CCCXIV.—*The Effect of the Solvent on the Rate of Acetylation of Ethyl Alcohol by Acetic Anhydride.*

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THE fact that solvents may, for a number of reactions, be arranged in an order which represents their accelerating influence, and that for certain reactions this order of solvents is inverted, was noticed by Patterson and Montgomerie (J., 1912, **101**, 26). One of us, in collaboration with Miss Richardson (J., 1929, 1873), has associated the inversion of the order of accelerating influences of solvents with the relative cohesions of the reaction products and reagents, polar solvents accelerating reactions producing polar products and retarding reactions in which the products are less polar than the reagents.

Some of the data supporting a retardation of reaction speed by solvents of high cohesion may possibly be explained by ionisation of a reacting substance in the more polar solvents (as in the decomposition of sulphoniun salts; von Halban, *Z. physikal. Chem.*, 1909, **67**, 129), and it was thus thought desirable to subject the evidence for this type of solvent effect to a further examination.

The acetylation of *iso*butyl and *iso*propyl alcohols by acetic anhydride, studied by Menschutkin (*Z. physikal. Chem.*, 1887, **1**, 611) in hexane, xylene, and benzene as solvents, was found to occur most rapidly in hexane. It has now been shown that the acceleration of the rate of acetylation of ethyl alcohol by solvents of low polarity is not due, as was possible, to the formation of reactive associated molecules of the alcohol, masking the more usual solvent influence.

In benzene, as typifying non-polar solvents, the reaction rate is proportional to the concentration of the alcohol up to 0·3*M*. At higher concentrations the bimolecular velocity coefficient, k_2, falls. The results obtained at different initial alcohol concentrations are shown in Table I, and definitely negative the formation of associated molecules which are more easily acetylated.

TABLE I.

Effect of association of ethyl alcohol on its rate of acetylation.

Solvent, benzene. Temperature, 50°. Initial [Ac_2O],0·216*M*.

Initial EtOH	0·172*M*	0·259*M*	0·345*M*	0·517*M*	0·690*M*
k_2	0·00390	0·00399	0·00405	0·00363	0·00319
Initial EtOH	0·862*M*	1·034*M*	1·379*M*	1·724*M*	
k_2	0·00306	0·00269	0·00235	0·00195	

The decrease in velocity coefficient at the higher concentrations of alcohol is due to some extent to the medium effect of the alcohol, and the velocity coefficients cannot be regarded as indicating the degree of association of the alcohol. No appreciable association of the alcohol appears to occur, however, at concentrations at which freezing-point methods indicate association (Raoult, *Ann. Chim.*, 1884, **2**, 66; Beckmann, *Z. physikal. Chem.*, 1888, **2**, 715; Paternò, *Ber.*, 1889, **22**, 1430). A similar behaviour is shown by ions which react at speeds proportional to their molarity although freezing-point and allied measurements indicate their association. The kinetic behaviour of ethyl alcohol is thus understandable if association consists, at least in the more dilute solutions, of electrostatic attractions between dipoles (Smith and Engel, *J. Amer. Chem. Soc.*, 1929, **51**, 2669).

The catalysis of the acetylation by acids and bases has been studied and the uncatalysed reaction appears to predominate over a considerable range of acid and base concentration. A similar conclusion was reached in the analogous reaction of the hydrolysis of acetic anhydride studied by Skrabal (*Z. Elektrochem.*, 1927, **33**, 322) and by Kilpatrick (*J. Amer. Chem. Soc.*, 1928, **50**, 2891).

The values obtained for the velocity coefficients of the uncatalysed reaction in a series of solvents are given in Table II, together with values calculated for the relative cohesions of the solvents (Hildebrance, "Solubility," N.Y. 1924).

Although the solvent effect is only slight in the present example, as would in fact be anticipated if the relative polarities of products and reagents determine the solvent effect, the order of accelerating

TABLE II.

Acetylation of ethyl alcohol at 50°.

Solvent.	$\frac{E_\sigma}{V^{\frac{1}{3}}}$.	$\frac{L_\nu}{V}$.	$\frac{(1/\alpha + 2 \times 293)}{V}$	k_2.
Hexane	9·45	243·3	9·61	0·0119
Heptane	—	239·4	9·56	0·0126
Carbon tetrachloride	13·61	310·0	14·76	0·0113
Chlorobenzene	14·68	360·8	15·96	0·00533
Benzene	15·29	275·0	15·99	0·00462
Anisole	14·84	340·0	—	0·00293
Chloroform	15·50	361·1	17·10	0·00404
Nitrobenzene	17·17	400·3	17·48	0·00245*

* Extrapolated from measurements at 60°, 70°, and 80°.

influence conforms fairly closely with the order of cohesions of the solvents.

EXPERIMENTAL.

Measurement of the Reaction Speed.—The composition of the reaction mixture at various times was determined by estimation of the residual acetic anhydride and of the acetic acid produced in the reaction (Menschutkin, *loc. cit.*), the acid titre when the reaction is complete being half the initial titre. Satisfactory titration end-points could only be obtained if the acetic anhydride was first allowed to hydrolyse by standing in contact with water for 24 hours. Blank experiments showed that no detectable hydrolysis of ethyl acetate occurred under such conditions. An alternative method of analysis of the mixture by direct estimation of the residual acetic anhydride (Orton and Bradfield, J., 1927, 983) necessitates the use of solvents stable to bromine and thus would limit the range of solvents available.

Purification of Materials.—Apart from physical constants, the test of purity of solvents was supplied by comparison of the speed of acetylation before and after further purification by suitable methods. The ethyl alcohol, after distillation from metallic calcium, had $d^{20°}$ 0·7898, corresponding to 99·86%, assuming water was the impurity. Experiments showed that the addition of water, at a concentration of 0·005*M*, had no appreciable effect on the speed of acetylation in benzene. The acetic anhydride employed was purified by fractional distillation through a 12-pear stillhead, and boiled from 139·3—139·5°/764·2 mm. The acids and bases used as catalysts were B. D. H. (A.R.) and Kahlbaum specimens, except quinoline, which after purification distilled at 235—235·4°/755 mm.

Effect of Acetic Acid on the Reaction Rate.—Although experiments, in which the concentration of each reagent was doubled in turn, showed that the reaction is dependent on the first power of the concentration of each reagent, the bimolecular coefficient decreases as the reaction proceeds. This decrease is due, not to a slight reversibility of the reaction, but to a retarding influence of acetic acid. The effect of added acetic acid is also similar, in its depressing influence on the reaction rate, to the effect of that produced in the reaction.

TABLE III.

Rate of acetylation of ethyl alcohol in carbon tetrachloride.

Initial [Ac_2O],0·216*M* ; [EtOH],0·345*M*.

% Change	30	41	51	64	acid added
[HAc] present	0·065*M*	0·088*M*	0·110*M*	0·140*M*	0·429*M*
k_2	0·00996	0·00992	0·00947	0·00933	0·00823

In acetone as well as in carbon tetrachloride, acetic acid exerts a retarding effect on the rate of acetylation, but in ethyl alcohol a slight acceleration is experienced.

Effect of Acids and Tertiary Bases on the Reaction Rate.—The effect of bases on the rate of acetylation in carbon tetrachloride, acetone, and ethyl alcohol has been studied. The results obtained with carbon tetrachloride and acetone as solvents are in Table IV. $K_{b'}$ represents the Brønsted association constant of the base (*Rec. trav. chim.*, 1923, **42**, 718 ; *J. Physical Chem.*, 1926, **30**, 777).

TABLE IV.

Effect of tertiary bases on the rate of acetylation.

Base.	$K_{b'}$.	$k_2^{50°}$ in carbon tetrachloride.	$k_2^{100°}$ in acetone.
No added base	—	0·0113	0·0148
0·169*M* Triphenylamine	—	—	0·0169
0·040*M* Dimethylaniline	$2·42 \times 10^4$	0·00883	—
0·079*M* ,,	,,	0·00787	—
0·237*M* ,,	,,	0·00682	—
0·169*M* ,,	,,	—	0·0170
0·085*M* Quinoline	$3·2 \times 10^4$	0·0100	—
0·169*M* ,,	,,	0·00895	0·0171
0·339*M* ,,	,,	—	0·0165
0·063*M* Pyridine	$1·41 \times 10^5$	0·0197	—
0·125*M* ,,	,,	0·0249	—
0·250*M* ,,	,,	0·0331	—
0·375*M* ,,	,,	0·0357	—
0·169*M* ,,	,,	—	0·0220

Although correction was made in evaluating the constants obtained in acetone for its slight simultaneous acetylation, the velocity coefficients in this medium decrease as the reaction proceeds. It was evident, however, that bases which retarded the acetylation in carbon tetrachloride accelerated it in acetone. In ethyl alcohol as medium the unimolecular velocity coefficient in the absence of any added base or acid had a value of 0·00466, whilst in the presence of 0·169*M*-quinoline it had a value of 0·0106. Addition of base to carbon tetrachloride, which is of low cohesion, would cause a greater change in the cohesion of the medium than would such addition to acetone and alcohol, and in carbon tetrachloride the normal slight accelerating influence of the base may be overshadowed by its medium effect.

The effect of weak acids is not unlike that of weak bases. Acetic and propionic acids, at a concentration of 0·3*M*, retard the reaction somewhat in carbon tetrachloride and in acetone but accelerate it slightly in ethyl alcohol. Benzoic and *o*-chlorobenzoic acids, however, accelerate the reaction in acetone in proportion to their strengths. A possible explanation of the retardation by acetic and propionic acids is the formation of an inactive complex of alcohol and acid by co-ordination, resulting in a decrease of speed except in ethyl alcohol medium where the formation of such a complex does not reduce appreciably the concentration of free alcohol present.

Measurement of the Effect of Solvent on the Rate of Acetylation.—The addition of the weak base quinoline has little effect on the rate of acetylation but, by its combination with the acetic acid formed, prevents an autoretardation of the speed. The rate under these conditions conforms closely to a bimolecular law. The value of the velocity coefficient in carbon tetrachloride, extrapolated to zero concentration of quinoline (Table II), agrees fairly closely with the value of the coefficient, in the absence of quinoline, extrapolated to the moment of initiation of the reaction when no acetic acid is present. The former extrapolation was selected as being the more precise, and measurements, in duplicate, of the rate of acetylation in the series of solvents were carried out at concentrations of quinoline of 0·169*M* and 0·339*M*. The values are in Table V.

TABLE V.

Effect of quinoline on the rate of acetylation at 50°.

Solvent.	k_2 in presence of 0·169*M*-quinoline.	k_2 in presence of 0·339*M* quinoline.	Solvent.	k_2 in presence of 0·169*M*-quinoline.	k_2 in presence of 0·339*M* quinoline.
Hexane	0·00969	0·00750	Benzene	0·00406	0·00350
Heptane	0·01060	0·00858	Anisole	0·00283	0·00273
Carbon tetrachloride * ...	0·00895	—	Chloroform ...	0·00372	0·00342
Chlorobenzene	0·00472	0·00409	Nitrobenzene	0·00215	0·00185

* In the presence of 0·085*M*-quinoline, k_2 in carbon tetrachloride as medium = 0·0100.

The values of the velocity coefficients in the various solvents, extrapolated to zero concentration of quinoline, are given in Table II, together with values for the relative cohesions of the solvents.

Discussion.

The confirmation of the relation of solvent effect to the relative polarities or cohesions of products and reagents leads to an interesting deduction of the solvent effect on a balanced reaction.

$$A + B \underset{2}{\overset{1}{\rightleftharpoons}} P + Q$$

The replacement of a solvent of low by one of high cohesion will be either to accelerate the forward reaction 1 and retard reaction 2, or vice versa, depending on the relative cohesions of products and reagents; that is, in many cases, the solvent effect on the speeds of direct and reverse reactions will be reciprocal, causing a change in the equilibrium constant with change of solvent (compare Dimroth, *Annalen*, 1913, **399**, 91). To explain this reciprocal effect is difficult if the solvent anomaly is due entirely to a deactivating influence of the solvent molecules on the critically energised complexes of the reagents (Norrish and Smith, J., 1928, 129). On this explanation, the replacement of one solvent by another should, since the same intermediate complex is involved, result in either a retardation or an acceleration of both forward and reverse reactions. The view, however, that the degree of resolution of the highly energised critical complexes into products depends on the nature of the solvent (J., 1929, 1873), such that polar solvents favour the formation of polar substances, would be in harmony with this reciprocal effect.

Further support for this theory is afforded by the work of Moesveld (*Z. physikal. Chem.*, 1923, **103**, 486) on the effect of pressure on the rate of the reactions

$$CH_3{\cdot}CO{\cdot}O{\cdot}C_2H_5 + OH' \longrightarrow CH_3{\cdot}CO{\cdot}O' + C_2H_5{\cdot}OH$$

and

$$5HBr + HBrO_3 \longrightarrow 3Br_2 + 3H_2O,$$

the latter of which may probably be represented kinetically by the consecutive reactions

$$\begin{aligned} 2H^{\bullet} + Br' + BrO_3{}' &\longrightarrow HBrO + HBrO_2 \\ HBrO + HBr &\longrightarrow Br_2 + H_2O \\ HBrO_2 + 3HBr &\longrightarrow 2Br_2 + 2H_2O \end{aligned}$$

the first stage being slow and determining the reaction speed. In the ester hydrolysis there is no change in the ion concentration but the polar alcohol replaces the relatively non-polar ester. In the bromate–bromide reaction, ions disappear to form non-ionised substances. Both reactions are attended by an increase in volume (Moesveld, *loc. cit.*; Benrath, *Z. physikal. Chem.*, 1909, **67**, 501). The effect of increase of pressure, however, which causes an increase in the inter-molecular forces in the liquid solvent, is, in the former case, where a polar substance is being produced from a relatively non-polar substance, to increase the reaction speed, and in the latter case, where non-ionised molecules are being produced from polar ions, to decrease it. This would be anticipated if an increase of the internal forces in the liquid were to favour a resolution of the highly energised intermediate critical complex into polar substances. The intermediate critical complex may be envisaged as oscillating between two unstable states, one corresponding to a resolution into products, the other into reagents. The change of solvent may cause a greater fraction of one of these unstable forms to decompose.

Moreover, if the proportion of critical complexes which break up into reaction products varies with temperature, an explanation might be forthcoming of the marked, and apparently haphazard, changes in the observed energies of activation of a reaction in different solvents.

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