32. *The Kinetics of the Esterification of Acetic Anhydride in Ethyl-alcoholic Solution.*

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THE rate at which several bimolecular reactions proceed in solution is in good agreement with that calculated by means of the equation : Number of molecules reacting = number of collisions × $e^{-E/RT}$, where E is the energy of activation given by the Arrhenius equation (Moelwyn-Hughes, *Chem. Reviews*, in the press). On the other hand, the observed rate of certain reactions, notably the formation of ternary ammonium salts, is several powers of ten smaller than that given by this formula (Christiansen, *Z. physikal. Chem.*, 1924, **113**, 35; Norrish and Smith, J., 1928, 129). The reaction studied here, *viz.*, $(CH_3{\cdot}CO)_2O + C_2H_5{\cdot}OH \longrightarrow CH_3{\cdot}CO_2C_2H_5 + CH_3{\cdot}CO_2H$, belongs to the latter category; and it is with a view to learn something about the cause of the discrepancy between theoretical and experimental rates that the present work was undertaken.

The course of the reaction has been followed by Menschutkin's method (*Z. physikal. Chem.*, 1887, **1**, 611). Samples of the reaction mixture were removed at intervals, and kept in distilled water until the acetic anhydride was completely converted into acetic acid, which was then estimated in the usual way. The initial titre should always be double the " infinity " titre. The reaction between acetic anhydride and ethyl alcohol in various solvents is bimolecular, but when the latter is used as solvent, the reaction should be unimolecular with respect to the former, the constant being independent of its concentration. The data given in Table I bear this out; k is the unimolecular constant given by the equation

$$k = 1/t \, . \ln (T_0 - T_\infty)/(T_t - T_\infty),$$

TABLE I.

Acetic anhydride in ethyl alcohol at 50·5°.

Initial conc. of anhydride = 0·0952 g.-mol./litre.			Initial conc. of anhydride = 0·1936 g.-mol./litre.		
Time (mins.).	T, c.c.	$k \times 10^5$ (secs.$^{-1}$).	Time (mins.).	T, c.c.	$k \times 10^5$ (secs.$^{-1}$).
0	26·20	—	0	53·20	—
24	24·75	8·14	17	51·15	7·86
54	23·20	8·03	47	47·70	8·21
97	21·25	8·16	75	44·94	8·26
129	20·05	8·19	119	41·40	8·21
173	18·55	8·45	177	37·75	7·76
276	16·70	7·80	309	32·90	7·77
455	14·65	7·82	379	31·20	7·72
Inf.	13·10	—	Inf.	26·60	—
Average $k = 8{\cdot}08 \times 10^{-5}$ sec.$^{-1}$			Average $k = 7{\cdot}97 \times 10^{-5}$ sec.$^{-1}$		

in which T_0 and T_∞ are the initial and final titrations respectively, and T_t is the titration after t seconds, 0·0364N-baryta being used.

The influence of temperature on the reaction rate is shown below, from which it will be seen that the observed velocity constants are in good agreement with the Arrhenius equation $k = 4{\cdot}70 \times 10^8 \times e^{-18,820/RT}$.

Acetic anhydride in ethyl alcohol prepared for conductivity purposes.

Temp.	50·5°	55·1°	60·0°	65·2°	70·2°	75·2°
$k \times 10^4$, obs.	0·803	1·27	1·95	2·88	4·24	6·63
$k \times 10^4$, calc.	0·816	1·24	1·87	2·96	4·48	6·63

The concentration of acetic anhydride used in these experiments varied by ± 5% from an average of 0·195 g.-mol./litre. The ethyl alcohol employed was a very pure specimen prepared for conductivity purposes, kindly given by Sir Harold Hartley, F.R.S., and Mr. O. L. Hughes. Several reactions occurring in solutions are sensitive to traces of impurity in the solvent; it was therefore thought advisable to study the kinetics of the reaction in a sample of ethyl alcohol prepared by another process.

Ordinary absolute alcohol (99·8%), which had been refluxed for two days over freshly fired quick-lime, was fractionated, the constant-boiling distillate being then used as solvent. The results obtained are given below, the Arrhenius equation now taking the form

$$k = 4{\cdot}05 \times 10^8 \times e^{-18,710/RT}.$$

Acetic anhydride in ethyl alcohol dried over calcium oxide.

Temp.	50·4°	59·9°	70·1°
$k \times 10^4$, obs.	0·826	1·95	4·42
$k \times 10^4$, calc.	0·833	1·94	4·44

The results are seen to be accurately reproducible, so that the rate is not influenced by traces of dissolved gases or by other impurities in the solvent. The average value of the velocity constants given by three experiments at 50·45° is $8{\cdot}10 \times 10^{-5}$ sec.$^{-1}$. Combining this with the best value for E (18,800 cals.) we may summarise the kinetics of the esterification of acetic anhydride in ethyl alcohol solution by the relation $k = 4{\cdot}4 \times 10^8 \times e^{-18,800/RT}$. We shall now compare the observed rate of reaction with values calculated from a knowledge of the number of collisions of various types which occur in solution.

Calculation of Reaction Rate from Number of Collisions between Acetic Anhydride and Ethyl Alcohol Molecules.—If chemical change results when a molecule of acetic anhydride collides with sufficient violence against a neutral alcohol molecule, the reaction rate should be proportional to the number of collisions of this kind. The number of alcohol molecules encountered per second by each molecule of acetic anhydride is $Z = 3\pi\sigma\eta/2m$, where η is the viscosity of ethyl alcohol, σ is the diameter, and m the mass of the acetic anhydride molecule (Moelwyn-Hughes, this vol., p. 95). At 50·5°, $\eta = 7{\cdot}0 \times 10^{-3}$ g./cm.-sec.; $m = 1{\cdot}68 \times 10^{-22}$ g.; $\sigma \cong 6{\cdot}0 \times 10^{-8}$ cm., hence $Z = 1{\cdot}20 \times 10^{13}$. The fraction of this number of collisions which is effective is $e^{-E'/RT}$, where E' is equal to the Arrhenius value for the energy of activation plus a correction which allows for the variation with temperature of the collision frequency. For ethyl alcohol at 50—70°, the correction amounts to 2,440 cals., so $E' = 18{,}770 + 2{,}440 = 21{,}210$ cals. This value can also be obtained more directly by plotting the logarithm of (k/η) against the reciprocal of the absolute temperature. The numerical value of $e^{-21{,}210/RT}$ is $4{\cdot}27 \times 10^{-15}$, hence $k = Z \, . \, e^{-E'/RT} = 5{\cdot}10 \times 10^{-2}$ at 50·5°. The observed unimolecular constant is $8{\cdot}1 \times 10^{-5}$. The reaction thus proceeds at a rate which is about 630 times as slow as that calculated on the assumption that chemical change occurs whenever neutral acetic anhydride and ethyl alcohol molecules collide with a kinetic energy equal to or exceeding 21,210 cals. per g.-mol.

Discussion.

Moelwyn-Hughes and Hinshelwood (preceding paper) have shown that the energy of activation for this reaction in carbon tetrachloride and in hexane solution is 13,400 and 12,400 cals. respectively. The observed bimolecular constants in both solvents are lower by a factor of about 10^8 than the values calculated for hypothetical gas reactions with these critical increments. The idea, however, that the discrepancy is due to deactivation by solvent molecules must be abandoned, for experiment has shown that the " gas " reaction, in spite of pronounced catalysis by the walls of the vessel, proceeds at about the same rate as the reaction in these two " inert " solvents. Two alternative explanations are advanced to account for the apparent abnormality of these reactions : (1) it is possible that the molecules must collide with a special orientation, or that they must be in a suitable internal phase at the moment of impact, before chemical change can set in ; (2) the reaction may be preceded by the ionisation of reactant molecules : recombination of some of the ions to produce the original, uncharged, reactant molecule would then be a partial deactivation.

In attempting to determine which of these two factors is more likely to be true, the following facts are relevant : (*a*) It has been concluded, from a general examination of bimolecular reactions in solution (Moelwyn-Hughes, *Chem. Reviews*, 1932), that the Arrhenius critical increment is not the true critical increment for reactions of the type studied here. The idea that ionisation enters into the problem gives us at once a reason for the false observed values, since in that case they would involve the heats of ionisation. It is difficult, on the other hand, to see how the necessity for a special phase condition at the moment of impact can alter the true energy of activation, particularly when the activation process is a simple one, not involving internal degrees of freedom, as would appear to be the case here. (*b*) The energy of activation for this reaction varies from solvent to solvent, the values for hexane, carbon tetrachloride, and ethyl alcohol being 12,400, 13,400, and 18,800 cals. respectively. The phase factor, being an inherent property of the reacting molecule, should not be greatly influenced by its environment (compare the decomposition of nitrogen pentoxide in the gaseous phase and in solution), and thus leaves the true solvent effect unsolved. Ionisation, on the other hand, is known to vary considerably with the nature of the solvent, and we should anticipate the heats of ionisation, and consequently the observed critical increment, to change from solvent to solvent. Finally, (*c*) the bimolecular constant for the esterification reaction in hexane solution (Moelwyn-Hughes and Hinshelwood, *loc. cit.*) and in benzene solution (Soper and Williams, J., 1931, 2297) increases with dilution. This becomes readily intelligible on the ionisation view, since the number of ions alters with the concentration; but the possible influence of the dilution on the phase factor is more difficult to understand.

There is really, however, no need to stress any further the superior claim of the ionisation view, for this, of the two suggestions now under consideration, is the only one which can at present be tested. We shall proceed to do so in an approximately quantitative manner.

Calculation of Reaction Rate from Number of Collisions between Acetic Anhydride Molecules and Ethoxide Ions.—If we assume that reaction takes place only between acetic anhydride molecules and ethoxide ions :

$$(CH_3{\cdot}CO)_2O + C_2H_5{\cdot}O^- \longrightarrow CH_3{\cdot}CO_2C_2H_5 + CH_3{\cdot}COO^-,$$

we can obtain the observed bimolecular constant for the process by dividing the observed unimolecular constant by the concentration of ethoxide ion present in ethyl alcohol :

$$k_{\text{bi.}} = -\frac{d[(CH_3{\cdot}CO)_2O]}{dt}\cdot\frac{1}{[(CH_3{\cdot}CO)_2O][C_2H_5{\cdot}O^-]} = \frac{k_{\text{uni.}}}{[C_2H_5{\cdot}O^-]}.$$

Macfarlane and Hartley (*Phil. Mag.*, in the press), from a study of the potential of the hydrogen electrode in ethyl alcohol, give the dissociation constant at 25° as $K = [C_2H_5{\cdot}O^-][H^+] = 1{\cdot}9 \times 10^{-19}$. It has not been possible to find how this varies with temperature, but we can assume as a first approximation that dK/dT will be the same for ethyl alcohol as for methyl alcohol, for which we have a heat of dissociation of 11,200 cals. This figure is the calorimetrically determined heat of neutralisation of strong acids with sodium methoxide (Wolfenden, Jackson, and Hartley, *J. Physical Chem.*, 1927, **31**, 850): $CH_3{\cdot}O^- + H^+ \longrightarrow CH_3{\cdot}OH$. From these two data we can estimate the concentration of ethoxide ion in ethyl alcohol at various temperatures: $[C_2H_5{\cdot}O^-] = K^{1/2} = 5{\cdot}75 \times 10^{-6} \times e^{-5,600/RT}$. Now $k_{\text{uni.}}$ at 50·5° is $8{\cdot}10 \times 10^{-5}$ sec.$^{-1}$ and $[C_2H_5{\cdot}O^-] = 7{\cdot}31 \times 10^{-10}$ g.-ion per litre; hence the "observed" bimolecular constant is $1{\cdot}11 \times 10^5$ litre/g.-mol./sec.

In order to calculate the bimolecular constant, we use the equation:

$$\text{rate} = [\text{number of collisions between } (CH_3{\cdot}CO)_2O \text{ molecules and EtO}' \text{ ions per sec.}] \times e^{-E_{\text{bi.}}/RT}.$$

In the absence of a more rigorous treatment, we must use the collision equation as deduced for a gas: the error thus introduced is probably not as great as it is sometimes considered to be. The numerical value of the collision frequency is about $1{\cdot}8 \times 10^{11}$. The critical increment of the bimolecular reaction is found in the following manner:

$$k_{\text{bi.}} = k_{\text{uni.}}/[C_2H_5{\cdot}O^-] = k_{\text{uni.}} \times K^{-1/2},$$
$$\ln k_{\text{bi.}} = \ln k_{\text{uni.}} - 1/2 \ln K.$$

Differentiating each term with respect to temperature, and dividing throughout by RT^2, we obtain

$$E_{\text{bi.}} = E_{\text{uni.}} - 1/2Q = 18{,}800 - 5{,}600 = 13{,}200 \text{ cals.}$$

On this basis, the calculated reaction rate at 50·5° becomes $2{\cdot}15 \times 10^2$, *i.e.*, about 520 times *less* than the observed value. The calculation admittedly involves several assumptions and has ignored the solvation of the ethoxide ion, but although only approximate, it is considered to be qualitatively correct.

The results obtained for this reaction, therefore, show that the experimental rate lies between the rates calculated on the assumptions that the reaction is entirely (i) $(CH_3{\cdot}CO)_2O + C_2H_5{\cdot}OH \longrightarrow CH_3{\cdot}CO_2C_2H_5 + CH_3{\cdot}CO_2H$ or (ii) $(CH_3{\cdot}CO)_2O + C_2H_5{\cdot}O^- \longrightarrow CH_3{\cdot}CO_2C_2H_5 + CH_3{\cdot}COO^-$. Possibly the observed rate is a composite value, both mechanisms being concerned simultaneously; but on account of the approximate nature of the calculations it is not possible to say in what proportion the two rates are shared. The composite velocity constant is not, of course, the average of the two calculated values, and can only be evaluated when more accurate figures become available for the true critical increment for each reaction.

Summary.

The kinetics of the esterification of acetic anhydride in ethyl alcohol as solvent have been investigated over a range of temperature in two different preparations of alcohol. The two series of experiments give concordant results, the unimolecular velocity constant being given by the relation $k = 4{\cdot}4 \times 10^8 \times e^{-18,800/RT}$ sec.$^{-1}$. The observed rate lies between the theoretical values calculated on the assumptions that reaction takes place between acetic anhydride molecules and (i) ethyl alcohol molecules, with an energy of activation of 21,200 cals., and (ii) ethoxide ions, with an energy of activation of 13,200 cals. The observed E has been corrected under assumption (i) to make allowance for the variation with temperature of the collision rate, and under assumption (ii) for the heat of ionisation of ethyl alcohol. The results of these calculations suggest that both mechanisms may be involved. The important point, however, is that the rates of abnormally slow reactions, of which esterification is but one instance, can be accounted for by introducing the idea of ionisation, and further work in this direction is contemplated, the chief difficulty being the scanty data as to the minute ionisation of substances such as ethyl alcohol in inert solvents.

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