaction from the gas phase to solution should be to change the entropy of activation by an amount approximately equal to the entropy of solvation of one of the reactant molecules. We have estimated the latter quantities to be about -12 cal./mole deg.; hence, on the assumption just stated the entropy of activation should be increased about 12 or become approximately 2 as compared to the experimentally observed values of -8.78 and -7.17.[10]

Since a large proportion of the collisions between the photoactivated β-naphthylamine and carbon tetrachloride lead to reactions in the gas phase the same condition is probably fulfilled in solution. Therefore, the rate in solution is determined by the rate with which the molecules diffuse together modified by a factor expressing what fraction of such encounters lead to reaction. The diffusion coefficients for the reactants in the solvents we have used are not known; hence, it is not possible to calculate the rate from experimental diffusion data. Many people have attempted the calculation on the basis of theoretical considerations which make use of certain other types of experimental observations. These attempts can be grouped into those which utilize (1) a quasi-crystalline theory[11] and (2) Smoluchowski's diffusion theory.[12] The latter theory treats the solvent as a continuous medium and discusses the movement of the solute particles through such a medium. The former theory considers the solvent and solute molecules as being at least locally distributed over the lattice sites in a crystal. In both types of treatment it is necessary to find some way to evaluate the diffusion coefficients. In the quasi-crystalline approach these coefficients may be estimated by means of Eyring's equation[13] which correlates the separation of the equilibrium positions (identified with the lattice sites) and the viscosity of the medium with the diffusion coefficient. The other approach bases the estimate of the diffusion coefficient on the assumption of reasonable sizes for the molecules of solute, the viscosity of the solvent, and the validity of the Stokes–Einstein equation. We have applied both types of calculation to our system but find that the uncertainties in the calculations are such that it is not possible to decide between the relative merits of the methods nor to calculate a value for the rate constant which shows anything more than that the experimental rate is of a magnitude which is not incompatible with the idea that in a system with the high efficiency of reaction observed by us the rate is determined by diffusion. However, it is also proper to say that in solution in an inert solvent the rate with which the molecules come together and react is not greatly different in solution from what it is in the gas phase. In that sense it may be said that our work supports the old simple picture advocated by Moelwyn-Hughes although many may think that the idea is more elegantly expressed by the later theories.

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[8] Paper presented by G. K. Rollefson before the Physical and Inorganic Division of the American Chemical Society at Detroit, April, 1950.

[9] H. E. Boaz and G. K. Rollefson, This Journal, **72**, 3435 (1950).

[10] The details of these calculations are contained in the Ph.D. thesis of H. G. Curme, University of California, 1950.

[11] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936); E. Rabinowitch, *ibid.*, **33**, 1225 (1937); R. H. Fowler and N. B. Slater, *ibid.*, **34**, 81 (1938); B. Williamson and V. K. LaMer, This Journal, **70**, 717 (1948); R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950).

[12] K. C. Hodges and V. K. LaMer, This Journal, **70**, 722 (1948); J. Q. Umberger and V. K. LaMer, *ibid.*, **67**, 1099 (1945); S. Chandrasekhar, *Rev. Modern Phys.*, **15**, 1 (1943); B. Williamson and V. K. LaMer, ref. 11; P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942); E. W. Montroll, *J. Chem. Phys.*, **14**, 202 (1946).

[13] S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," p. 519.