CHEMICAL KINETICS IN GAS PHASE AND IN SOLUTION

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Chemical reactions in solution are much more abundant than reactions in the gas phase, but they have been thought to involve greater difficulties of interpretation. They are more important from a practical standpoint because the syntheses of organic chemistry, the procedures of analytical chemistry, and all the reactions of biology involve reaction in solution.

From the theoretical standpoint, however, our knowledge of gases is much more complete than our knowledge of solutions. The kinetic theory of gases is well established, and exact mathematical formulas are available for calculating the frequency with which molecules collide. The crystalline state is well understood also, through the development of x-ray methods. But very little is known of the liquid state, and because of its pioneer character this field is intriguing.

The molecules of a liquid are held closely together by van der Waals forces, and in many cases there is undoubtedly an association or combination of molecules. Sometimes this association involves the formation of double molecules, and in other cases there may be larger groupings. Recent progress in the theory of the liquid state seems to indicate that there are statistical deviations in the distribution of molecules and that they are involved in the diffraction patterns produced when a beam of x-rays is passed through a liquid. Very little is known regarding the nature of solution and solvation, and one hardly knows whether to emphasize a physical or a chemical combination of the solute with the solvent.

It would be valuable to compare a given reaction in the gas phase with the same reaction in solution. It would be desirable to take over some of the formulas which have been established in the kinetic theory of gases and apply them to solutions. But direct experimental comparison is extremely difficult for several reasons. The temperature range of solvents is limited by the boiling points of the solvents, and only a few gas reactions are known which proceed with measurable velocity in this temperature range. Many gas reactions are complicated by wall effects. Chains are stopped or initiated at the walls, and a catalytic effect of the walls themselves or of materials deposited on the walls may greatly affect the reaction rate. In solution, on the other hand, the reactions are complicated by combination with the solvent. In the gas phase the products of the reaction are immediately lost in the mass of independent molecules, whereas in solution the products may be kept by molecular collision very near to their starting places.

It is an open question as to which is simpler for theoretical study,—reactions in the gas phase where wall effects can predominate, or reactions in solution where solvation may be an important factor.

AQUEOUS AND NON-AQUEOUS SOLUTIONS

Reactions in aqueous solutions are the most common, and an enormous number of rate measurements have been made. Water is unique in many of its properties, and accordingly it is among the reactions in non-aqueous solutions that the closest relation to gas-phase reactions is to be found.

In water and a few related solvents the dissociation of the solutes into ions becomes a very important factor, which is not ordinarily present in the gas phase and in many of the non-aqueous solvents. In spite of the extra variable of an electric charge, reactions between ions may be simpler because the other factors become relatively less important. Marked success has followed the application of two well-known theories of electrolytes to the problem of velocities of reactions involving ions. It is possible to predict the influence of electrolytes on reaction rates by application of the Debye-Hückel theory, and the Brönsted-Bjerrum theory of intermediate complexes.

Reactions involving ions are known also in the gas phase. They may be produced by radium rays, cathode rays, or electrical discharges, but there seems to be no direct correlation between ionization reactions in gases and in solution. Any correlation that could help in bringing these two fields closer together would lead to further progress.

Many ionic reactions proceed so rapidly that they can not be utilized in the study of chemical kinetics. Electrovalent linkages lead to rather complete ionization, and an ion may be considered an activated molecule which needs no extra energy of activation and accordingly no time lag for accumulating it from molecular collisions. Covalent linkages, on the other hand, require so much energy that reactions which involve their rupture do not ordinarily proceed at a measurable rate in the temperature range in which liquid solvents can exist. This leaves reactions involving coördinate linkages as the most common for study in solution.

THE DECOMPOSITION OF NITROGEN PENTOXIDE

The simplest reaction which has been studied directly in the gas phase and in solution is the decomposition of nitrogen pentoxide (2, 3). It is not a chain reaction and it is free from wall effects. The gas-phase reaction seems to be free from complications, and it has been checked in many laboratories. It is an excellent unimolecular reaction and gives practically the same specific decomposition rate from 50 atmospheres osmotic pressure down to 0.05 mm. gas pressure. Inert solvents have very little effect on the decomposition rate. Liquid nitrogen tetroxide causes the decomposition to proceed about twice as fast as in the gas phase, where vacuum may be considered as the "solvent." In nitromethane the decomposition is slightly slower than in the gas phase. Other solvents give intermediate values, as shown in table 1. The energy of activation is the same within the limits of experimental accuracy.

When 100 per cent nitric acid is used as the solvent the decomposition is much slower and the energy of activation is about 3600 calories greater. This greater energy of activation gives such a large temperature coefficient that decomposition at the lower temperatures is barely detectable. The results may be explained on the assumption that an intermediate complex is formed between nitrogen pentoxide and nitric acid which decomposes more slowly,—i.e., it requires more energy for activation.

TABLE 1

The specific decomposition rate of nitrogen pentoxide in various solvents

SOLVENT	VALUES OF $k \times 10^4$			ENERGY OF ACTIVATION
	15°C.	20°C.	25°C.	
				calories
Nitrogen tetroxide	0.159	0.344		25,000
Ethylidene chloride		0.322		24,900
Chloroform		0.274	0.554	24,600
Ethylene chloride		0.238	0.479	24,400
Carbon tetrachloride		0.235	0.469	24,200
Pentachloroethane		0.220	0.430	25,000
Bromine	0.114	0.215		24,000
Gas phase	0.079	0.165		24,700
Nitromethane	0.075			24,500

In the case of the other solvents listed the solvation is probably slight, and in some cases the solvated molecules of nitrogen pentoxide appear to decompose faster than the unsolvated molecules.

The decomposition in saturated solutions is particularly interesting. The oxygen evolved from the solution, which is a measure of the rate of reaction, is contributed by the unsolvated and the solvated nitrogen pentoxide. When the solutions contain an excess of solid crystals the activities of unsolvated nitrogen pentoxide molecules must be the same in all solvents. This gives an opportunity to separate the behavior of the solvated and unsolvated molecules, and to draw conclusions regarding the relative merits of using concentrations or activities in calculating reaction rates. The activities calculated from vapor pressures should all be the same, but the concentrations vary from 0.01 mole per liter in the gas phase to 4.78 moles per liter in carbon tetrachloride at 15°C. If the solvated molecules do not decompose at all, the rate of decomposition would be the same in all solutions. If the solvated and unsolvated molecules decompose at the same rate, the *specific* decomposition rates would be the same in all solutions. Neither situation is found. The specific decomposition rates are of the same order of magnitude in gas phase and in the inert solvents, a fact which indicates that concentrations are more significant than activities in calculating reaction rates. In nitric acid solution the case is different, and further investigation is in progress.

BIMOLECULAR REACTIONS

It would be highly desirable to study a bimolecular reaction in both gas phase and solution, as has been done for the unimolecular decomposition of nitrogen pentoxide. Knowing the collision frequency in the gas phase and the specific reaction rates and the energies of activation in the two media, it should be possible to make a direct calculation of the frequency of collision in solution. Unfortunately it is extremely difficult to find an uncomplicated, bimolecular reaction which goes by the same mechanism in the gas phase and in solution. Research in this direction is important.

An idea of the difficulties of such research may be gathered from the interaction of oxalyl chloride and water (4), which occurs both in the gas phase and in inert solvents. In carbon tetrachloride solution it is an excellent second-order reaction, but in the gas phase it is of a definite fractional order, suggesting a chain reaction. The value of the specific velocity constant varies with the initial concentration, and a solid product is produced as an intermediate step and condensed temporarily on the walls of the vessel. In the gas phase the reaction is more exothermic than in solution, and the conditions are more favorable for chain reactions. In spite of all these complications it can be stated that the specific decomposition rate in the gas phase is several powers of ten faster than the reaction in carbon tetrachloride solution. This fact may be significant or it may simply mean that the mechanisms in the two cases are quite different. This unsatisfactory state of affairs is quite common when one tries to compare a gas phase reaction with the same reaction in solution.

THE DECOMPOSITION OF TRICHLOROACETATES

It has been known for some time that various solutions of trichloroacetic acid decompose according to a good first-order reaction in the neighborhood of 100°C. to give carbon dioxide and chloroform. A much higher temperature is required for decomposition in the gas phase, and then a different set of products is obtained. The reaction is interesting because it illustrates how in at least one case the solvent effect and a whole mass of complex data can be nicely interpreted.

It has been found (11) that it is the trichloroacetate ion which undergoes unimolecular decomposition, and that the ionizing power of the solvent and the addition of electrolytes affect the rate by determining the effective concentration of the ion. Trichloroacetic acid decomposes in water, aniline, and basic solvents, but it does not decompose in benzene, carbon tetrachloride, glacial acetic acid, and non-ionizing solvents. In water the various salts of trichloroacetic acid decompose at about the same rate, because the dissociation is practically complete. In alcohol the sodium salt gives a first-order reaction throughout, but the barium salt changes its specific reaction rate during the decomposition. An increase in ionic strength through the addition of electrolytes gives an increase in the decomposition rate.

The solvent effect involves the degree of ionization, but it involves also a solvation effect. The solvents in which one would expect the greatest solvation, such as water, give the slowest reaction and the largest temperature coefficient. These effects can be explained on the assumption that in the process of solvation extra energy is evolved, and to effect decomposition of the trichloroacetate ion the energy equivalent to solvation must be supplied in addition to the energy required for decomposition.

THE SOLVENT EFFECT

The effect of the solvent in chemical kinetics may be due to a variety of causes. Combination with solvent (solvation) may give an intermediate complex of high stability or low stability, as already explained. If the complex is stable the reaction will go more slowly; if unstable it will go faster. According to a somewhat more indefinite concept the solvent effect may be due to an electrostatic or electromagnetic influence of the solvent on the solute. The solvent effect can sometimes be explained as due to a varying degree of electrolytic dissociation, as in the case of the decomposition of the trichloroacetates.

There are several ways in which a so-called solvent effect may be without any theoretical significance because it is due to secondary complications. For example, bromine dissolved in carbon tetrachloride may react with a certain organic substance rather slowly as bromine molecules, but bromine dissolved in water may react more rapidly as hypobromous acid. The extent to which the carbon tetrachloride or other inert solvent contains dissolved water will determine, under these conditions, the rate of the reaction. The same type of complication may result from dissolved air. For example, the rate of bromination of cinnamic acid depends on the amount of oxygen dissolved in the solution (1), and the order in which different solvents affect the rate of bromination may depend chiefly on the relative solubilities of atmospheric oxygen.

In still other reactions dissolved alkali from the glass may be an important factor in changing the rate in different solvents. This is particularly true of keto–enol transformations. In still other cases the appearance of a heterogeneous phase may lead to erratic changes in velocity which are not fundamental. For example, it was found (4) that the chilling of the carbon tetrachloride solution of oxalyl chloride and water led to a great increase in reaction rate. This unexpected behavior was traced to the precipitation of water droplets at the low temperature, and this colloidal water remained for a long time after the solution was again heated. Other solvent effects can sometimes be traced to chain-stopping properties of the solvent or of impurities which it contains.

It is an important question, not yet fully decided, whether or not most of the so-called solvent effects are due to secondary complications such as have been suggested. If the solvent effects can be rendered comparatively slight by removal of these secondary complications, comparison with the gas reaction may be significant. When secondary complications exist there is no point in trying to compare the reactions in solution with those in the gas phase.

CALCULATION OF COLLISION FREQUENCY IN SOLUTIONS

Extensive efforts have been made to provide a means for calculating collisions in the liquid phase. There seems to be good support for the formulas which give the frequency of collisions between molecules of solute. It is a familiar fact that the osmotic pressure of a dilute solution and other related properties can be calculated from the simple gas laws on the assumption that the solute behaves as a gas. It is probably safe to use the standard formula

$$Z_{1,2} = \sigma_{1,2}^2 n_1 n_2 \sqrt{8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$$

where Z is the number of collisions per second per cubic centimeter between solute molecules 1 and 2, n is the number of molecules per cubic centimeter, M is the molecular weight, and $\sigma_{1,2}$ is the average diameter of the two different molecules. The molecular diameter can not be determined as accurately as in the case of gases but, fortunately, useful calculations of collision frequencies may be made even when the diameters are inaccurately known. Fairly satisfactory results may be obtained with a formula involving the cube root of the molar volume, V, of the pure liquid or solid solute,

$$\sigma = 1.33 \times 10^{-8} \sqrt[3]{V}$$

On the basis of collisions calculated in this way Moelwyn-Hughes (7) has examined a large number of bimolecular reactions in solution. He has calculated the specific reaction rate, k, using the formula

$$k = se^{-E/RT}$$

where s is the collision frequency of the solute molecules and E is the energy of activation calculated from the temperature coefficient. He then compares the calculated rate with the observed rate, and if the two agree the reaction has a "normal velocity." In general, reactions between a neutral molecule and a charged ion give normal velocities. An example of this type is the reaction in alcohol solution between an alcoholate and an alkyl iodide such as

$$C_2H_5I + C_2H_5O^- + Na^+ = (C_2H_5)_2O + I^- + Na^+$$

Reactions between uncharged molecules are abnormally slow by this criterion. For example, the reaction

$$C_2H_5Br + (C_2H_5)_3N = (C_2H_5)_4NBr$$

in acetone at 60°C. has a calculated specific reaction rate of 1×10^4 and an observed value of 1.7×10^{-4}. Other reactions of this general type range from one ten-thousandth to one billionth of the calculated velocity.

This classification is striking. Hinshelwood (5) has suggested that the perturbing influence of an electrically charged ion is necessary to effect successful reaction on collision of activated molecules. It is quite important to extend this examination of normal and slow reactions to radically different types to see if these classifications are completely general. A repetition of some of the earlier experimental work, with special attention paid to the possibility of secondary complications, would also be desirable.

Attempts to calculate the frequency of collision between solute and solvent molecules are much less satisfactory than the calculations of collisions between solute molecules alone. The formulas are given by Moelwyn-Hughes (8). One depends on the viscosity of the solvent, and another on the diffusion coefficient of the solution. Corrections are made for free space between molecules and for other factors. In spite of some experimental checks, these formulas remain of doubtful significance, because the very definition of a collision involving the solvent is uncertain. In the gas phase a collision can be considered as a definite meeting and parting of two molecules,—as a collision between billiard balls. In solution a collision is more likely a continuing process, and the solvent probably undergoes persistent or sticky collisions with the solute molecules. The time of collision or the frequency is then rather indefinite.

SLOW IONIC REACTIONS

As explained before, reactions between ions are usually immeasurably fast, for example such as the neutralization of acids and bases or the reactions between silver and chloride ions. A few slow ionic reactions are known and their interpretation is interesting.

In some cases a certain orientation of the ions or molecules is necessary in order to effect the reaction. Not every collision of activated molecules is effective, and it is necessary to multiply the collision frequency by a steric factor, less than unity. La Mer (6) has studied reactions of this type, for example, the reaction between β-bromopropionate ion and thiosulfate ion.

Another slow type involves the transfer of an atom from one ion to the other. Possibly this is a special case of orientation. The oxidation of arsenite by tellurate in aqueous solution at 100°C. is an example (10), as shown by the following equation

$$TeO_4^{--} + AsO_3^{---} = TeO_3^{--} + AsO_4^{---}$$

A striking relation leading to slow ionic reactions has been pointed out by Shaffer (9). Oxidation-reduction reactions involving two ions are immeasurably fast, but reactions which require triple or quadruple collisions for the stoichiometrical reaction are usually slow. For example the reaction

$$2Ce^{++++} + Tl^{+} = 2Ce^{+++} + Tl^{+++}$$

requires a triple collision for the transfer of the two electrons from a thallous ion to two ceric ions. The reaction is very slow. The reduction of ceric ion by ferrous ion is however a fast reaction, for in this case a collision between two atoms is sufficient. The case for the slow oxidation of thallous ion is further supported by the fact that manganese ions are excellent catalysts. Manganese ions can exist as Mn^{++}, Mn^{+++}, and Mn^{++++}, and transfer of the two electrons can be effected by a series of simple collisions, which of course occur much more frequently. Further investigation along this line is important.

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SYMPOSIUM QUESTIONS

The following questions were suggested for general discussion at the symposium:

1. What is the definition of a collision in solution, and how may collision frequency be calculated?
2. What is the significance of a, s, and E in $k = ase^{-E/RT}$?
3. Where can more experimental facts be obtained for the direct comparison of reactions in solution and in the gas phase?
4. What is the mechanism by which solvents produce minor differences in the rate of a unimolecular reaction, such as are found with nitrogen pentoxide in inert solvents?
5. Are large solvent effects significant or are they due to secondary complications?
6. Is the formation of "intermediate complexes" of varying degrees of stability frequently responsible for changing reaction rates in different solvents?
7. Should concentrations rather than activities be used in calculating reaction rates, except in the case of ions?
8. Is the requirement for orientation at collision the cause of many slow reactions?
9. Is the requirement for multiple collisions significant in explaining slow ionic reactions?
10. Should bimolecular reactions in solution be classified into (a) reactions between ions and molecules giving normal calculated velocities, and (b) reactions between uncharged molecules giving abnormally slow velocities? What is the theoretical explanation of such a classification?

Insofar as general conclusions may be drawn from the limited discussion it can be stated that questions 6–9 seemed to be answered in the affirmative. Answers to 4 and 10 seemed to be uncertain.

With reference to question 1 there was uncertainty regarding the definition of a collision in solution. It was suggested that the collision frequency may be related to the collision frequency in the gas phase through the partial pressure of the solution.

In question 2 the generally accepted significance of the various terms in the Arrhenius equation for collision frequency, orientation at collision, and energy of activation seemed satisfactory. No suggestion of entirely new meanings for these terms was offered.

No suggestions were forthcoming in question 3 as to favorable reactions for direct comparison of gas phase and solution. The importance of such experimental investigations was emphasized.

Discussion of question 5 was not definite. More experimental facts and new reactions are necessary before the general importance of these secondary complications can be decided.

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