

Elementary Reactions in Solution

When a reaction takes place in solution, the solvent usually is present in much larger amounts than the reactants. The solvent concentration therefore remains essentially unchanged during the course of a reaction, and if the method of integration is used to analyze the results, the effect of the solvent will not be revealed. The same is true if the differential method is used to analyze initial rates at different reactant concentrations.

For many reactions the stoichiometric equation does not involve the solvent. For others the solvent does enter into the equation, or there may be reason to believe that the solvent takes part in the chemical change but is regenerated at the end of the process. In these cases the solvent exerts some chemical effect as well as a purely environmental effect.

Theories of liquids are intrinsically more complicated than those of gases. Therefore, the understanding of reactions in solution is less straightforward than that of gas reactions, and sometimes it is preferable to apply different theoretical procedures. So far the treatments involving partition functions have rarely been applied to solution reactions; thermodynamic approaches have proved more useful.

6.1 SOLVENT EFFECTS ON REACTION RATES

solvate
Valuable evidence concerning the influence of the solvent on reactions in solution has come from investigations of two kinds. A few measurements have been made on reactions that occur both in solution and in the gas phase. However, the number of such studies is not large, since many reactions in solution (e.g., those involving ions) will not easily occur in the gas phase. Therefore, much of the information on solvent

TABLE 6.1 COMPARISON OF KINETIC PARAMETERS FOR THE DECOMPOSITION OF NITROGEN PENTOXIDE

Medium	$k/10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C	$\log_{10} (A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E_a/\text{kJ mol}^{-1}$
Gas phase ^a	3.38	13.6	103.3
Carbon tetrachloride ^b	4.09	13.8	106.7
Carbon tetrachloride ^c	4.69	13.6	101.3
Chloroform ^b	3.72	13.6	102.5
Chloroform ^c	5.54	13.7	102.9
Ethylene dichloride ^c	4.79	13.6	102.1
Ethylidene dichloride ^c	6.56	14.2	104.2
Pentachloroethane ^c	4.30	14.0	104.6
Nitromethane ^c	3.13	13.5	102.5
Bromine ^c	4.27	13.3	100.4
Nitrogen tetroxide ^c	7.05	14.2	104.6
Nitric acid ^c	0.147	14.8	118.4
Propylene dichloride ^c	0.510	14.6	113.0

^a F. Daniels and E. H. Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).^b R. H. Lueck, *J. Am. Chem. Soc.*, **44**, 757 (1922).^c H. Eyring and F. Daniels, *J. Am. Chem. Soc.*, **52**, 1473 (1930).

influences has come from the second type of investigation, in which the kinetics of reactions are compared in different solvents.

1 Comparison between Gas-Phase and Solution Reactions

Reactions that occur in the gas phase as well as in solution often show similar behavior in solution as in the gas phase and are affected little by a change of solvent. An example of such a reaction is the thermal decomposition of nitrogen pentoxide,§ some data for which are shown in Table 6.1. The rate constants, pre-exponential factors, and activation energies are much the same in most of the solvents as they are in the gas phase. An exception is with nitric acid, which plays a more active role in the reaction than the other solvents. Similar results are found with the dimerization of cyclopentadiene and the reverse dissociation of the dimer.¹ As seen in Table 6.2, solvents have relatively little effect.

It appears that when a reaction occurs in the gas phase as well as in solution, the solvent usually plays a relatively subsidiary role; it seems to act merely as a space filler and has only a minor influence on the kinetics.

1.2 Comparisons between Different Solvents

It would be unwise, however, to conclude from this evidence that solvent influences are not important in general. Reactions that occur in the gas phase as well as in

§ This reaction is actually composite (Section 8.4.6). The fact that its rate is affected very little by the solvent suggests that this is also true of the elementary reactions involved in the mechanism.

TABLE 6.2 COMPARISON OF KINETIC PARAMETERS FOR THE DIMERIZATION OF CYCLOPENTADIENE AND THE REVERSE DISSOCIATION

Medium	Dimerization		Dissociation	
	$\log_{10} (A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E/\text{kJ mol}^{-1}$	$\log_{10} (A/\text{s}^{-1})$	$E/\text{kJ mol}^{-1}$
Gas phase	6.1	69.9	13.1	146.0
Pure liquid	5.7	66.9	13.0	144.3
Carbon tetrachloride	5.9	67.8	—	—
Carbon disulfide	5.7	74.1	—	—
Benzene	7.1	29.7	—	—
Paraffin	8.1	33.9	13.0	143.1

solution are a special type of reaction. When reactions that do not occur in the gas phase are studied, rates usually vary much more widely from solvent to solvent.

A good example is provided by the reaction between triethylamine and ethyl iodide, studied many years ago by Menshutkin² in 22 different solvents. He measured no activation energies, but this was done later by Grimm, Ruf and Wolff,³ some of whose results are shown in Table 6.3. There is a considerable variation in k , A , and E_a from solvent to solvent. A similar wide variation was found in the reaction between pyridine and methyl iodide.⁴

An interesting feature of such reactions is that the pre-exponential factors are often markedly different from those predicted by simple collision theory, namely, 10^{10} – $10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; similar values are predicted by transition-state theory for reactions between simple molecules (Section 4.6.2). The values in Table 6.3, however, are much lower. In many cases the low A factors appear to be an intrinsic property of the reaction, arising from complexity of the reactants, rather than a specific solvent effect. This is certainly true of the dimerization of cyclopentadiene (Table 6.2), where low A factors occur for the reaction in the gas phase as well as in various solvents.

6 FACTORS DETERMINING REACTION RATES IN SOLUTION

A reaction between two molecules in solution can be thought of as involving three steps: (1) diffusion of the reactant molecules to each other, (2) the actual chemical

TABLE 6.3 COMPARISON OF KINETIC PARAMETERS FOR THE REACTION BETWEEN TRIETHYLAMINE AND ETHYL IODIDE IN VARIOUS SOLVENTS

Solvent	$k/10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 100°C	$\log_{10} (A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E_a/\text{kJ mol}^{-1}$
Hexane	0.5	4.0	66.9
Toluene	25.3	4.0	54.4
Benzene	39.8	3.3	47.7
Bromobenzene	166.0	4.6	52.3
Acetone	265.0	4.4	49.8
Benzonitrile	1125.0	5.0	49.8
Nitrobenzene	1383.0	4.9	48.5

transformation, and (3) the diffusion of the products away from each other. For most processes with which chemists are concerned, the chemical transformation, step 2, is much slower than the diffusion processes: the overall rate therefore is controlled by the chemical change. If this were not the case, the viscosity of the solvent would exert an important influence on the rate, since diffusion and viscosity are related closely: this, however, is found rarely. Another line of evidence relates to activation energies, which for a diffusion process are not usually greater than about 20 kJ mol^{-1} . Most chemical reactions have values much higher than this and therefore are not controlled by diffusion.

There are some rapid reactions, however, that are controlled partly or almost completely by the rate at which the reactants come together: examples are ion combinations (such as $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$) and certain fluorescence quenching processes in solution. The theory of these diffusion-controlled reactions is dealt with in Section 6.7. In the meantime, a discussion is given of some of the theoretical treatments of solution reactions for which the rate is controlled by the chemical interaction that takes place when the reactants come together.

6.1 Collisions in Solution

In 1924 Christiansen⁵ suggested that collision frequencies in solution should be similar to those in the gas phase. During the next few years Hinshelwood, Moelwyn-Hughes, and others investigated a number of reactions in a variety of solvents, and whenever possible they studied the same reactions in the gas phase. The general conclusion that they reached is that certain solvents, such as carbon tetrachloride and benzene, do appear to have a relatively minor effect on rates, but that others have a much stronger effect. They realized that simple collision theory, in which the reactants are regarded as spheres, often greatly exaggerates collision frequencies: therefore, abnormally low A factors may be due to this cause rather than to specific solvent effects. For example, for certain reactions between tertiary amines and alkyl iodides, Hinshelwood and Moelwyn-Hughes concluded⁶ that in solvents such as carbon tetrachloride the A factors are approximately those that would be found if the reactions occurred in the gas phase. Larger A factors found for other solvents were attributed to specific effects, such as solvation.

Another important collision-theory approach to reactions in solution was made by Rabinowitch,⁷ who based a treatment on a distribution function for mercury that had been given by Debye and Menke.⁸ He made a theoretical calculation of the frequency of collisions between a given pair of mercury atoms and compared this frequency with the frequency in the gas phase. He found that in the liquid the frequency is two to three times greater than that in the gas phase. It must be noted that mercury has less structure than solvents such as water and alcohols, so that this conclusion may not apply to them.

The important question of both the frequency and the *distribution* of collisions in solution was investigated by Rabinowitch and Wood⁹ by means of a model experiment involving a tray on which balls were allowed to roll. Agitation of the tray caused the balls to move around, and an electrical device was employed to record collisions between a given pair of balls. When very few balls were on the tray, the collisions

between a given pair occurred individually, with relatively long intervals between successive collisions (see Fig. 6.1, record I). This represents the behavior in the gas phase. The effect of solvents was simulated by adding additional balls until there was fairly close packing. Then it was found that the frequency of collisions was not changed much when the additional spheres were added, but that the distribution of collisions between a given pair of spheres was very different when many spheres were present. When the gas-phase behavior was simulated, individual collisions usually were separated by fairly long periods of time. When the additional spheres were added, collisions instead tended to occur in sets, as shown schematically in Fig. 6.1, record II. Such a set of collisions, occurring in rapid succession, is referred to as an *encounter*. For example, there might be an average of four collisions in each encounter, but the interval between successive encounters would tend to be about four times the interval between collisions in the gas phase. The overall collision frequency therefore is much the same in solution as in the gas phase. The reason for the successive collisions is that in the liquid phase the surrounding solvent molecules form a "cage," which holds the colliding spheres together and causes them to collide a number of times before

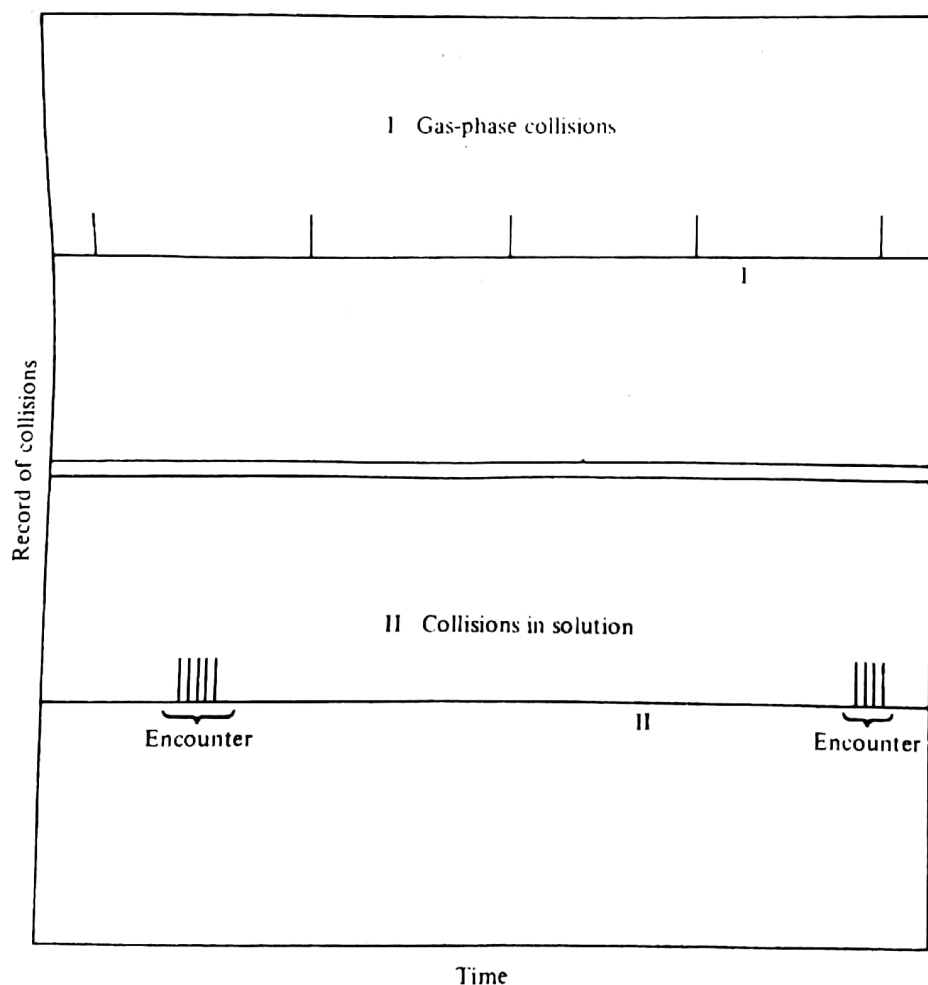


Figure 6.1 Distribution of collisions between solute molecules, as shown by the demonstration of Rabinowitch and Wood. Record I shows schematically the gas-phase collisions, while record II shows the distribution of collisions when a solvent is present.

they finally separate. This tendency for collisions to occur in sets has no effect on ordinary reactions, which involve an activation energy, since reaction may occur at any collision within the set. With reactions that do not involve an activation energy, such as free-radical combinations, this tendency of collisions to occur in sets makes a difference to the pre-exponential factors since reaction occurs at the first collision in any set, with the result that the remaining collisions do not contribute to the rate. Therefore, the pre-exponential factor is related to the reciprocal of the average time elapsing between successive sets of collisions, that is, between successive encounters.

This cage effect, also known as the *Franck-Rabinowitch effect*,¹⁰ has other important consequences. In photochemical reactions in solution, for example, a pair of free radicals produced initially may recombine before they can separate from each other, owing to their being caged in by the surrounding solvent molecules. This phenomenon is known as *primary recombination*, as opposed to *secondary recombination* which occurs after the free radicals have separated.

6.2.2 Transition-State Theory

*solvent
rates
thermodynamic
of solvate*

Transition-state theory¹¹ was applied to reactions in solution first by Wynne-Jones and Eyring¹² and later by Evans and Polanyi¹³ and by Bell.¹⁴ Since it is difficult to formulate partition functions for substances in the liquid state, it has proved more fruitful to use the thermodynamic formulation of CTST [Eq. (4.97)] and to make use of activity coefficients.

The basis of CTST is that rates are proportional to concentrations of activated complexes [Eq. (4.45)]:

$$v \propto [X^\ddagger] \quad (6.1)$$

For a reaction between two species A and B, the activated complexes are in quasi-equilibrium with A and B:

$$\frac{[X^\ddagger]}{[A][B]} \frac{\alpha_\ddagger}{\alpha_A \alpha_B} = K^\ddagger \quad (6.2)$$

where K^\ddagger is the equilibrium constant and the α 's are the activity coefficients. It is satisfactory to neglect these for reactions in the gas phase, but they must now be included since for a solution they may differ markedly from unity. Equations (6.1) and (6.2) give

$$v \propto [A][B] K^\ddagger \frac{\alpha_A \alpha_B}{\alpha_\ddagger} \quad (6.3)$$

and the rate constant is thus

$$k \propto K^\ddagger \frac{\alpha_A \alpha_B}{\alpha_\ddagger} \quad (6.4)$$

For an ideal gaseous system, the activity coefficients are unity, so that the rate constant reduces to

$$k_g \propto K^\ddagger \quad (6.5)$$

Therefore, the rate constant in solution can be related to that in the gas phase by the equation

$$k = k_g \frac{\alpha_A \alpha_B}{\alpha_{\ddagger}} \quad (6.6)$$

This equation can be used for relating the rate constant in solution not only to that in the gas phase but also to that in very dilute solution, where the substances behave ideally; this will be considered later.

If the rates in solution and in the gas phase are to be equal, the activity-coefficient factor $\alpha_A \alpha_B / \alpha_{\ddagger}$ must be equal to unity. This may arise easily for a unimolecular reaction, for which the appropriate factor is $\alpha_A / \alpha_{\ddagger}$. If the reactant and the activated complex have similar structures, as is often the case, α_A and α_{\ddagger} will not differ greatly, and the rate in solution will be similar to that in the gas phase. This similarity in rates applies to the decomposition of nitrogen pentoxide in a number of solvents (Table 6.1). The abnormally slow rate of decomposition in nitric acid and propylene dichloride and the correspondingly high energies of activation may be due to the formation of a complex between the reactant and the solvent. Such compound formation decreases α_A and consequently the rate of reaction.

An alternative and very useful approach is to express the rate constant in terms of entropies and energies of activation [Eq. (4.97)]:

$$k = e \frac{kT}{h} e^{\Delta S^\ddagger / R} e^{-E_a / RT} \quad (6.7)$$

Empirical values for entropies of nonpolar molecules in solution were used by Bell¹⁵ to make estimates of entropies of activation for reactions between such molecules. He deduced in this way that the pre-exponential factor for a reaction in solution should be approximately three times that in the gas phase. This is in agreement with the conclusion that Rabinowitch drew on the basis of collision theory.

6.2.3 Influence of Internal Pressure effect on solvent in rxn

Application of transition-state theory also leads to some useful conclusions about the effect on the rate of the internal pressure of the solvent. The activity coefficient α which appears in Eq. (6.6) is proportional to the activity coefficient γ which relates the behavior of a solute in any solution to its behavior in an ideal solution. The rate therefore can be expressed as

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma_{\ddagger}} \quad (6.8)$$

where k_0 is now the rate constant in the ideal solution [rather than that in the gas phase as in Eq. (6.6)]. A *regular* solution is one in which the molecular distribution is random in spite of nonideality, and for such a solution the activity coefficient γ_2 of a solute can be expressed as¹⁶

$$RT \ln \gamma_2 = V_{m,2} \left(\frac{x_1 V_{m,1}}{x_1 V_{m,1} + x_2 V_{m,2}} \right)^2 \left[\left(\frac{E_{v,1}}{V_{m,1}} \right)^{1/2} - \left(\frac{E_{v,2}}{V_{m,2}} \right)^{1/2} \right]^2 \quad (6.9)$$

where x is the mole fraction, V_m is the molar volume, and E_v is the energy of vaporization, and the subscripts 1 and 2 refer to solvent and solute, respectively. For a

sufficiently dilute solution, $x_2 V_{2,m}$ can be neglected in comparison with $x_1 V_{1,m}$, and the equation reduces to

$$RT \ln y_2 = V_{m,2} \left[\left(\frac{E_{v,1}}{V_{m,1}} \right)^{1/2} - \left(\frac{E_{v,2}}{V_{m,2}} \right)^{1/2} \right]^2 \quad (6.10)$$

To a crude approximation the quantities E_v/V_m may be set equal to the *internal pressures* P_i . Thus,

$$RT \ln y_2 \approx V_{m,2} (P_{i,1}^{1/2} - P_{i,2}^{1/2})^2 \quad (6.11)$$

This is written conveniently as

$$RT \ln y_2 \approx V_{m,2} \Delta \quad (6.12)$$

where Δ , always a positive quantity, is equal to $(P_{i,1}^{1/2} - P_{i,2}^{1/2})^2$. Taking logarithms of Eq. (6.8) and inserting the expressions for $\ln y$ using Eq. (6.12), we obtain

$$RT \ln k = RT \ln k_0 + V_A \Delta_A + V_B \Delta_B - V_{\ddagger} \Delta_{\ddagger} \quad (6.13)$$

This equation gives a useful interpretation of rates in solution in terms of internal pressures.

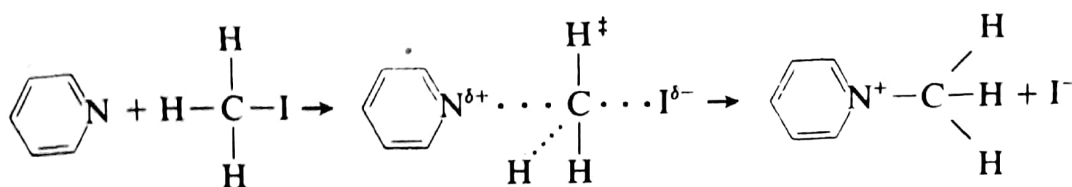
The molar volumes do not vary greatly, so that the internal pressure factors Δ are the most important. If the internal pressures of the solvent, of A and B, and of the activated complexes are all similar, the Δ terms in Eq. (6.10) are all small, and the rate is the same in a particular solvent as it is in a solvent in which there is ideal behavior. If the internal pressure of the solvent is similar to the values for the reactants (i.e., if Δ_A and Δ_B are small) but is different from that of the activated complex (Δ_{\ddagger} is large), k is less in the solvent than in an ideal solvent. Conversely, if the solvent is such that its internal pressure is similar to that of the activated complex but different from those of the reactants, the rate will be high. In general, the internal pressure of the activated complexes is intermediate between that of the reactants and of the products. It therefore follows as a useful rule that if the reaction is one in which the products are of higher internal pressure than the reactants, it will be accelerated by solvents of high internal pressure: if the products are of lower internal pressure than the reactants, the reaction will be accelerated by solvents of low internal pressure. This rule was first found empirically by Richardson and Soper,¹⁷ and it was arrived at theoretically by Glasstone,¹⁸ whose argument was similar to that just given.

The rate constants listed in Table 6.3 provide a useful example of the application of this rule. The product, the quaternary ammonium salt, is ionized and has a much higher internal pressure than the reactants. The activated complex therefore is expected to have a higher internal pressure than the reactants. The rule predicts that the reaction is accelerated by solvents of high internal pressure, and this is generally the case.

6.2.4 ^{effect} Influence of Solvation

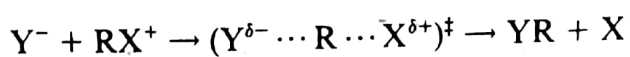
Another useful approach to solvent effects is in terms of the extent of solvation of the reactants and activated complex. The treatment of reactions from this point of view is due largely to Hughes and Ingold.¹⁹ Consider, for example, the reaction between a tertiary amine such as pyridine and an alkyl iodide such as methyl iodide:

6.3 REACTIONS BETWEEN IONS



The products are two separated ions, and in the activated complex there is partial ionization, as represented above. In a polar solvent such as nitrobenzene there is more solvation of the activated complex than of the reactants. The effect of solvation is to lower the activity coefficient: thus, α_{\ddagger} in Eq. (6.6) is expected to be low compared to α_A and α_B , and as a result the rate is high, in agreement with experiment (compare Table 6.3 for an analogous reaction).

On the other hand, in a reaction of the type



there is a decrease in polarity as the activated complex is formed. A polar solvent therefore solvates the activated complex less than the reactants; now the activity coefficients are smaller for the reactants than for the solvent, and such a solvent reduces the rate.