THE KINETICS OF CERTAIN BIMOLECULAR REACTIONS IN SOLUTION

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The rate at which bimolecular reactions proceed in gaseous systems can, in the majority of cases, be accounted for on the assumption that reaction takes place whenever two molecules collide with a combined kinetic energy equal to or greater than E, the heat of activation. In other words, the so-called simple-collision theory, independently advanced by Strutt (1) and by Lewis (2), is here tenable; and as Hinshelwood (3) points out "there is no absolute necessity to look any further for the interpretation of bimolecular reactions." The position of the theory in relation to bimolecular reactions in solution is by no means as assured as this, and in fact but few attempts have been made to apply it to existing data. Norrish and Smith (4), who approached the problem by comparing the observed rates of certain reactions in solution with the rates of the corresponding hypothetical gaseous reactions, have shown that the experimental value of the bimolecular constant is generally about 10^{-8} times the calculated value. These authors, while admitting the possibility of alternative explanations, favor Christiansen's view (5) that the reason for the discrepancy is to be sought in the deactivating influence of solvent molecules. Whether this or some other explanation should prove to be the correct one, it is clear that we are here dealing with a certain type of bimolecular reaction which is profoundly influenced by the solvent, and which proceeds in all solvents at a rate which is very much lower than that which we would anticipate it to have in the gaseous phase. In direct contrast to this behavior we have the case of chlorine monoxide (6), which reacts at the same rate and possesses the same energy of activation in the gaseous state as in a solution of carbon tetrachloride. This observation naturally suggests that there may exist other bimolecular reactions of the same type, i.e., those that are not markedly influenced by the presence of a solvent. Direct experimental comparison between the rates in solution and in the gaseous state being impossible, we follow the treatment of the earlier workers (5, 4) and compare the observed rates of reactions in solution with the rates calculated for the hypothetical gaseous reactions possessing the same critical increments.

The calculated values of the bimolecular velocity constants are determined in the following manner (2, 3). The number of molecules reacting per second per cubic centimeter is

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \sqrt{2}\,\pi\sigma^2 n^2 \bar{u} \cdot e^{-E/RT} \tag{1}$$

where σ is the molecular diameter, n the number of molecules per cubic centimeter, $\bar{u}$ the root-mean-square velocity at temperature T, and E the energy of activation. The bimolecular velocity constant k, expressed in liters per gram-molecule per second, is

$$k = -\frac{\mathrm{d}n}{\mathrm{d}t} \cdot \frac{1}{n^2} \cdot \frac{N}{1000} \tag{2}$$

in which N is the Avogadro constant. Combining equations 1 and 2, replacing $\bar{u}$ by $\sqrt{3RT/M}$, and substituting numerical values for the constants,

$$k = 5.71 \times 10^{25} \cdot \sqrt{T/M} \cdot \sigma^2 \cdot e^{-E/RT} \tag{3}$$

When reaction occurs between different species of molecules, we must substitute the mean molecular diameter $\left(\frac{\sigma_1 + \sigma_2}{2}\right)$ for σ, and the term $\left(\frac{M_1 + M_2}{M_1 M_2}\right)^{1/2}$ for $M^{-1/2}$, hence,

$$k = 5.71 \times 10^{25} \cdot T^{1/2} \left(\frac{M_1 + M_2}{M_1 M_2}\right)^{1/2} \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 e^{-E/RT} \tag{4}$$

This equation as it stands does not take into account the possible influence of the orientation of the colliding molecules at the moment of impact, nor does it allow for the fact that the actual volume of the molecules may become comparable with the total volume of the system. The steric effect is known to be small in the case of gases (5), and the free-space correction does not amount to more than 30 per cent in the cases that are to be considered here. These two terms are therefore omitted. Calling the collision term Z, we can rewrite the equation thus:

$$k = Z \cdot e^{-E/RT} \tag{5}$$

This makes it readily comparable with

$$k_{\text{observed}} = S \cdot e^{-E/RT} \tag{6}$$

in which S is now the empirical, non-exponential term of the Arrhenius equation. The temperature range to which an investigation of reactions in solution must be confined is generally so small that we can regard both Z and S as being independent of temperature.

In order to calculate the diameters of the reacting molecules, we assume (7) that molecules in the solid or liquid states at low temperatures are closely packed, occupying 74 per cent of the total space: σ is then related to the molecular volume V_m by the equation:

$$\sigma = 1.33 \times 10^{-8}\, V_m^{1/3} \tag{7}$$

To avoid confusion it will be as well, perhaps, to emphasize that all values of velocity constants, observed and calculated, given below are expressed in liters per gram-molecule per second.

THE CONVERSION OF AMMONIUM CYANATE INTO UREA IN AQUEOUS SOLUTION

$NH_4CNO \rightarrow (NH_2)_2CO$

The bimolecular constants obtained by Walker and Hambly (8) for this reaction at temperatures ranging between 25° and 80°C. may be summarized thus:

$$k_{\text{observed}} = 4.27 \times 10^{12} \cdot e^{-23{,}170/RT}$$

The fact that these authors found k to vary slightly with the salt concentration led Doyle (9) to reinvestigate the effect of dilution on the value of the constant. His results (table 1) show that the rate is sensibly independent of the dilution. There is therefore no reason to regard the reaction as being other than truly bimolecular. In calculating the constants allowance has, of course, been made for the influence of the reverse reaction. The kinetics of the reaction over the range of 45° examined by Doyle are given by the equation:

$$k_{\text{observed}} = 4.68 \times 10^{12} \cdot e^{-23{,}160/RT}$$

a result in excellent agreement with the earlier work.

TABLE 1

Effect of dilution on the bimolecular constant for the conversion of ammonium cyanate into urea

TEMPERATURE	INITIAL CONCENTRATION OF NH_4CNO	$k \times 10^4$
°C.	*gram-molecules per liter*	*liters per mole per second*
35	0.20	1.47
	0.10	1.45
	0.05	1.50
55	0.20	16.0
	0.05	16.7

Assuming the rate to depend on collisions between unionized molecules of ammonium cyanate, and ascribing to these a diameter of 4.73 × 10^{-8} cm., we obtain by means of equation 3 the following expression for the velocity constant:

$$k_{\text{calculated}} = 2.95 \times 10^{11} \cdot 3e^{-23{,}165/RT}$$

Thus the observed rate is at all temperatures about 15 times as great as the calculated value.

THE REACTION BETWEEN SODIUM ETHOXIDE AND VARIOUS ALKYL IODIDES IN 99.5 PER CENT ETHYL ALCOHOL SOLUTION

$$C_2H_5ONa + RI \rightarrow C_2H_5OR + NaI$$

The rate of formation of ethers in alcoholic solution has been studied extensively and with great precision by Conrad and his collaborators (10), who measured the velocity of reaction at four or five temperatures covering a range of 30° to 36°C. The data are in excellent agreement with the Arrhenius equation—except in the case of heptyl iodide, which is omitted on that account—and are summarized in the second and third columns of table 2. The calculated rates (column 4) were obtained by means of equation 4, the theoretical collision numbers (Z) for the six reactions varying by 6 per cent from the average value of 4.55×10^{11}. It will be shown later that the agreement between theory and practice is actually somewhat closer than is represented by the ratios given in the last column, since the observed velocity constants for very dilute solutions are greater than those given in the table, which refer to solutions which are one-half normal with respect to either reactant.

TABLE 2

Rate of formation of ethers in alcoholic solution

REACTION	E	$k_{30°C.} \times 10^4$		$\frac{k_{\text{calculated}}}{k_{\text{observed}}}$
		Observed	Calculated	
	calories			
$C_2H_5ONa + CH_3I$	19,490	19.1	34.1	1.8
$C_2H_5ONa + C_2H_5I$	20,650	1.71	5.15	3.0
$C_2H_5ONa + C_3H_7I$	19,840	0.60	21.2	35.3
$C_2H_5ONa + C_3H_5I$	19,180	28.9	62.2	2.2
$C_2H_5ONa + C_3H_5Cl$	20,220	0.30	10.9	36.1
$C_2H_5ONa + C_6H_5CH_2Cl$	19,900	0.58	17.4	30.3

THE REACTION BETWEEN SODIUM PHENOXIDE AND VARIOUS ALKYL IODIDES IN ETHYL ALCOHOL SOLUTION

$$C_6H_5ONa + RI \rightarrow C_6H_5OR + NaI$$

Segallar (11) has measured the rate at which several alkyl iodides react with sodium phenoxide in absolute alcohol solution. The initial concentration of both reactants was usually 0.1 gram-molecule per liter, and velocity constants were determined at four temperatures over a range of 50°C. The critical increments (E) given in column 3 of table 3 may therefore be considered accurate to within less than 1000 calories. The molecular diameters of the iodides, given in column 2, have been calculated from the densities of these liquids by means of equation 7; the diameter of the sodium phenoxide molecule is taken to be 6.19×10^{-8} cm., this being the "density value" for chlorobenzene, which is of similar structure and molecular weight. There is on the whole considerable harmony between theory and observation.

The approximate constancy of the observed critical increments for all the reactions considered here is characteristic of many other bimolecular reactions, both catalyzed and uncatalyzed, for which the value of E seems to be determined by the type of reaction rather than by the nature of the reactant molecules. In this sense, then, there appears to be a sharp contrast between bimolecular and unimolecular reactions, for the latter, at all events when uncatalyzed, exhibit wide variations in the value of the energy of activation although the type of reaction may be the same in all cases (12).

TABLE 3

Values of E and k for the reaction between sodium phenoxide and alkyl iodides

IODIDE	MOLECULAR DIAMETER	E	$k_{42.5°C.} \times 10^5$		$\frac{k_{\text{calculated}}}{k_{\text{observed}}}$
			Observed	Calculated	
	cm. $\times 10^8$	*calories*	*liters per mole per second*		
CH_3I	5.28	22,120	101.00	19.1	0.2
C_2H_5I	5.75	22,000	22.50	22.7	1.0
C_3H_7I	6.12	22,450	8.67	11.4	1.3
C_4H_9I	6.45	22,090	8.08	21.0	2.6
$C_5H_{11}I$	6.75	22,280	3.50	16.1	4.6
$C_6H_{13}I$	7.00	22,000	7.73	26.2	3.4
$C_7H_{15}I$	7.22	22,230	7.52	18.5	2.5
$C_8H_{17}I$	7.47	22,500	7.23	12.5	1.7
$C_{16}H_{33}I$	9.01	22,430	7.15	16.1	2.3
C_3H_7I (iso)	6.17	22,100	7.58	20.4	2.7
C_4H_9I (iso)	6.46	21,790	3.22	33.3	10.3
$C_5H_{11}I$ (iso)	6.82	22,250	4.75	17.5	3.7
C_4H_9I (tertiary)	6.51	22,110	202.00	20.2	0.1

Segallar's results for the reaction between sodium phenoxide and six secondary alkyl iodides have been omitted from table 3 because they illustrate no new feature; inclusion of these cases leaves the mean values of both E and $\frac{k_{\text{calculated}}}{k_{\text{observed}}}$ unaltered.

THE REACTION BETWEEN SODIUM-β-NAPHTHOXIDE AND ETHYL IODIDE IN VARIOUS ALCOHOLS

$$C_{10}H_7ONa + C_2H_5I \rightarrow C_{10}H_7OC_2H_5 + NaI$$

The critical increments and bimolecular velocity constants determined by Cox (13) for the formation of β-naphthyl ethyl ether in a series of alcohols are quoted in the second and third columns of table 4, along with the calculated rates (column 4). The diameter of the sodium naphthoxide molecule is taken to be 6.75×10^{-8} cm., a value based on comparison with molecules of similar structure. The theoretical rate is, on the average, 47 times as great as the experimental, but it is noteworthy that the agreement between calculation and observation is best when relatively large values of E are involved, and *vice versa*. Now whereas the variation in the energy of activation indicated in this table may be real, indicating a slightly differing influence of the solvents on the reaction, it is equally possible that the highest value of E (21,000 cal.) is the true critical increment for this reaction in all these solvents, the lower values indicating a slight depression in E caused by the presence of traces of impurity.

TABLE 4

Values of E and k for the formation of β-naphthyl ethyl ether in alcohols

SOLVENT	E	$k_{40°C.} \times 10^5$		$\frac{k_{\text{calculated}}}{k_{\text{observed}}}$
		Observed	Calculated	
	calories			
CH_3OH	21,010	7.67	74	9.6
C_2H_5OH	19,840	13.16	574	44
C_3H_7OH	21,300	7.37	55	7.4
C_4H_9OH	19,650	6.73	774	115
C_3H_7OH (iso)	19,990	10.76	445	41
C_4H_9OH (iso)	19,650	6.65	774	116
$C_5H_{11}OH$ (iso)	20,240	3.72	301	81
$C_5H_{11}OH$ (tertiary)	21,190	0.89	64	72
$C_6H_5CH_2OH$	20,650	4.55	154	34

The approximate constancy in the energy of activation for this reaction in these nine alcohols should be contrasted with the variation of 5000 calories exhibited by a unimolecular reaction—the decomposition of acetonedicarboxylic acid (14)—in the same solvents.

THE REACTION BETWEEN METHYL IODIDE AND VARIOUS BASES IN ETHYL ALCOHOL SOLUTION

$$CH_3I + RONa \rightarrow CH_3OR + NaI$$

The results for another series of etherification reactions, which offer themselves as suitable bimolecular reactions to study from the point of view of chemical kinetics on account of their quantitative nature and their consequent freedom from complications due to reverse changes, are given in table 5. The values used for the molecular diameters of sodium methoxide, sodium ethoxide and the three sodium cresolates are 5.00×10^{-8}, 5.47×10^{-8} and 6.42×10^{-8} cm., respectively. The agreement in the last three examples is probably not quite as close as the table would suggest, for velocity constants were determined at but two temperatures, thus rendering the value of E liable to error.

TABLE 5

Values of E and k for the formation of various ethers

REACTION	E	$k_{30°C.} \times 10^4$		$\frac{k_{calculated}}{k_{observed}}$
		Observed	Calculated	
	calories			
$CH_3I + CH_3ONa$ (10)	21,180	5.18	2.00	0.4
$CH_3I + C_2H_5ONa$ (10)	19,490	19.1	34.1	1.8
$CH_3I + C_6H_5ONa$ (11)	20,900	2.51	3.17	1.3
$CH_3I +$ *o*-$CH_3C_6H_4ONa$ (15)	20,240	2.93	9.16	3.2
$CH_3I +$ *m*-$CH_3C_6H_4ONa$ (15)	20,510	3.23	5.78	1.8
$CH_3I +$ *p*-$CH_3C_6H_4ONa$ (15)	21,220	3.72	1.79	0.5

THE FORMATION OF TRIETHYLSULFONIUM BROMIDE IN BENZYL ALCOHOL–GLYCEROL MIXTURES

$$C_2H_5Br + (C_2H_5)_2S \rightarrow (C_2H_5)_3SBr$$

This reaction is the reverse of that which has been studied so extensively by von Halban (16). Corran (17) determined the rate (k_1) at which triethylsulfonium bromide decomposes in mixtures of varying amounts of benzyl alcohol and glycerol, using that form of the unimolecular velocity constant equation which allows for the influence of a reverse bimolecular change. He also measured the equilibrium constants (K), and studied the influence of temperature on both k_1 and K. From his data, therefore, it is an easy matter to derive values for the bimolecular constant (k_2) and the critical increment E which characterize the reaction between ethyl bromide and diethyl sulfide. These values are given in the second and third columns of table 6, for comparison with the theoretical rates (column 4) which have been calculated by means of equation 4, taking the diameters of the ethyl bromide and diethyl sulfide molecules as 5.57×10^{-8} and 6.31×10^{-8} cm. respectively. The accordance between theory and observation lies well within the limits of experimental uncertainty—a result of particular interest, since we are here dealing with a reaction which proceeds about 10^{12} times as slowly as those which have previously been considered.

TABLE 6

Values of E and k for the reaction between ethyl bromide and diethyl sulfide

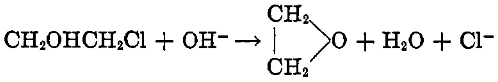
COMPOSITION OF SOLVENT IN MOLECULAR PERCENTAGE OF BENZYL ALCOHOL	E	$k_{85°C.} \times 10^{14}$		$\frac{k_{\text{observed}}}{k_{\text{calculated}}}$
		Observed	Calculated	
	calories			
100	43,400	2.69	0.14	19
89	42,000	9.12	1.02	9
78	40,600	109.6	7.41	15
65	39,600	1479.0	30.2	49

THE INTERACTION OF *o*- AND *p*-DINITROBENZENE WITH SODIUM METHOXIDE AND WITH SODIUM ETHOXIDE IN THE CORRESPONDING ALCOHOLS

$$C_6H_4(NO_2)_2 + NaOR \rightarrow C_6H_6(NO_2)OR + NaNO_2$$

The experimental values for the kinetics of these reactions given in table 7 were measured by Steger (18), who worked with solutions that were 0.05 N with respect to each reactant. The reactions are quantitative, and in three out of the four cases, the velocity coefficients determined at three temperatures are in excellent agreement with the Arrhenius equation. The theoretical collision number for all assumes a value of about 4.96 × 10^{11}.

THE REACTION BETWEEN ETHYLENE CHLOROHYDRIN AND HYDROXYL ION IN DILUTE AQUEOUS SOLUTION



$$CH_2OHCH_2Cl + OH^- \rightarrow \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!O + H_2O + Cl^-$$

The kinetics of the reaction between numerous chlorohydrins and alkali have been investigated by Evans (19). Bimolecular constants for a solution containing both ethylene chlorohydrin and potassium hydroxide at an initial concentration of 0.02 gram-equivalents per liter were determined at three temperatures, the results being in excellent conformity with the equation:

TABLE 7

Action of dinitrobenzenes with sodium methoxide and with sodium ethoxide

REACTION	SOLVENT	E	$k_{35°C.} \times 10^4$ Observed	$k_{35°C.} \times 10^4$ Calculated	$\frac{k_{\text{observed}}}{k_{\text{calculated}}}$
		calories			
o-$C_6H_4(NO_2)_2$ + $NaOC_2H_5$.........	C_2H_5OH	20,590	13.4	10.8	1.2
o-$C_6H_4(NO_2)_2$ + $NaOCH_3$.........	CH_3OH	20,480	8.17	14.3	0.6
p-$C_6H_4(NO_2)_2$ + $NaOC_2H_5$.........	C_2H_5OH	22,030	119	1.04	115
p-$C_6H_4(NO_2)_2$ + $NaOCH_3$.........	CH_3OH	22,290	24.6	0.67	37

$$k_{\text{observed}} = 2.55 \times 10^{12} \cdot e^{-19,870/RT}$$

It is a matter of some difficulty, if indeed it is at all possible at present, to apply the collision mechanism of chemical change to cases of reactions involving ions. We are more likely to succeed if we treat a relatively simple case, such as the one under discussion, where chemical change depends on the number of encounters between an ion and a neutral molecule, rather than cases where both colliding molecules are charged, because in the former case the velocity of the dissolved ion (although profoundly affected by the presence of other ions) may be regarded as unaltered in so far as its influence in determining the number of collisions with neutral molecules is concerned. Furthermore, it is now appreciated that there may be many types of effective collisions, leading to several simultaneous bimolecular reactions, or to the existence of complexes, each of which may undergo chemical change at a rate characterized by its "specific reactivity." In certain examples of catalyzed unimolecular reactions, however, the influence of the reactivity of one kind of complex on the reaction rate is so much greater than even the combined effect of the reactivities of other species of complexes that the latter may be ignored in comparison. By analogy it is to be expected that, for certain examples of bimolecular reactions involving ions, the effectiveness of collisions of a given type may be sufficiently predominating to allow us legitimately to neglect all other types of collisions. As we are here concerned with the application of the collision theory in its broadest possible outline, we will therefore make the assumption that reaction rate in the case under discussion is dependent on the number of effective collisions of one type only, i.e., between the organic molecule ($\sigma = 5.68 \times 10^{-8}$ cm.) and an hydroxyl ion, which is considered to be moving with the same mean velocity as a neutral gaseous molecule having the same mass, and to possess a diameter equal to a (monohydrol) water molecule, i.e., 3.47×10^{-8} cm. On this admittedly crude basis, we arrive at the following equation for the theoretical velocity coefficient:

$$k_{\text{calculated}} = 5.73 \times 10^{11} \cdot e^{-19{,}870/RT}$$

Such close harmony with the experimental value ($k_{\text{obs.}}/k_{\text{calc.}} = 4.4$) is almost certainly fortuitous. Nevertheless, the result is not without interest.

Evans has studied also the rate at which potassium hydroxide reacts with dimethyl- and dichloro-ethylene chlorohydrin, but he found k to diminish perceptibly with increase in time. Smith (20), in a recent repetition of this work, shows that this is caused by isomerism of the chlorohydrin and by the attack of atmospheric carbon dioxide on the alkali. The reaction is strictly bimolecular over its complete course, the velocity coefficient being the same for ethylene chlorohydrin and for propylene chlorohydrin, and being independent of the concentration of alkali over a fourfold change in the neighborhood of $[OH^-] \doteq 0.01$ gram-equivalent per liter.

THE HYDROLYSIS OF ALIPHATIC AMIDES BY AQUEOUS HYDROCHLORIC ACID

$$RCONH_2 + H_2O + H^+ \rightarrow RCOOH + NH_4^+$$

Crocker (21) has shown that the acidic hydrolysis of amides in aqueous solution is bimolecular with respect to the amide and hydrogen ion. The calculated rates included in table 8 have been evaluated on the assumption that reaction occurs whenever a hydrogen ion and an amide molecule collide with the necessary increment of energy. The velocity of the hydrogen ion is taken as equal to that of a hydrogen atom at the same temperature, and its diameter is arbitrarily assessed as 1.0×10^{-8} cm. The error introduced by making this approximation is not as great as it appears to be, for a glance at equation 4 shows that if the value of σ were taken to be one-tenth of this figure, the calculated velocity constant would be reduced by about one-third of its previous value. The reason for this is that the specific part played by the hydrogen ion in determining the number of collisions is influenced far less by the magnitude of its diameter than it is by its great speed. The agreement between theory and practice is seen to be

TABLE 8

Acidic hydrolysis of amides

AMIDE	$\sigma \times 10^8$	E	$k_{61.4°C.} \times 10^2$ Observed	$k_{61.4°C.} \times 10^2$ Calculated	$k_{\text{observed}}/k_{\text{calculated}}$
	centimeters	*calories*			
$HCONH_2$	4.28	19,070	1148	22.9	50
CH_3CONH_2	4.91	20,710	69.2	2.4	29
$C_2H_5CONH_2$	5.47	19,770	83.2	11.8	7
$C_3H_7CONH_2$	5.82	20,090	42.7	8.3	5
$C_3H_7CONH_2$ (iso)	5.85	19,430	50.1	21.9	2.3
$C_4H_9CONH_2$	6.13	20,040	11.0	9.8	1.1

quite good except in one case, which, as before, is that involving the lowest value of E, and in fact the only value of E which shows any marked deviation from the mean. Crocker's results, determined at four temperatures, were summarized by him in the form of equation 6, and show clearly that the non-exponential term S of the Arrhenius equation decreases regularly with increase in molecular weight of the amide, the value of S for the first member (formamide) being 25 times as great as that for the sixth member (valeramide): the calculated collision number (i.e., Z of equation 5), on the other hand, increases slightly as we ascend the series, the sixth value of Z being 80 per cent greater than the first. This is a rather surprising feature, which would require closer examination if it transpired to be true in other cases: the results of Segallar (11), however, which also relate to the reactions of a homologous series, reveal no such disparity, and are, furthermore, somewhat more precise.

DISCUSSION

In all the examples which have been examined here, the observed rates of reaction in solution have been of the same order of magnitude as the rates of the corresponding hypothetical gaseous reactions. The experimental rate has been sometimes greater than and sometimes less than the calculated value, but seldom has the difference between the two rates been greater than can be accounted for by an error of about 1000 calories in the energy of activation. Greater harmony between theory and observation has resulted in those instances where it was possible to compare the rate of the gaseous reaction with that occurring in very dilute solution. The actual values of k have differed by the order of 10^{12}. This approximate agreement must be either (*1*) illusory, due to the fortuitous compensation of rival influences, such as catalysis by traces of impurity and intervention of the solvent in alcohol solutions, or electrical influences and the superposition of simultaneous reactions in aqueous solution, or (*2*) real, indicating that we have been examining systems which are relatively free from most of the unknown complications usually implied in the term "solvent effect," and for which the collision theory in its simple form can reasonably be expected to apply. This latter conclusion seems in most respects to be the more likely, and gains in probability when it is recalled that at least one instance has been encountered in practice—i.e., that of chlorine monoxide in carbon tetrachloride solution (6)—of a bimolecular reaction proceeding in solution in all respects as it does in the gaseous phase.

The general agreement of the simple theory with observation may be presented in an alternative form. Reverting to equation 6, it will be seen that the term S must now be a collision number, and cannot therefore vary beyond fairly narrow limits, defined by the temperature and size of the molecules. Hence, for two different reactions, we have the approximation:

TABLE 9

Comparison of critical increments and temperatures at which reactions proceed at the same rate

REACTION	SOLVENT	E	$T_{k=1}$
		calories	*°Absolute*
$(C_2H_5)_2S + C_2H_5Br$	$C_6H_5CH_2OH$	43,400	731
$(C_2H_5)_2S + C_2H_5Br$	$C_6H_5CH_2OH$ + $C_3H_5(OH)_3$	39,600	647
$NH_4CNO \rightarrow (NH_2)_2CO$	H_2O	23,160	402
p-$C_6H_4(NO_2)_2 + NaOR$	HOR	22,160	357
$C_6H_5ONa + RI$	C_2H_5OH	20,810	418
$C_{10}H_7ONa + C_2H_5I$	HOR	20,390	437
$NaOC_2H_5 + RI$	C_2H_5OH	20,050	385
$CH_2OHCH_2Cl + OH^-$	H_2O	19,930	361
$RCONH_2 + H^+$	H_2O	19,850	359

$$\ln k_1 + \frac{E_1}{RT} \sim \ln k_2 + \frac{E_2}{RT}$$

If we now confine attention to those temperatures at which both reactions proceed at unit rate ($k_1 = k_2 = 1$):

$$\frac{E_1}{T_1} \sim \frac{E_2}{T_2}$$

There should therefore be a *rough* parallelism between the critical increments and the temperatures at which reactions proceed at the same rate, arbitrarily taken as $k = 1$. This is borne out in a general manner by the results given in table 9. The difficulty of finding uncomplicated bimolecular reactions exhibiting a wide variation in E is met with in considering gaseous systems, and appears in a more acute form when we come to deal with reactions in solution, where the temperature of investigation is usually limited by the boiling point of the solvent.

If the collision mechanism is, as we suppose, sufficient to account for the rates at which these reactions proceed, then the factor which determines the order of magnitude of the velocity constant is the exponent $e^{-E/RT}$. Compared with this, the contribution made by all other factors, including deactivation, will be of a secondary character and may even be negligible. Brief reference will be made to some of these auxiliary influences.

1. The dilution effect

The alteration in the value of the velocity constant with a change in the concentration of the reactants has been studied very thoroughly in some of the examples quoted. The rate at which *o*-dinitrobenzene reacts with sodium alkoxides in methyl alcohol and ethyl alcohol is not disturbed by changing the dilution from 20 to 100 liters per gram-molecule (18); within narrower limits the same is true of the conversion of ammonium cyanate into urea in aqueous solution (9). On the other hand, k for the reaction between sodium ethoxide and the alkyl iodides increases with increase in dilution in such a way that the values for 0.01 N solutions are about double the values for normal solutions (22). Cox (13) concludes that the velocity of formation of β-naphthyl ethyl ether in various alcohols at infinite dilution would be about five times the value observed by him for approximately normal solutions. These and similar results for other reactions are usually interpreted by the "dual" hypothesis of Bredig, Snethlage and Acree, which postulates the existence of two concurrent reactions—those between neutral molecules of one reactant (e.g., ethyl iodide) with both neutral molecules and ions of the other reactant (e.g., sodium ethoxide and the ethoxide ion). The change in the value of the observed constant with dilution can on this basis be quantitatively accounted for; the specific reaction rates for both neutral molecules and ions are found to be independent of their concentration and, in the case of the ions, of the components with which they were originally associated. The bearing of these observations on the problem of applying the collision mechanism to reactions in solution is twofold. In the first place, the fact that some reactions proceed more quickly in dilute solutions than in concentrated ones brings about a closer agreement between the theoretical rates calculated for gaseous reactions and the observed rates in solution; the numerical values of the factors $k_{\text{calculated}}/k_{\text{observed}}$ given in the last column of table 2 (and probably also of table 3) should be halved, and the ratios given in table 4 should be divided by 5. In the second place, inasmuch as the "dual" theory implies that there is no necessity to draw a distinction between the manner in which both ion and neutral molecule react with the second neutral molecule, the extent to which the hypothesis is established may be regarded as evidence for the validity of the treatment followed here; that is, for calculating the number of collisions between an ion and a neutral molecule the ion can be treated as if it were itself uncharged (23). Finally, experiment shows that the reactivity of the ion is always, as far as it is known, greater (by a small factor) than that of the neutral molecule (24); this is to be expected as a consequence of its smaller mass and greater velocity. The critical increment is apparently not affected by the relative amounts of ions and neutral molecules present.

2. *The orientation factor*

When a homologous series of reactions is considered (cf. tables 2, 3 and 8), there is a tendency for the ratio $k_{\text{calculated}}/k_{\text{observed}}$ to increase with the molecular weight. If the orientation of the molecules at the moment of impact is in any way a determining factor in the activation process, this result becomes readily explicable, for the steric effect, if operative at all, must be greater the larger the molecule. In order to make $k_{\text{calculated}}$ identical with k_{observed}, it would be necessary, in the absence of any other correction, to ascribe to the relatively large molecules an effective diameter (for collision purposes) equal to about one-third of those used in the calculations. It is unlikely, however, that the orientation factor should be as great as this.

3. The viscosity of the solvent

It is a little difficult to see how the viscosity of the medium influences the rate of reaction. Lewis (25), reviewing Menschutkin's data (28) on the rate of formation of tetraethylammonium iodide, points out that *k* is 20 times greater in benzyl alcohol than in the more mobile solvent benzene. Considering the diffusion of non-electrolytes in water, Jowett (27) has shown that the number of collisions between solute and solvent molecules is proportional to the viscosity of the medium; Ölander (28), however, following another treatment, comes to a different conclusion. While there is insufficient data to test either view, it seems very likely that the rôle played by the viscosity is generally a minor one.

The important point to observe however, is that a very simple collision mechanism offers a fairly complete interpretation of the numerous reactions that have been discussed, without making any appeal to the concept of deactivation.

EXAMPLES SHOWING A WIDE DISPARITY BETWEEN OBSERVED AND CALCULATED RATES

The results given in table 10 refer to a class of reactions which are distinguishable from the type already considered by a marked lack of agreement between the experimental and theoretical values of the velocity coefficients. To this class belong also those cases which have been treated by Norrish and Smith (4), viz., the combination of trimethylamine with nitrobenzoyl chloride, of aniline with bromoacetophenone (13), and of pyridine with allyl bromide (19).

Perhaps the first point to which attention should be directed in dealing with these "anomalous" reactions is that they all involve the conversion of two reactant molecules (a halide with either an amine or a nitrogen base) into *one* molecule of resultant (a ternary ammonium salt). The suggestion naturally presents itself that the collision hypothesis should in some way be modified to allow for an essential difference between this type of change and the double decompositions which are more commonly encountered and to which the hypothesis is known to apply. Reference to gaseous reactions, however, shows that the collision theory accounts in a satisfactory manner for the rate of change, whether the resultant molecules number two (as in the cases of hydrogen iodide (35) and acetaldehyde (36)) or three (as in the cases of nitrous oxide (37) or nitrogen peroxide (38)). Furthermore, we have seen that no correction is necessary in calculating the velocity of combination of ethyl bromide and diethyl sulfide in solution. The divergence between theory and observation in the

TABLE 10

Reactions showing disparity between observed and calculated rates

REFERENCE	REACTION	SOLVENT	E	$k_{60°C.}$		$\frac{k_{\text{calculated}}}{k_{\text{observed}}}$
				Observed $\times 10^5$	Calculated $\times 10^{-2}$	
30	$(C_2H_5)_3N + C_2H_5Br$	C_6H_6	11,190	1.28	239	1.9×10^9
31	$C_6H_5N(CH_3)_2 + CH_3I$	$C_2H_2Cl_4$	11,680	45.4	93.1	2.1×10^7
30	$(C_2H_5)_3N + C_2H_5Br$	$(CH_3)_2CO$	11,710	17.5	108	6.2×10^7
33	p-$H\phi NH_2 + H\phi Cl$*	$99.6\% C_2H_5OH$	11,860	9.80	36.1	3.7×10^7
30	$(C_2H_5)_3N + C_2H_5Br$	$50\%(CH_3)_2CO$ $50\% C_6H_6$	12,040	8.97	65.5	7.3×10^7
30	$(C_2H_5)_3N + C_2H_5Br$	$80\%(CH_3)_2CO$ $20\% C_6H_6$	12,100	16.0	59.7	3.7×10^7
30	$(C_2H_5)_3N + C_2H_5Br$	$20\%(CH_3)_2CO$ $80\% C_6H_6$	12,180	4.92	53.0	1.1×10^8
31	$C_6H_5N(CH_3)_2 + CH_3I$	$C_6H_5NO_2$	13,020	6.65	12.4	1.9×10^7
31	$C_5H_5N + CH_3I$	$C_2H_2Cl_4$	13,220	182	9.04	5.0×10^5
33	$C_6H_5NH_2 + H\phi Cl$	$99.6\% C_2H_5OH$	13,450	13.8	3.25	2.4×10^6
32	$CS(NH_2)_2 + CH_3I$	$(CH_3)_2CO$	13,620	383	4.45	1.2×10^5
32	$C_6H_5N(CH_3)_2 + C_2H_5I$	$(CH_3)_2CO$	13,680	3.11	4.81	1.6×10^7
31	$C_6H_5N(CH_3)_2 + CH_3I$	$C_6H_5CH_2OH$	14,400	250	1.50	6.0×10^4
32	$CS(NH_2)_2 + C_2H_5I$	C_2H_5OH	14,620	143	0.973	6.8×10^4
33	$C_6H_5NH_2 + p$-$NO_2\phi Cl$	$99.6\% C_2H_5OH$	14,680	5.77	0.548	9.5×10^5
34	$(CH_3)_2NH + C_3H_5I$	C_2H_5OH	14,740	275	1.10	4.0×10^4
34	(*iso* $C_5H_{11})_3N + C_3H_5I$	C_2H_5OH	15,190	180	0.577	3.2×10^4
33	p-$H\phi NH_2 + H\phi Cl$	$99.6\% C_2H_5OH$	16,050	25.2	0.063	2.5×10^4

* $\phi = -C_6H_4CH_2-$ or $-CH_2C_6H_4-$.

examples studied here cannot therefore be attributed to the additive nature of the reactions.

Secondly, it should be observed that the experimental values of the velocity coefficients are generally of the same order of magnitude as most of the reactions which have been discussed in the earlier section of this paper, although the general activation theory of chemical change (of which the collision theory is one variant) would lead us to expect much faster rates for reactions possessing such low critical increments. The interpretation given by Christiansen (5) and by Norrish and Smith (4) is that the rate of activation is in fact very fast, as would be the rate of reaction were it not for the deactivating influence of the solvent. In other words, the increase in k which would be expected from such a low value of E is compensated by the decrease in k brought about by the deactivating influence of the solvent. Now although deactivation to this extent has no analogy in the scanty data available for bimolecular reactions in gases, there is nothing inherently improbable in the mechanism suggested, or in the necessarily very specific nature of the deactivation process with regard to both solute and solvent molecules. Nevertheless, the deactivation theory alone leaves the true solvent effect unsolved, for it cannot account for the change in the critical increment which one and the same reaction exhibits in various solvents. If, however, deactivations be an operating factor in solutions, it becomes a matter of importance to inquire into the relation between the probability that a collision should be effective in the deactivating sense and the energy transfer during such a collision. The empirical data for thirteen gaseous unimolecular reactions (conveniently summarized by Ramsperger and Leermakers (39)) make it clear that the probability that an activated molecule will undergo chemical change increases with the value of the energy of activation. It is not improbable that a similar function connects the excess energy possessed by an activated molecule with the chance of transition, by collision with a normal molecule, into a lower quantum state. If this were so, we would expect the number of deactivations to be greatest for activated molecules with the largest critical increments; the greater the excess energy possessed by the activated molecule, the more readily could it be expected to part with it. An examination of the results given in table 10 shows that the reverse is in fact the case, for it is evident that the highest value of E coincides with the least divergence between calculated and observed rates of reaction.

This observation indicates the line along which the explanation for the discrepancy is to be sought. Considering the results of table 10 broadly, we see that rates which for "normal" reactions would be associated with an energy of activation of about 21,000 calories are here related to reactions which in all cases show values of E considerably below this figure. Furthermore, the divergence between the experimental and theoretical k's diminishes steadily as the observed value of E increases, finally disappearing as E approaches that quantity (21,000) which is characteristic of "normal" reactions proceeding with this rate. It would appear, therefore, that the observed critical increments given in this table are false, in the sense that—by some unknown mechanism—they have been depressed from the normal values.

The problem thus resolves itself into tracing the cause for the low values not only of S (of the Arrhenius equation—6) but also of E_{observed}. As we have seen, the deactivation hypothesis deals with the first of these terms only. Several mechanisms could be invented to account for the simultaneous lowering of S and E_{observed} from their normal values, but they all prove unsatisfactory in some particular.

Thus, if we postulate, in the first place, that the depression in E_{observed} is due to the introduction of several internal degrees of freedom of the reacting molecules, it can be shown that the collision term required to satisfy these conditions is of the wrong order. The argument is as follows. In order to estimate the value of the true energy of activation we assume that the velocity of reaction is unaffected by the mechanism, so that, by eliminating k_{observed} and $k_{\text{calculated}}$ from equations 6 and 5, we have:

$$E_{\text{true}} = E_{\text{observed}} + RT \ln \frac{Z}{S} \qquad (8)$$

The number of energy terms involved (see reference 40) is

$$n = 2\left(\frac{E_{\text{true}} - E_{\text{observed}}}{RT}\right) + 2 \tag{9}$$

On substituting values of n obtained in this manner in the equation

$$k = Z' \cdot e^{-E/RT}\left(\frac{E}{RT}\right)^{\frac{1}{2}n-1} \Big/ \underline{|\tfrac{1}{2}n-1} \tag{10}$$

Z', which should be of the same order as the normal collision numbers, turns out to be far too low. There is also the objection that E_{observed} should betray a detectable decrease with rise in temperature, which is, of course, not the case (41).

If we postulate, in the second place, the formation of a complex formed exothermically from the solvent and one of the reactant molecules A, and the establishment of the following equilibrium relations:

$$\text{A} + \text{Solvent} \rightleftarrows \text{Complex} + Q \text{ calories.} \quad K = \frac{[\text{A}]}{[\text{Complex}]} = W \cdot e^{-Q/RT} \tag{11}$$

it can be shown that

$$k_{\text{observed}} = \left(\frac{Z_c}{W}\right) e^{-(E_c - Q)/RT} \tag{12}$$

in which Z_c is the number of collisions between molecules of the complex and molecules of the second reactant B, and E_c is the critical increment for that process. This, like the preceding suggestion, will explain the low value of E_{observed}, but before this equation can tally completely with the experimental relation

$$k_{\text{observed}} = S \cdot e^{-E/RT}$$

it would be necessary for W to be of a fairly high order of magnitude—a condition that is forbidden by the Nernst heat theorem.

The possibility should not be overlooked that, for certain reactions, deactivations by solvent molecules, the calling into play of a large number of internal degrees of freedom, the stoichiometric intervention of the solvent and other factors may operate simultaneously. But it seems premature to speculate beyond this stage.

The object of this paper has been to demonstrate the existence of numerous reactions in solution which appear to be free from the complications that have just been discussed, and for which the collision theory offers a fairly complete interpretation. In this connection, one or two points remain to be mentioned. To conclude that hydroxy bodies generally act as normal solvents, which allow reactions to proceed in them at about the same rate as in the gas, would be erroneous: in those instances dealt with in the earlier section of this paper they appear to exert no disturbing influence on the rate. The division of reactions into two groups, according to whether they harmonize or clash with the simple collision theory, appears to be genuine and not in any sense due to the random repression of 'intermediate' cases. Finally, catalysis by hydrogen ion and hydroxyl ion will not, of course, usually lend themselves to such facile treatment as that given here; it is proposed to return to this aspect of the problem in a forthcoming publication.

SUMMARY

The simple collision theory of chemical reaction rate has been shown to be in harmony with the experimental results obtained for numerous and fairly diverse reactions in alcoholic and aqueous solutions. The instances examined include several etherification processes, other double decompositions, an intramolecular change, an addition reaction, catalysis by hydrogen ion and reactions involving hydroxyl ion. The interpretation given by theory is moderately complete without introducing the concept of deactivation.

Several examples are also quoted of reactions proceeding at rates much slower than the corresponding hypothetical gaseous reactions. The ideas of deactivation by solvent molecules, of the introduction of a large number of internal degrees of freedom of the reactant molecules, and of the stoichiometric intervention of the solvent appear to be insufficient to account separately for this;

and it is difficult to see in exactly what the departure from normal behavior consists.

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