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second-order effects. Although Margenau's calculations do not apply to smaller distances, it appears that the correction would be very much larger at such distances.

The results of this paper show that the measurement of total collision cross sections of high velocity particles can be used as a sensitive method for determining intermolecular repulsive potentials if the experimental results reveal a large dependence of cross section on velocity. In such cases it is found that the greater the slope of the cross section *versus* velocity curve, the softer will be the potential required to reproduce the experimental points. An extreme illustration of this point is found in the collision cross section for rigid spheres, which has no velocity dependence and is the result of an infinitely steep repulsive potential.

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The Efficiency of the Primary Photochemical Process in Solution

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A study has been made of the effect of an inert solvent on the efficiency of the primary process in the photolysis of oxalyl bromide and nitrosyl chloride. The oxalyl bromide was studied at the wave-lengths 2650, 3130, 3650, 4047, and 4358A, the nitrosyl chloride at 3650, 4047, 4358, 5461, and 5790A. In order to eliminate the back reaction between nitric oxide and chlorine, oxygen was introduced which converted the nitric oxide into nitrogen dioxide. The solvent used was carbon tetrachloride. Quantum yields for nitrosyl chloride showed only a slight trend ranging from 0.7 at 3650A to 0.5 at 5790A as compared to approximately 2 at all wave-lengths in the gas phase. Oxalyl bromide gave approximately the same quantum yield in solution as in the gas phase at 2650A, i.e., ~ 0.9, and the values in solution decreased to ~ 0.3 at 4358A with most of the change occurring between 3130 and 3650A. The results are discussed in terms of the Franck-Rabinowitch hypothesis and it is pointed out that they are most readily accounted for by assuming a deactivating action of the solvent rather than a high efficiency of recombination. A new quartz capillary arc of high intensity is described. The equilibrium $N_2O_4 = 2NO_2$ has been studied in carbon tetrachloride solution and the equilibrium constant at 25°C found to be 6.4×10^{-6}, concentrations expressed in mole fractions.

THE effect of a solvent on the efficiency of a primary photochemical process has been discussed by Franck and Rabinowitch.[1] According to their view the quantum yield of the initial step should be lower in a solvent than in the gas phase because of (1) deactivation by solvent molecules, or (2) a higher efficiency of recombination due to the fragments of the original molecule being held together by a "cage" of solvent molecules. The chief difficulty in applying these views to most systems lies in the fact that secondary processes are involved and it is impossible to determine how much of an observed solvent effect is caused by a modification of the secondary reactions. In order to avoid such complications we have studied two systems in which the fragments produced by photodissociation of the absorbing molecule do not react with the solvent molecules and any secondary reactions are unaffected by the solvent or do not affect the yield of the primary process. The reactions are (1) the photolysis of oxalyl bromide and (2) the photo-oxidation of nitrosyl chloride. Both were studied in carbon tetrachloride solution and some experiments were performed with nitrosyl chloride in hexane solution in which case action with the solvent had to be considered.

EXPERIMENTAL METHODS AND APPARATUS

The light source (Fig. 1) used in most of the experiments was a thick-walled capillary arc. Quartz capillary of about 1.5 mm wall thickness and internal diameter between 2.7 and 3.3 mm has been used on various arcs; a bore of around 3 mm and a length of about 4.5 cm for the working part seemed to give the best results. The bottom tungsten lead is sealed into the large quartz tube with De Khotinsky cement, and the

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[1] Franck and Rabinowitch, Trans. Faraday Soc. **30**, 120 (1934).

arc filled with mercury to the upper bulb. The tube is pumped on to remove most of the gas trapped on the walls, though there is no need for great care in removing air, since gas bubbles do not tend to collect in the capillary. After the rest of the tube is filled with mercury and the screw clamp tightened on the rubber tubing, mercury may move slowly through it, but sudden oscillations are prevented. The upper part of the holder into which the arc is screwed may be filled with water, so that the rubber and upper part are kept cold. The arc was operated on 220 d.c. (the top is connected to the negative side of the line) with a resistance in series. The resistance is adjusted to give a current of around 10 amperes, and the arc struck by breaking the mercury column near the bottom bulb with a small flame. A brisk stream of cooling water should be turned on immediately and the jacket (a quartz tube for filter work—a metal tube with a quartz window for the monochromator) screwed up so that the arc is entirely surrounded by flowing water. During operation, the resistance in series is varied between 10 and 15 ohms, depending on the arc's characteristics and the intensity desired. Around a kilowatt was the average power used, though arcs have been operated on as much as 1500 watts for several hours. They will not operate well on 110 d.c. with little or no resistance in series. After forty or fifty hours of operation it is advisable to clean the capillary with hydrofluoric acid and repair any small cracks which may develop. None of these arcs have ever broken down violently except when the water supply failed. One was operated (with perhaps a dozen or more cleanings) almost 1000 hours on about 900 watts. A tungsten lead which has been used for a long time in the bottom of an arc seems to help prevent blackening of the capillary.

Zeiss monochromat filters *A*, *B*, and *C* were used for the 5790, 5461, and 4358A mercury lines, respectively, Corning 586 filter (8 mm) for 3650A, and Corning 587 (3.9 mm) with Corning 330 (noviol 0, 2 mm) for the 4047 A line. A large fused quartz prism monochromator was used to separate the 2650 and 3130A radiations.

Nitrogen dioxide was prepared by heating C. P. lead nitrate. The gas was passed through phosphorus pentoxide and freed from gaseous impurities by repeated freezings and pumpings. The solid nitrogen tetroxide was colorless. Apiezon grease "L" was not attacked noticeably by short exposures to nitrogen dioxide. A weighed ground joint with a small bulb attached was pumped out in the vacuum line. A known volume and pressure of nitrogen dioxide was condensed into the bulb which was then sealed off and weighed, along with the rest of the ground joint. Weights of nitrogen dioxide thus obtained checked to within less than 1 percent of the weights calculated from the volume-pressure measurements, using the equilibrium constants for nitrogen dioxide and nitrogen tetroxide of Verhoek and Daniels.[2]

Chlorine was prepared from tank chlorine, which was bubbled into water at 0°C until a considerable amount of chlorine hydrate had formed. On warming to 10°C the gas was evolved and passed through calcium chloride and phosphorus pentoxide. The chlorine was distilled in a vacuum line, the first and last fractions being discarded.

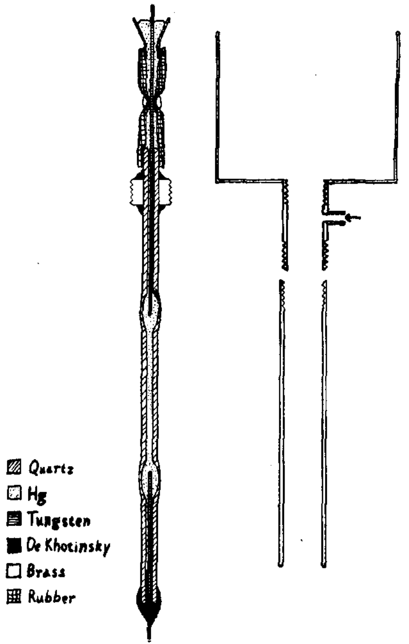

FIG. 1.

Nitric oxide was prepared by a modification of the method of Johnston and Giauque.[3]

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[2] Verhoek and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).

[3] Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929).

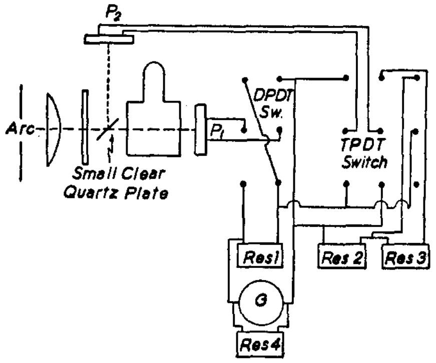

Fig. 2.

Nitrosyl chloride was prepared by a method similar to that of Taylor and Denslow.[4]

Nitric oxide (in excess) and chlorine were allowed to react in a three-liter flask. When the chlorine was practically all used up the gases were repeatedly condensed in liquid air and evaporated until pressure measurements showed complete reaction. Then the gases were condensed in liquid oxygen and non-condensible nitric oxide pumped off, the operation being repeated until no gas was uncondensed by liquid oxygen. Finally the nitrosyl chloride was distilled, with the first and last fractions discarded. Some preparations were made in a system using greaseless glass valves; others were made in a system containing stopcocks greased with Apiezon grease "L." The grease, which was protected from light when in contact with nitrosyl chloride, was not affected visibly. No effect of stopcock grease on the gas photolysis was found. Weights of nitrosyl chloride were checked against pressure-volume measurements by the method used with nitrogen dioxide. These different values checked to within about $\frac{1}{2}$ percent.

Oxalyl bromide, prepared from oxalyl chloride and hydrogen bromide in a system using greaseless glass valves, was kindly supplied by Dr. Tuttle. Titration of the acid formed on hydrolysis of oxalyl bromide checked within about 3 percent of the pressure-volume measurements. Free halogen in the material amounted to less than 0.1 percent.

Sulfur-free carbon tetrachloride, saturated with chlorine, was exposed to sunlight for several days, but was found to produce acid on illumination with chlorine even after such treatment. Finally chlorine dioxide was bubbled through and the solution illuminated with a 150-watt bulb for five days, chlorine dioxide being renewed as it was used up. Chlorine dioxide was prepared by the method of Bray.[5] Finally the carbon tetrachloride was washed with alkali and distilled from phosphorus pentoxide, the end fractions being discarded.

Crude hexane was shaken with small amounts of concentrated sulfuric acid until the acid took up no color. Then the hexane was shaken several times with 0.1 N potassium permanganate in 10 percent sulfuric acid, and a few times with 0.1 N potassium permanganate in 10 percent sodium hydroxide solution. The fraction distilling between 65–70°C was used.

Pressures of the corrosive gases were measured with a click gauge connected to a sulfuric acid manometer. Samples of the various gases were condensed and sealed off in small bulbs which could be broken by shaking in the reaction cells. Two cells were used—one cylindrical Pyrex cell 40 mm in diameter and 30.4 mm long, the other a rectangular quartz cell 30 by 40 mm and 24.2 mm long, used in the work below 3650A.

The experimental set-up is shown in Fig. 2. Absorption of substances in the cell could be measured in two ways. Direct reading of currents from photo-cell P_1 with the cell in and out of the light path may be made, or both photo-cells may be used in a potentiometric arrangement. The beam reflected from the quartz plate to photo-cell P_2 measures the incident light intensity; the voltage of P_2 is applied across the full resistance of the potentiometer (resistance boxes 2 and 3). The two methods gave identical results, but it was more convenient to use the first method

Table I. *Calibration of the sensitivity of the photronic cell.*

Wave-Length, A	(Moles/min. ×mm) ×10⁶		
	Nitrosyl Chloride	Uranyl Oxalate	Thermopile
3650	0.57	0.49	0.59
4358	1.22	1.44	1.08
5461	5.0	—	6.8
5790	7.8	—	7.3

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[4] Taylor and Denslow, J. Phys. Chem. **31**, 374 (1927).

[5] Bray, Zeits. f. physik. Chemie **54**, 463 (1906).

when the cell could be moved rapidly back and forth from the light path. When the cell could not be moved, it was necessary to use the latter method, since it corrects for fluctuations in the intensity of the arc. When absorption measurements were used for analytical purposes dense screens, cutting out about 97 percent of the light, were used, so that photochemical reaction during the measurement would be negligible. Analytical measurements were often made at one or two wave-lengths on a reaction initiated by light of another wave-length.

The absolute number of quanta entering the reaction cell was determined from current outputs of photo-cell P_1, which was calibrated against actinometers and a thermopile. Uranyl oxalate[6] was used as an actinometer between 2537 and 4358A. This actinometer alone was used at 2650 and 3131A. Nitrosyl chloride gas, assuming a quantum yield of 2.0, was used between 3650 and 5790A, and those calibrations checked against a Moll large surface thermopile. Photocell sensitivities from these actinometers and the large surface thermopile calibrated against a standard lamp are compared in Table I. The nitrosyl chloride gas values were used in calculating the nitrosyl chloride solution yields, while uranyl oxalate values were used for the oxalyl bromide quantum yields.

TABLE II. *Oxalyl bromide absorption coefficients in carbon tetrachloride solution.*

WAVE-LENGTH, A	$M\times10^3$	K
2650	1.8	~200
3130	2.3	~120
3650	2.1– 8.3	30.9±1.7
4047	6.0–18.0	5.9±0.2
4358	2.3–18.0	1.78 (2.43–1.58)

M = concentration of oxalyl bromide in moles/liter.
l = length of cell.
$K = 1/lM \times \log_{10} I_0/I$.

TABLE III. *Quantum yields for the photolysis of oxalyl bromide in carbon tetrachloride solution.*

WAVE-LENGTH	OBSERVED VALUES	AVERAGE
2650	0.94, 0.91, 0.82, 0.91, 0.87	0.89
3130	0.81, 0.79, 0.81, 0.74	0.79
3650	0.37, 0.39, 0.34, 0.38, 0.38, 0.35	0.37
4047	0.29, 0.23	0.26
4358	0.22, 0.32, 0.33, 0.30, 0.26	0.29

TABLE IV.

STOICHIOMETRIC MOLE FRACTION OF $NO_2\times10^5$	$K=\frac{(N_{NO_2})^2}{N_{N_2O_4}}\times10^5$ $T=25°C$
1.1	5.65
3.3	5.69
9.7	5.55
19.3	6.18
29.0	6.15
38.6	6.34
48.3	6.42
58.1	6.41
77.3	6.40
96.5	6.49
145.0	5.68
173.9	5.73
4250	1.4*

Henry's law constants $=\frac{\text{fugacity (atmos.)}}{\text{mole fraction}}$ $T=25°C$ $NO_2=74.6$ $N_2O_4=2.5$

* Cundall, J. Chem. Soc. **51**, 1076 (1891); **67**, 794 (1895).

PHOTOCHEMICAL DECOMPOSITION OF OXALYL BROMIDE IN CARBON TETRACHLORIDE SOLUTION

The decomposition of oxalyl bromide was followed by bromine absorption measurements, and iodometric titration of the bromine liberated. Since oxalyl bromide has a much smaller absorption coefficient than bromine at 4358A, light absorption at that wave-length was used for analysis in the work at all wave-lengths. Titration and absorption measurements gave checks within 5 percent, except in runs at 2537 and 2650A. At these wave-lengths the carbon tetrachloride itself absorbs light and liberates oxidizing material. As the concentration of oxalyl bromide is increased, the discrepancy decreases, since the solvent then absorbs a smaller fraction of the light. If a correction is made for oxidizing material produced from the solvent the two methods of analysis are brought into good agreement, even at low oxalyl bromide concentrations. The photolysis of oxalyl bromide appears to be unaffected by the accompanying carbon tetrachloride decomposition, except insofar as the solvent acts as an inner filter. The inner filter action of the bromine at the longer wave-

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

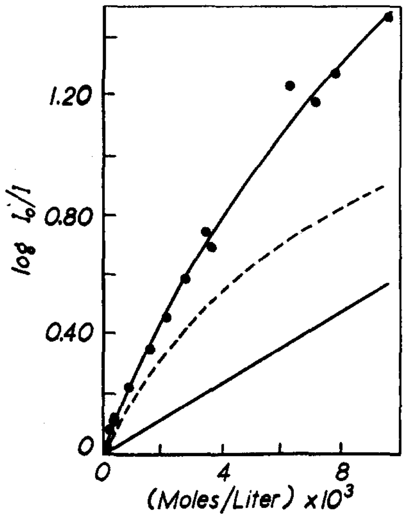

FIG. 3. 3650A. —·—·— ($\Delta \log I_0/I)_1$ *vs.* stoichiometric NO_2 conc.; ———— $(\Delta \log I_0/I)_{2+3}$ *vs.* NOCl conc.; ------ $\Delta \log I_0/I$ *vs.* NOCl conc. decrease.

lengths was eliminated by using initial rates for the calculation of quantum yields.

Two runs were made at 2537A, using a low pressure, gas-filled mercury arc which furnishes over 90 percent of its radiation at 2537A. The set-up in these two experiments was different from that in the others. A lower limit for the quantum yield was about 0.6; the geometry of the system indicated an upper limit of 1.2.

Errors in the 4358A measurements are larger than those at the other wave-lengths, since the absorptions are small and the quantum yield is low. There appears to be a slight change in absorption coefficient with concentration at 4358A, though the errors in measurement at the low concentrations are large. Table II shows the absorption coefficients of oxalyl bromide in solution, Table III summarizes the quantum yield data.

Illumination of a solution of nitrosyl chloride in carbon tetrachloride caused no measurable amount of decomposition. Experiments with mixtures of nitric oxide and chlorine in solution in the same solvent showed that the back reaction was so fast (at least 100 times as fast as in the gas phase) that the photostationary state which could be set up by our light source was not measurable. In order to eliminate this back reaction oxygen was introduced into the system. Control experiments showed that oxygen reacts very much faster than chlorine with nitric oxide in carbon tetrachloride. With oxygen present the net reaction on illumination is $2NOCl+O_2=2NO_2+Cl_2$. This reaction can be followed readily by measurement of the increase in the absorption of light by the solution. The presence of any water in the carbon tetrachloride interfered with this measurement by reacting with the nitrogen dioxide. In order to eliminate this difficulty it was necessary to distill the carbon tetrachloride through fluffy phosphorus pentoxide and condense it directly in the reaction vessel which was then sealed off.

The nitrogen dioxide exists in the solutions in equilibrium with the tetroxide. From absorption measurements in very dilute solutions, in which the dissociation of the tetroxide is essentially complete, it was possible to determine the absorption coefficients for the dioxide at the wave-lengths 4358 and 3650A. Since only the dioxide absorbs at 4358A, it is possible to obtain the data necessary for the calculation of equilibrium constants by measuring the absorption and the total amount of dissolved oxides at higher concentrations. The constants obtained in this way are tabulated in Table IV.

In order to follow the course of the oxidation of nitrosyl chloride by light absorption it is necessary to set up a relationship between the change in the light absorption and the amount of the nitrosyl chloride which has reacted. The change in $\log I_0/I$ may be written

$$\Delta \log I_0/I = k_1\, \Delta C_{NO_2} + k_2 \Delta C_{Cl_2} + k_3 \Delta C_{NOCl}.$$

From the stoichiometry of the net reaction $\Delta C_{Cl_2} = -\frac{1}{2}\Delta C_{NOCl}$. The correlation between ΔC_{NO_2} and ΔC_{NOCl} is not so simple because of the equilibrium between the dioxide and tetroxide. However, if we speak of the total tetravalent nitrogen as a stoichiometric C_{NO_2} then the ΔC_{NO_2} corresponding to this is numerically equal to ΔC_{NOCl}. Thus the above equation can be reduced to a function of ΔC_{NOCl}. The simplest way to use this expression for analytical purposes is to prepare a graph of $\Delta \log I_0/I$ against ΔC_{NOCl}. Each term of the equation is plotted; the last two give straight lines but the first gives a curve because of the equilibrium between the dioxide and tetroxide. The contribution of each term for a given ΔC_{NOCl} is read from the graph and the three are combined to give a point for the desired curve. The curve obtained with λ4358A could be used only for small values of ΔC_{NOCl} because $\Delta \log I_0/I$ changed very little at the higher values. The curve obtained for λ3650A was quite satisfactory and was used in most of the analyses with checks against the one for λ4358A. The agreement between the two was found to be satisfactory. Figure 3 shows the curves for λ3650A. In this figure the contributions of the second and third terms have been combined into the single straight line.

The quantum yields for the oxidation reaction are listed in Table V. It was found that unless the oxygen pressure over the solution was controlled considerable variation was noted in the results. The effect of varying the oxygen pressure is shown in the values for 3650A. High oxygen pressures apparently have some inhibiting action although oxygen must be present for the reaction to go. At the other wave-lengths the oxygen pressure was fixed at one atmosphere.

The recombination of the nitric oxide and chlorine atoms formed in the photolysis of nitrosyl chloride may be prevented by carrying out the reaction in a solvent which reacts with chlorine atoms. Hence some experiments were performed with hexane as a solvent. No nitrogen dioxide was formed in this system under any conditions and the absorption decreased as the reaction proceeded. The reaction could not be run to completion since the solution became cloudy due to the separation of some hexane-insoluble product. Some experiments were tried with a solution of hexane in carbon tetrachloride and in these the reaction was carried to completion; the absorption dropped to zero. The quantum yields for these experiments are contained in Table VI.

TABLE V. *Quantum yields for the oxidation of nitrosyl chloride in carbon tetrachloride solution.*

WAVE-LENGTH	OXYGEN PRESSURE	OBSERVED VALUES	AVERAGE
3650	0.2 atmos.	0.70	0.70
	1	0.66, 0.67, 0.67, 0.68, 0.64	0.66
	1.5	0.56	0.56
	2	0.48, 0.45	0.47
4358	1	0.68, 0.76	0.72
5461	1	0.48, 0.51, 0.42, 0.43, 0.50	0.47
5790	1	0.48, 0.44, 0.58	0.50

TABLE VI. *Quantum yields for the photolysis of nitrosyl chloride in hexane solution.*

WAVE-LENGTH	OBSERVED VALUES	AVERAGE
3650	0.91, 0.87, 0.96, 1.19, 1.10	1.0
4358	0.69	0.69
5790	0.27, 0.30, 0.33, 0.32, 0.37	0.32
3650 Solvent 0.05 mole fraction of hexane in CCl_4	0.50, 0.60	0.55

DISCUSSION

According to the hypothesis of Franck and Rabinowitch[1] the quantum yield of simple reactions such as are considered here should be less in liquids than in the gaseous state. Our results show that this is true at all wave-lengths in the case of nitrosyl chloride and at long wave-lengths with oxalyl bromide but not at short wave-lengths where our results are essentially the same as found by Tuttle in the gas phase.[7] If the decrease in yield of the primary process is caused by a high efficiency of recombination of the molecular fragments brought about by a "cage" action of the solvent molecules it might be expected that the yield would vary with wave-length since at high frequencies the large kinetic energies possessed by the separating fragments would favor escape from the cage. The excess energy in the case of nitrosyl chloride amounts to 41 kcal. at 3650A and 11 at 5790A.[8] The products are the same at all wave-lengths except possibly that the chlorine atom may or may not be raised to the $P_{\frac{1}{2}}$ state, a difference of 2.5 kcal. The estimate of the excess energy for the oxalyl bromide depends upon what values are chosen for the carbon-carbon and carbon-bromine bonds. If we assume that the primary process is the same between 3650A and 4358A, the range in which an effect was noted, the variation in energy amounts to 13 kcal. Inspection of our results shows that in carbon tetrachloride solution there is only a slight trend in the yield with nitrosyl chloride and with oxalyl bromide the only change of importance occurs in a rather narrow wave-length range. Nitrosyl chloride in the presence of hexane shows a much greater variation. In this case a reaction with the solvent

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[7] J. E. Tuttle, Ph.D. Thesis, University of California, 1940.

[8] Dixon, Zeits. f. physik. Chemie **B24**, 328 (1934).

occurs and it is possible that the excess energy supplied at the shorter wave-length is required to supply an activation energy for such a reaction. A point in favor of this view is supplied by the experiments in the dilute solution of hexane in carbon tetrachloride. Under these conditions some of the excess energy could be taken up by the carbon tetrachloride before a reaction with hexane could occur and actually we find a quantum yield only half as great as in pure hexane at the same wave-length.

The results which have been presented are more readily accounted for by assuming a deactivating action of the solvent rather than a high efficiency of recombination. Such a deactivation need not involve a change of electronic state in the photoactivated molecule but only the removal of vibrational energy. Usually the absorption of light produces a strongly vibrating molecule; if vibrational energy is removed from such a molecule until the amount left is less than that required for the dissociation of that particular electronic state the molecule will remain intact. If the potential energy curve which could be drawn to represent the excited state has no minimum or only a very slight one it may not be possible to remove enough energy to prevent dissociation. Apparently such a situation is found with hydrogen iodide in hexane solution.[9] If we consider oxalyl bromide from this standpoint the difference in behavior at long and at short wave-lengths corresponds to excitation to two different electronic states. The one produced at short wave-lengths has no minimum in its potential energy function, hence the solvent cannot prevent the dissociation and the quantum yield is the same in solution and in the gas phase. At long wave-lengths two-thirds of the molecules in solution lose so much vibrational energy that they cannot dissociate and the quantum yield drops accordingly. In the case of nitrosyl chloride between two-thirds and three-fourths of the molecules are deactivated. The slight trend in the results is such that it could be said that with the larger energies there is a little less chance of the energy being lowered below the dissociation limit. According to Goodeve and Katz[10] the potential energy curves for the upper states of the nitrosyl chloride involved in the absorption process at all the wave-lengths we have used except 5790A are repulsion curves. However, these curves intersect one which does have a minimum and transfers of the type which are involved in predissociation occur between the states. If this set of energy levels is assumed to be correct then the deactivating action of the solvent would involve removal of vibrational energy plus this transfer to an excited state with a minimum in its potential energy function. Ultimately the molecule is deactivated further to the lowest state but the dissociation is prevented in the first action of the solvent.

The arguments which have been presented do not exclude the possibility that a great many cases may exist in which a low quantum yield in solution is due to recombination. That effect has probably been overemphasized in the literature. A deactivation by the removal of vibrational energy is better suited to account for some of the specific effects observed and the small or absent trends with wave-length. It also offers a possibility of predicting the effect of a solvent if any information is available concerning the potential energy function of the excited state.

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[9] Warburg and Rump, Zeits. f. Physik **47**, 305 (1928). They found the quantum yield the same in the gas phase and in solution at 2820A. At shorter wave-lengths their results were complicated by absorption of the solvent they used.

[10] Goodeve and Katz, Proc. Roy. Soc. London **A172**, 432 (1939).