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Primary Photochemical Processes in Solution

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The effect of an inert solvent on the efficiency of photodissociation processes is discussed. It is shown on theoretical considerations that under the usual experimental conditions a close analogy between reactions in solution and in the gas phase cannot be accounted for by assuming a symmetrical retardation of both the dissociation and recombination processes by the solvent. It is shown experimentally by means of the radioactive indicator method that even in the ideal case of chlorine in carbon tetrachloride the atoms produced in the photodissociation process do not react with the solvent.

IN considering the nature of the primary process in photochemical processes in solution it is customary to assume that the reaction occurring is the same as would be found in a gaseous system. Thus if we are dealing with absorption corresponding to the continuum of one of the halogens we assume that atoms are formed in solution just as they would be in the gas phase. Dickinson¹ has presented a review of a number of reactions which have been studied both in the gas phase and in solution and he has shown that the behavior of such systems is usually in accord with the above assumption. Franck and Rabinowitch,² however, have advanced the argument that the quantum yield of such a primary dissociation process must be small on account of a high rate of "primary recombination." They argue that the atoms when first formed are hemmed in by solvent molecules so that they cannot escape from each other and therefore they recombine giving up the dissociation energy to the solvent molecules. An exception to this state of affairs arises if the atoms (or radicals) react with the solvent.³ Recently Rabinowitch and Wood⁴ have described some experiments with a mechanical model which they interpret as confirming these views. It is to be noted, however, that their results can be compared accurately only to reactions in which the atoms or radicals separate with approximately the same kinetic energy as the solvent molecules. This is usually not true of

photodissociations but rather we find the parts separating with abnormally high kinetic energies, thus increasing the possibility of forcing their way between the solvent molecules. The close correspondence between the reactions in gaseous and liquid systems as pointed out by Dickinson suggests that for dissociations of this type the primary recombination must be rather small.

In the interpretation of most of the data on chemical reactions we are concerned with the stationary state concentrations of atoms or radicals rather than their specific rates of formation and disappearance. Rabinowitch and Wood⁵ have remarked that if we assume that in such experiments only $1/n$ of the absorption processes result in dissociation and at the same time the recombination is reduced to $1/n$ of the gas phase rate then the stationary state is unchanged so it would be possible to observe the correlation mentioned above and yet have an inefficient primary process. Such a symmetrical modification of the dissociation and recombination processes is required by the principle of microscopic reversibility provided the reactions occur reversibly, i.e., if the separating atoms or radicals have the same kinetic energy as those which are recombining. Ordinarily this condition is not fulfilled but instead we find the dissociation process producing atoms with very high kinetic energies. Such atoms have an excellent chance of forcing their way between the solvent molecules or of reacting with the solvent molecules. The net effect would be that the dissociation would be affected less than the recombination process insofar as an inhibiting action of the solvent

¹ Dickinson, *Chem. Rev.* **17**, 413 (1935).

² Franck and Rabinowitch, *Trans. Faraday Soc.* **30**, 125 (1934).

³ Franck, *Chem. Rev.* **17**, 423 (1935).

⁴ Rabinowitch and Wood, *Trans. Faraday Soc.* **32**, 1381 (1936).

⁵ Reference 4, p. 547.

molecules is concerned. This would tend to produce higher concentrations of the atoms in solution if it were not for the fact that in solution the atoms can recombine at every collision with each other as there will always be some other molecule present to act as the third body.

The possibility of the atoms or radicals reacting with the solvent certainly exists in some systems but there are many examples of reactions in inert solvents where such a step seems impossible. Thus in reactions involving the absorption of light by iodine or bromine in solution in carbon tetrachloride the reactions of the atoms with the solvent are so markedly endothermic that they can be ruled out even when the atoms have quite high kinetic energies. With chlorine in carbon tetrachloride the possibility of a reaction, such as a chlorine atom adding on one side of the molecule while another chlorine atom leaves the other side, must be considered as the heat of the reaction is zero. The net result of such a process being merely the replacement of one chlorine atom by another it cannot be detected by ordinary chemical means but it can be detected by using the method of radioactive indicators. We have therefore carried out experiments to test this reaction using radioactive chlorine, obtained from Professor E. O. Lawrence, dissolved in carbon tetrachloride.

The essential steps in the experiment consisted of illuminating a solution of chlorine, some of which was radioactive, in carbon tetrachloride, removing the chlorine and testing the carbon tetrachloride for radioactivity. The chlorine was prepared from sodium chloride, which had been activated by the cyclotron, by oxidizing with manganese dioxide in acid solution. The gas was dissolved in carbon tetrachloride which had been washed with sodium hydroxide, dilute sulfuric acid, water, dried with anhydrous sodium sulfate, and distilled (b.p. $76 \pm 0.1^\circ$). The solution was divided into two parts, one to serve as a control, the other for the illumination. The latter was placed six inches from a quartz mercury arc (220 volt Cooper-Hewitt) with a piece of plate glass between the two to ensure the elimination of all wave-lengths which might affect the carbon tetrachloride. In order to obtain a measure of the effective light intensity two control reactions involving absorption of light in the same spectral

region as chlorine in carbon tetrachloride were used. The first was the decomposition of a solution 0.01 *M* in uranyl nitrate and 0.05 *M* oxalic acid for which an average quantum yield of 0.6 was assumed.⁶ The second was the decomposition of a solution of chlorine in 0.1 *M* hydrochloric acid for which Allmand⁷ gives an average quantum yield at these wave-lengths of 0.05. As the light was not monochromatic it is obviously impossible to obtain an exact check by such methods but these two tests agree within twenty percent in showing that in the course of thirty minutes illumination enough light would be absorbed by the chlorine in the carbon tetrachloride to dissociate all the molecules four times. After such a period of illumination the chlorine was removed from the carbon tetrachloride by shaking with a solution of sodium sulfite. This carbon tetrachloride was compared with the control solution of chlorine in carbon tetrachloride by means of a counter such as has been used in previous work on liquid systems in this laboratory.⁸ The liquid which had been given the treatment described above gave a count of 77.4 ± 2.3 , a blank run with carbon tetrachloride gave 82.6 ± 2.8 , for half-minute intervals. These values were obtained by taking readings with the two liquids alternating in the counter. Then the count for the control solution of chlorine was determined and found to be 256 ± 5 . Subtracting 80 as an allowance for the zero of the counter we find 176 ± 6 as the activity due to the chlorine. The mean time for this determination was 38 minutes later than for the tests on the carbon tetrachloride. This is approximately the half-life of radioactive chlorine, therefore before we can compare our results we must multiply our observed activity by two to get the activity which existed at the time of the tests on the carbon tetrachloride. The resulting value is 350 in round numbers. The difference between the treated and untreated samples of carbon tetrachloride was -5.2 ± 4 . Such a negative value must be attributed to fluctuations in the zero point as any appreciable amount of

⁶ Leighton and Forbes, *J. Am. Chem. Soc.* **52**, 3139 (1930).

⁷ Allmand, Cunliffe and Maddison, *J. Chem. Soc. (London)* **131**, 165 (1927).

⁸ Olson, Libby, Long and Halford, *J. Am. Chem. Soc.* **58**, 1313 (1936).

interchange involving the radioactive chlorine would give a positive value. Under the circumstances we feel that it is conservative to say that the amount of interchange which occurred is less than that necessary to give a difference of ten in the count. In other words, less than 10/350 or 0.029 of the chlorine reacted. As the total light absorbed was four times that necessary to dissociate all of the chlorine we can say that the quantum yield of the interchange process at room temperature is certainly less than 0.007.

The data which have been presented show that even in the most favorable case, chlorine in carbon tetrachloride, we cannot account for a high efficiency of a photodissociation process by assuming that the dissociation products react with the solvent. In the earlier paragraphs we have shown that the hypothesis that the rates of dissociation and recombination are both reduced

by the same factor so that the concentration of atoms in the photostationary state is comparable with that in the absence of a solvent is not tenable under the experimental conditions which have prevailed in most investigations. It seems necessary to assume, therefore, that the primary action of the light on a molecule must be of comparable efficiency in solution and in the gas phase if we have a close correlation between the behaviors of the two systems. The effect predicted by Franck and Rabinowitch should appear if we work with light of such frequency that the energy is just enough to bring about a dissociation. Even under such conditions it will not be observed experimentally unless the reaction mechanism is such that the active intermediates produced by the light are removed by some other reaction than a homogeneous recombination. A search is being made for a suitable reaction.

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The Temperature, Pressure and Volume Coefficients of the Viscosity of Fluids

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Since $(\partial\eta/\partial T)_p$ and $(\partial\eta/\partial T)_V$ are both positive for dilute gases and both are negative for ordinary liquids, they must be zero at some intermediate density. From data in the literature it is shown that these two coefficients do not become zero at the same state of the fluid, but that the former becomes zero at lower densities than does the latter. On this basis any state of a fluid can be placed in one of six categories, or loci, which are characterized by the signs and relative magnitudes of the two viscosity temperature coefficients. By the use of general mathematical equations relat-

ing four variables, the signs of the viscosity pressure and viscosity volume coefficients are deduced for the six loci. It is shown that the fluidity and volume of a normal liquid are linearly related for volume changes up to about 10 percent, as both properties are varied with the pressure at constant temperature, i.e., that $(\partial\varphi/\partial V)_T$ is a constant. This is analogous to Batchinski's relation, according to which $(\partial\varphi/\partial V)_p$ is a constant. From data in the literature it is shown that $(\partial\varphi/\partial V)_T$ is about $\frac{2}{3}$ to $\frac{3}{4}$ of $(\partial\varphi/\partial V)_p$, in agreement with relations deduced in this paper.

THE viscosity of a homogenous fluid is a function of the state only, just as are the pressure, temperature, and volume, and any of these four variables is fixed by fixing any two of the others. The commonest equations of state are those involving p , T and V , but formally at least, an equation relating p , T and η could equally well be called an equation of state. The volume pressure and volume temperature coefficients are well known to be negative and positive numbers, respectively, for any phase, gas, liquid or solid. The corresponding coefficients of

viscosity are however not so simple nor so well known, for instance the viscosity temperature coefficient is positive for gases and negative for ordinary¹ liquids, but its transition from the one sign to the other has never been investigated.

The following pages discuss all the viscosity coefficients of the four dimensional surface p - T - V - η for all fluid phases from the dilute gas to the highly compressed liquid. The data

¹ The term ordinary liquids will be used in the early part of this paper to mean a liquid below its normal boiling point. Later a more precise definition will be given the term from a viscosity standpoint.