

XIX.—*The Velocity Coefficient for Bimolecular Reactions in Solution.*

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THE application of the kinetic molecular theory to the problem of chemical reactivity, which has met with considerable success in the case of bimolecular reactions in gases at the hands of Hinshelwood and his co-workers, has given us the important concept of kinetic activation which would appear to be of far-reaching and funda-

mental importance to the understanding of the kinetics of dark reactions.

The velocity coefficient  $k$  of a bimolecular gaseous reaction can be calculated (Lewis, J., 1918, **113**, 471) by means of the equation

$$k_T = m \times 114 \times 10^{21} \left( \frac{\sigma_1 + \sigma_2}{2} \right)^2 \sqrt{u_1^2 + u_2^2} \cdot e^{-E/RT} \quad (1)$$

where  $\sigma_1$  and  $\sigma_2$  are the molecular diameters,  $u_1$  and  $u_2$  are the velocities of the reacting molecules,  $m$  is the number of resultant molecules formed at each collision, and  $E$  is the energy of activation obtained from the temperature coefficient of the reaction. The object of the present paper is to examine the above equation in the case of non-ionic reactions in solution.

For this purpose, reactions of the simplest possible type are required taking place in a non-ionising solvent with regular and measurable velocities. The test may then be carried out either (1) by comparing two closely similar reactions in the same solvent in order to eliminate effects of solvation, or (2) by finding an expression for the number of effective collisions per second between the dissolved reactants in terms of the critical increment determined from the temperature coefficient, and comparing the results given by the expression with the experimentally observed velocity. Both these methods have been adopted in the present paper.

No suitable reactions could be found in the literature to provide data for the present investigation. A careful study has therefore been made of the velocities and temperature coefficients of two reactions which were considered to approach closest to our ideal requirements—the interactions of trimethylamine with *m*- and with *p*-nitrobenzyl chloride in carbon tetrachloride and benzene solutions.

#### EXPERIMENTAL.

The *m*- and *p*-nitrobenzyl chlorides after recrystallisation from petroleum ether (b. p. 40–60°) melted at 45.5° and 72.5°, respectively, and gave correct analyses. The trimethylamine was obtained from its hydrochloride by treatment with concentrated potassium hydroxide solution and warming, the evolved gas being passed through three soda-lime tubes and absorbed in the cooled solvent. The strength of the solution was obtained by titration with *N*/10-hydrochloric acid, a mixture of methyl-orange and sodium indigo-tinsulphonate being used as indicator. The solvents, benzene and carbon tetrachloride, were purified in the usual manner, the thiophen-free benzene being frozen and distilled from phosphoric oxide, and the carbon tetrachloride washed with soda and distilled from fused calcium chloride.

The velocity measurements were carried out in nine boiling tubes. These were drawn out and placed in a bath of ice, and 10 c.c. of nitrobenzyl chloride solution and 10 c.c. of base were placed in each tube, which was then quickly sealed off and placed in the thermostat, the timing being started from this point.

The method of analysis varied with the solvent. In the case of benzene, the tube was opened and the contents were washed into a conical flask containing dilute nitric acid to stop the reaction, and a known quantity of silver nitrate solution. The whole was shaken with a considerable quantity of ether for about one minute in order to coagulate the silver chloride. The excess of silver nitrate was titrated with ammonium thiocyanate in the usual way.

Two thermostats were run side by side, and solutions for velocity measurements in each of them were made from the same stock solution, the reactions with the *m*- and *p*-isomerides being conducted at each temperature simultaneously. The strength of the silver nitrate solution was 0.04986*N*; *a* represents the concentration of the amine, *p* that of *p*-nitrobenzyl chloride, and *m* that of *m*-nitrobenzyl chloride. Tables I and II are specimens of the complete results with benzene as solvent, whilst Table III gives a summary of the results, the concentrations *a*, *m*, and *p* being expressed as normalities.

The logarithm of the velocity coefficient for both the *m*- and the *p*-nitrobenzyl chloride reactions was plotted against the inverse of the absolute temperature. In each case a straight line was obtained, from which Table IIIA was compiled.

TABLE I.

*p*-Nitrobenzyl chloride and trimethylamine at 30°.*p* = 0.08231*N*; *a* = 0.1276*N*.

Time (mins.).	AgNO <sub>3</sub> (c.c.).	<i>x</i> .	<i>k</i> . 10 <sup>3</sup> .	Time (mins.).	AgNO <sub>3</sub> (c.c.).	<i>x</i> .	<i>k</i> . 10 <sup>3</sup> .
1246	8.92	0.0224	2.19	2686	15.22	0.03794	2.18
1290	9.16	0.02283	2.18	3924	18.90	0.04712	2.19
2480	14.71	0.03667	2.23	3955	18.92	0.04718	2.17
2661	15.22	0.03794	2.20	3983	19.05	0.04794	2.19
							Mean 2.19

TABLE II.

*p*-Nitrobenzyl chloride and trimethylamine at 25°.*p* = 0.08231*N*; *a* = 0.1280*N*.

Time (mins.).	AgNO <sub>3</sub> (c.c.).	<i>x</i> .	<i>k</i> . 10 <sup>3</sup> .	Time (mins.).	AgNO <sub>3</sub> (c.c.).	<i>x</i> .	<i>k</i> . 10 <sup>3</sup> .
2776	13.03	0.03248	1.65	5614	19.38	0.04832	1.60
2806	13.05	0.03253	1.63	5661	19.40	0.04837	1.59
3897	16.00	0.03988	1.62	5676	19.44	0.04846	1.59
3934	16.05	0.04000	1.62	5728	19.47	0.04854	1.58
3955	16.07	0.04005	1.61				Mean 1.61

TABLE III.

Temp.	$\alpha$ .	$p$ .	$m$ .	Limits of $k \times 10^5$ .	$k \times 10^5$ .
35°	0.0842	0.1172	—	305—293	301
35	1.1319	—	0.07787	217—212	214
30	0.1276	0.08231	—	223—217	219
30	0.1290	—	0.08130	163—152	158
25	0.1280	0.08231	—	165—158	161
25	0.1301	—	0.08130	119—112	115

TABLE IIIA.

Reactant.	$k_{25}$ .	$k_{35}$ .	$k_{35}/k_{25}$ .	$E$ .
<i>p</i> -Nitrobenzyl chloride .....	0.00161	0.00298	1.851	11,210
<i>m</i> - „ „ .....	0.00115	0.00214	1.861	11,320

When carbon tetrachloride was used as solvent, consistent velocity coefficients could not be obtained. When an aqueous suspension of silver chloride, carbon tetrachloride, and ether is shaken, an unmanageable emulsion results, but this difficulty was overcome by filtering off part of the silver chloride and the whole of the carbon tetrachloride through a wet Swedish filter-paper before adding the ether. The reason for the irregularity has not been elucidated, but it may be due to the formation of a complex between trimethylamine and carbon tetrachloride, since a white solid is deposited from 0.3*N*-solutions of the amine in carbon tetrachloride.

#### Discussion of Results.

The main difficulties to be overcome in applying equation (1) to test the kinetic molecular hypothesis of reaction in solution are due to the uncertainty of the effect of the solvent upon the concentration and diameter of the dissolved molecules.

*The Calculation of ( $E_1 - E_2$ ) for Two Similar Reactions.*—The difficulties can, however, be *partly* eliminated by comparing the above two closely similar reactions in the same non-polar solvent. If we take the same concentrations of reactants in each case, it is probable that they will suffer the same number of molecular encounters, since no great difference in solvation or molecular velocity is to be imagined between the two isomerides in such a non-polar solvent as benzene. By applying equation (1) to the two reactions, we can therefore eliminate the  $\sigma$  and  $u$  terms by division, and obtain the relationship  $k_1/k_2 = e^{-E_1/RT}/e^{-E_2/RT}$  or  $(E_1 - E_2)/RT = \log_e k_2/k_1$ . Hence the difference between the critical increments can be calculated from the ratio of the velocity coefficients, and compared with that obtained directly from a measurement of the temperature coefficients of the reactions.

If the conditions described above for making the rôle of the solvent merely one of a medium for the reaction are successful, there

is no reason why  $E_1$ ,  $E_2$ , and  $(E_1 - E_2)$  should not be obtained with some accuracy. In the equation  $k_1/k_2 = e^{-(E_1 - E_2)/RT}$ , small changes in  $E_1 - E_2$  are considerably magnified in  $k_1/k_2$ , and hence a slight error in  $k_1/k_2$  will hardly influence  $E_1 - E_2$ . Similarly, in the equation  $\log_e k_{T_2}/k_{T_1} = E/R \cdot (1/T_1 - 1/T_2)$ , a small experimental error in  $k_{T_2}/k_{T_1}$  will have but little effect on  $E$ .

In Table IV, the results obtained in the present paper are compared with those obtained by Olivier (*Rec. trav. chim.*, 1923, 42, 516) for the hydrolysis of various benzyl halides with a mixture of equal parts of water and alcohol, and by Conant (*J. Amer. Chem. Soc.*, 1925, 47, 488) for the reaction of various benzyl chlorides with potassium iodide in acetone solution. In both these cases, the solvent was of a highly polar character, and in the second case one of the reactants was an ion. For these reasons, and also for reasons of steric hindrance where the reactions of *o*- and *p*-isomerides are compared, we should not expect the same close agreement between the two methods of determining  $(E_1 - E_2)$  as that to be obtained when precautions are taken to eliminate serious errors due to differences of solvation and steric hindrance in the isomeric substances employed. This, indeed, is seen to be the case, for in the present reaction where these disturbing effects have been reduced to a minimum, the concordance between the two methods of calculating  $(E_1 - E_2)$  is close, the two values differing only by 90 cal., while in the other cases cited the divergences vary from 560 cal. to 1660 cal.

TABLE IV.\*

	$E_1$ and $E_2$ from temp.	$E_1 - E_2$ coeff.	$E_1 - E_2$ .
<i>m</i> - and <i>p</i> -Nitrobenzyl chlorides + trimethyl-amine	11,320 } 11,210 }	110	200
<i>o</i> - and <i>p</i> -Bromobenzyl chlorides + KI	19,140 } 17,970 }	1,170	-250
<i>p</i> - and <i>o</i> -Chlorobenzyl chlorides + KI	18,330 } 17,610 }	720	160
$\omega$ -Chloro- <i>p</i> - and - <i>o</i> -xylenes + alcohol-water	20,460 } 19,860 }	600	-550
$\omega$ -Chloro- <i>p</i> - and - <i>m</i> -xylenes + alcohol-water	20,460 } 20,230 }	230	-1430

*The Calculation of the Velocity Coefficient, k.*—We will now consider the more general problem of the calculation of the velocity coefficient of a non-ionic reaction in non-polar solution, as Lewis (*loc. cit.*) and

\* Since writing this paper, we have found that Peacock (*J. Physical Chem.*, 1927, 31, 535), working from a different point of view, calculated  $E_1 - E_2$  by the two methods given in the text for certain reactions studied by himself and by Holleman. Neither of the sets of reactions was carried out in non-polar solvents, and the reactions studied by Peacock give velocity coefficients which vary with the initial concentration of the reactants.

Hinshelwood (J., 1923, **123**, 2730; 1924, **125**, 184) have done for gaseous systems.

The expression giving the number of collisions per c.c. per second between two gases containing  $n_1$  and  $n_2$  molecules per c.c. is

$$Z = \pi \left( \frac{\sigma_1 + \sigma_2}{2} \right)^2 n_1 n_2 \sqrt{u_1^2 + u_2^2} \quad . \quad . \quad (2)$$

where the symbols have the same significance as in (1). This expression, as Christiansen (*Z. physikal. Chem.*, 1924, **113**, 35) has suggested, will apply also to the case of the collisions between two solutes, but it will be subject to correction for the true values of  $\sigma_1$  and  $\sigma_2$  which are somewhat affected by the presence of the solvent.

It has been suggested (Lewis, "A System of Physical Chemistry," Vol. III, p. 225) that the number of collisions in the case of a bi-molecular reaction in solution can be calculated from the diffusion coefficient of the bodies involved. It is possible to show, however, that we obtain by this means the same result as is given by equation (2). If  $\Delta$  is the mean displacement in a given direction in time  $\tau$ , then the diffusion coefficient is given by  $D = \frac{1}{2}\Delta^2/\tau = \frac{1}{2}\Delta v$ , where  $v$  is the mean velocity of displacement. If  $\tau$  is made equal to the time between successive collisions between solute molecules,  $\Delta$  becomes their "linear" mean free path. Hence the number of collisions per second will be given by  $v/\Delta$ . Now the actual path of the solute molecule between collisions is irregular owing to collisions with the solvent; it will be described with a mean velocity equal to the average thermal velocity of agitation, and the total distance travelled will be  $L$ , approximately equal to the mean free path  $L$  in a gas at the same concentration. Now since  $\Delta$  is the algebraic sum of the resolved parts of the irregular path  $L$  in a given direction, and the resultant mean velocity  $v$  is obtained by resolving and summing the thermal velocity over the path  $L$  in the same way,  $v/\Delta = u/L =$  number of collisions calculated from gas theory. Calculation by the help of the diffusion theory, is, however, rendered impossible, since there is no way of obtaining  $\Delta$  independently, the Clausius equation being inadmissible. We shall therefore use equation (2) in the calculation of the number of collisions in solution allowing for the following secondary effects of the solvent :

(1) The free space, and therefore the concentration of the solute, will be affected by the actual volumes occupied by solvent molecules. This volume,  $s$ , can be determined from the critical data of the solvent or from the Clausius-Mossotti theory of dielectrics, and is of the order of 24 c.c. per g.-mol. for benzene. If  $V$  is the molecular volume of the solution, the effective concentration of a solute in benzene is thereby increased by the factor  $V/(V - s) = 1.26$ .

(2) Solvation. The molecular diameters of a number of solutes in various organic solvents have been calculated by the Stokes-Einstein diffusion expression by means of data obtained by Thovert (*Ann. Physique*, 1914, 2, 369), Ohlm (*Medd. K. Vetenskapsakad. Nobel.-Inst.*, 2, No. 24 and No. 26), Dummer (*Z. anorg. Chem.*, 1920, 109, 31), and Miller (*Proc. Roy. Soc.*, 1924, A, 106, 124), and they have been found to vary little from solvent to solvent, and also to be of the same order as the value determined for gases by Rankine. In subsequent calculations we have taken the value of the molecular diameter to be  $4 \times 10^{-8}$  cm. for all the cases considered.

*The Discrepancy between the Observed and the Calculated Values of the Velocity Coefficient.*—The experimentally determined values of the critical increment,  $E$ , now enable us to calculate the velocity coefficient by equation (1) corrected for solution as above :

$$k = 114 \times 10^{21} [V/(V - s)]^2 \times 16 \times 10^{-16} \sqrt{u_1^2 + u_2^2} \cdot e^{-E/RT}$$

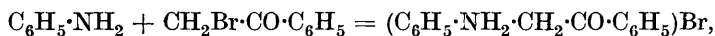
Taking the critical increment  $E$  as 11,200 cal., we obtain the velocity coefficient at  $30^\circ$  for the reaction between *p*-nitrobenzyl chloride and trimethylamine as  $1.2 \times 10^5$ , whereas that determined experimentally is 0.00219.

The reason for this large discrepancy must undoubtedly be bound up with the nature of the liquid state : in the solvent, the mean free path is of the same order as the molecular diameter. Nearly every collision between potentially reactant solute molecules must therefore of necessity partake of the nature of a ternary collision at least, in which the third body is a solvent molecule. The energy of collision must therefore be divided between three (at least) instead of only two molecules, and the solvent, according to its molecular structure, may take up a large or small quantity of the energy which would otherwise lead to chemical reaction. It may thus happen that the number of fruitful contacts between molecules is small compared with the number calculated from the simple bimolecular theory. To allow for this deactivating action of the solvent we may reintroduce the probability factor  $P$  into the velocity-coefficient equation;  $P$  therefore represents the fraction of effective to total collisions taking place between molecules possessing the required energy of activation, and is equal to  $0.00219/1.2 \times 10^5 = 1.9 \times 10^{-8}$  for the above reaction.

*Other Reactions.*—It appeared of interest to see how  $P$  varies from solvent to solvent, or in the same solvent for two similar reactions. The following reactions have been employed :

I. The reactions studied above.

II. The reaction between bromoacetophenone and aniline,



studied by Cox (J., 1921, **119**, 142) in several solvents and at more than one temperature.

III. The reaction between pyridine and allyl bromide,  $C_5H_5N + C_3H_5Br = (C_5H_5N \cdot C_3H_5)Br$ , studied by Hawkins (J., 1922, **121**, 1170).

The result of these calculations is shown in Table V. The volume occupied by the molecules in 1 g.-mol. of solvent,  $S$ , is taken as one-quarter of the volume at absolute zero, except in the cases of butyl alcohol and chloroform, where it is obtained from the Clausius-Mossotti theory of dielectrics.

TABLE V.

Reaction and solvent.	Temp.	$S$ .	$E$ .	$k$ (obs.).	$k$ (calc.).	$P \times 10^8$ .
III. Acetophenone ...	28°	24.5	12,100	0.01040	$1.84 \times 10^4$	56.4
I. Benzene .....	30	24	11,200	0.00219	$1.2 \times 10^5$	1.9
II. Benzene .....	38	24	8,088	0.00098	$2.44 \times 10^7$	0.004
III. Benzene .....	28	24	14,400	0.00030	$4.6 \times 10^2$	64.8
III. Toluene .....	28	21.6	15,100	0.00023	$1.23 \times 10^2$	187.2
II. Chloroform .....	38	21	10,760	0.00188	$3.1 \times 10^5$	0.59
II. Acetone .....	38	14	11,080	0.02690	$1.6 \times 10^5$	16.8
III. Acetone .....	28	14	13,600	0.00505	$1.46 \times 10^3$	356.0
II. Nitrobenzene ...	38	21.7	13,470	0.01350	$3.4 \times 10^3$	400.0
III. Nitrobenzene ...	28	21.7	13,300	0.01290	$2.46 \times 10^3$	524
II. Methyl alcohol	38	7.7	12,400	0.07480	$1.73 \times 10^4$	432
II. Ethyl alcohol ...	38	11.2	13,910	0.06260	$1.62 \times 10^3$	3872
III. Ethyl alcohol ...	28	11.2	15,100	0.00251	$1.19 \times 10^2$	2100
II. Butyl alcohol ...	38	22	14,060	0.05500	$1.42 \times 10^3$	3888
II. Benzyl alcohol	38	22	14,290	0.04400	$8.9 \times 10^2$	4920

Although the three reactions considered are of the same type, these values of  $P$  show but little uniformity in their variation from solvent to solvent. However, they seem to be generally much smaller for non-polar than for polar solvents, and uniformly high for the alcohols. This may conceivably be due to the fact that the polar solvent molecule at the moment of collision forms a momentary complex with the potentially reactant molecules, which retains the energy in the system long enough for reaction to take place; the non-polar solvent, on the other hand, must be imagined to act only as a diluent to the energy in collisions between solute molecules, reducing largely the number of effective collisions.

*The Rôle of the Solvent.*—It is well known that variation of the solvent has in most cases a very great effect on the velocity of a given reaction. In many cases, as, for example, in the mutarotation of sugars (Lowry and Faulkner, J., 1925, **127**, 2883), the solvent itself undoubtedly enters into the reaction as an intermediate reactant. In other cases, limiting factors, such as solubility and ionisation of one or more of the components, may affect the course of a reaction. Such cases must be separately considered on their



own merits. The formation of quaternary ammonium complexes, however, does in a general way appear to be linked up with the polar nature of the solvent (McCombie, Scarborough, and Smith, J., 1927, 802), and it has been suggested that in such cases the general action of the solvent is due to the electrical environment it provides for the reacting molecules (Norrish, J., 1923, 123, 3006). A polar solvent may by close association create an induced polarity in the reacting molecules with the absorption of energy, and the consequent lowering of the critical increment of the reaction. We should therefore expect an increased velocity in the more polar solvents.

The facts now presented, however, make it clear that this is not the only general effect, and that we must also take account of the deactivating effect of the solvent as represented by the factor  $P$ , treated in the last section. It follows that, while a solvent may increase the velocity of a reaction by lowering the critical increment, yet there is always a reverse effect, due, as we believe, to the removal of energy from the potentially reactant molecules at the moment of collision by the molecules of the solvent.

#### *Summary.*

(1) An attempt is made to apply the theory of kinetic activation to the investigation of reaction velocity in non-polar solution.

(2) The velocity of reaction between *m*- or *p*-nitrobenzyl chloride and trimethylamine in benzene solution has been determined for three temperatures.

(3) The difference in the critical increments of the two reactions has been obtained by a comparison of their velocities and found to agree with that calculated from the temperature coefficients.

(4) The expression for the number of collisions between dissolved reactants has been considered, allowance being made for the more important effects of the solvent.

(5) The calculated velocity coefficients are in all cases greater than those determined experimentally.

(6) It is suggested in explanation that the probability factor connecting the number of potentially reactant with the number of reacting molecules is not unity, as in the case of gases, but is lowered by a deactivating effect of the solvent.

(7) This deactivating effect is considered to be connected with a removal of energy of activation by one or more of the solvent molecules at the moment of collision between the reactants.

(8) The rôle of the solvent is considered in the light of the probability factor in the reaction-velocity equation.

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