CCLXXVIII.—*Esterification in Mixed Solvents.*

By BALWANT WASUDEO BHIDE and HERBERT EDMESTON WATSON.

PREVIOUS experiments (Bhide and Sudborough, *J. Indian Inst. Sci.*, 1925, **8***A*, 89) have shown that the equation $(r - a) \log a/(a - x) - x = kt$ suggested by Goldschmidt and Udby (*Z. physikal. Chem.*, 1907, **60**, 728) gives satisfactory values for the velocity coefficient k in numerous cases of esterification of organic acids with ethyl alcohol, and thus allows for the effect of the water formed during the reaction. The question as to the actual catalytic agent is, however, still obscure. Of the theories which have been put forward (compare Lapworth, J., 1911, **99**, 1427; Rice *et al.*, *J. Amer. Chem. Soc.*, 1923, **45**, 2808; 1924, **46**, 2405; 1925, **47**, 379), that of Goldschmidt (*Z. physikal. Chem.*, 1913, **81**, 30; 1920, **94**, 233), according to which both the hydrogen ions and the undissociated molecules are assumed to act as catalysts, has given satisfactory results in explaining the enolisation of acetone, the decomposition of diazoacetates, and the esterification of certain acids with methyl and ethyl alcohols, for a range in concentration of the catalyst from 0·05 to 0·2*N*. As the degree of dissociation between these limits only changes by approximately 10%, the relative effects of the ions and molecules cannot be determined with great accuracy.

In order to study the question through a greater range of ionic concentration, it was decided to examine the effects obtained in the presence of non-dissociating solvents. Kailan (*Z. physikal. Chem.*, 1914, **88**, 63) has shown that the velocity coefficient for the esterification of benzoic acid by ethyl alcohol is largely increased when benzene is added, but he has not worked with solutions containing more than 75% of benzene.

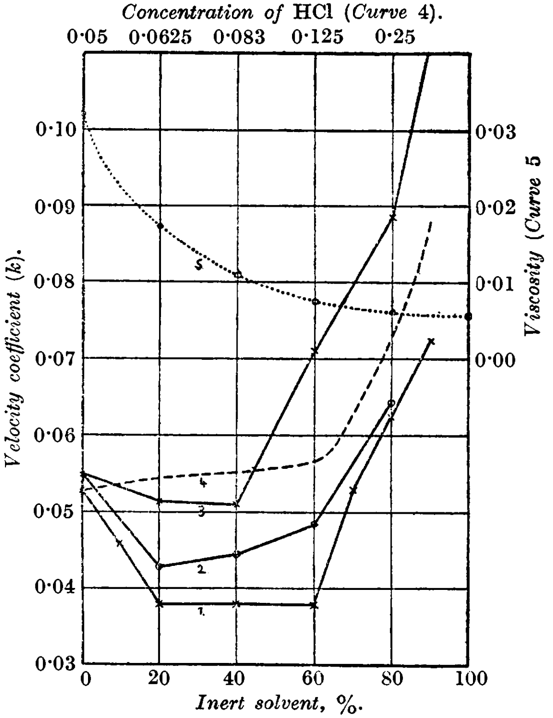
In the present experiments, mixtures of *iso*amyl alcohol with benzene or ligroin have been used. As acids, suberic and *n*-butyric were selected on account of their convenient rates of esterification. The former is moderately easily soluble in *iso*amyl alcohol (5·15 g. per 100 g. of solvent), but almost insoluble in benzene and ligroin. The latter is miscible in all proportions with all three solvents.

EXPERIMENTAL.

The *iso*amyl alcohol was very carefully purified and dried, the final drying agent being anhydrous copper sulphate, as metallic calcium was found to give rise to traces of ammonia which increased the conductivity. At 30°, it had *d* 0·8026 and specific conductivity 2×10^{-7} mho. The suberic acid had m. p. 140°; *n*-butyric acid, b. p. 156—157°/685 mm.; and benzene, $d_{4^\circ}^{30^\circ}$ 0·8658. The ligroin dried over sodium had b. p. 80—90°/685 mm., and did not decolorise bromine. Throughout the preparation and subsequent use of these materials, the utmost care was taken to exclude moisture.

The composition of mixtures is given as % by vol., and density determinations showed that the change of volume on mixing was negligible.

FIG. 1.



Curve 1. *Suberic acid–benzene.* 2. n-*Butyric acid–benzene.* 3. n-*Butyric acid–ligroin.* 4. *Suberic acid–*iso*amyl alcohol with varying* HCl. 5. *Viscosity:* iso*amyl alcohol–benzene.*

Several determinations of the viscosity and conductivity of the solutions were made in order to ascertain whether these properties could be correlated with the velocity coefficients.

Viscosity measurements were made with an Ostwald viscometer at 30° ± 0·05° and the results are in Table I and Fig. 1 (Curve 5).

When hydrogen chloride is dissolved in *iso*amyl alcohol, the viscosity increases regularly with the concentration, rising from 0·0321 for the pure alcohol to 0·0354 for a 0·142N-solution.

TABLE I.

Viscosity of mixtures of *iso*amyl alcohol and benzene.

Benzene, %.	Time of flow (secs.).	$d^{30^\circ}_{4^\circ}$.	η.	Benzene, %.	Time of flow (secs.).	$d^{30}_{4^\circ}$.	η.
0	419·0	0·8026	0·0321	60	95·0	0·8397	0·00760
20	222·4	0·8147	0·0173	80	76·4	0·8525	0·00621
40	137·4	0·8266	0·0108	100	68·0	0·8658	0·00562

Conductivity measurements of solutions of hydrogen chloride in the anhydrous solvents were made, but were rendered difficult by the large decrease in conductivity caused by traces of water. Table II shows the effect of water upon the equivalent conductivity (Λ) of a 0·1*N*-solution of hydrogen chloride in *iso*amyl alcohol;

TABLE II.

Conductivity of 0·1*N*-*iso*amyl alcohol solutions of HCl containing water.

H_2O (mols./litre)	0·0	0·078	0·163	0·203	0·248	0·31	0·62	1·05
Λ	2·18	1·62	1·494	1·491	1·490	1·64	1·99	2·33

it will be observed that the conductivity drops rapidly to a minimum and then steadily rises. Analogous results have been obtained by Goldschmidt (*Z. physikal. Chem.*, 1915, **89**, 129) in the case of ethyl alcohol. Consistent results could only be obtained by making a fresh solution in the conductivity cell itself for each determination.

Table III gives the results obtained for *iso*amyl alcohol alone and for 20 and 40% benzene solutions.

TABLE III.

Conductivity of HCl in *iso*amyl alcohol.

HCl (*N*)	0·00565	0·0166	0·0216	0·0303	0·055	0·071	0·086	0·110	0·164
Λ	2·42	2·33	2·28	2·21	2·18	2·16	2·15	2·20	2·27

Conductivity of HCl in *iso*amyl alcohol containing 20% of benzene.

HCl (*N*)	0·0133	0·0250	0·0385	0·0425	0·0675	0·0773
Λ	1·040	0·917	0·883	0·886	0·923	0·958

Conductivity of HCl in *iso*amyl alcohol containing 40% of benzene.

HCl (*N*)	0·0171	0·0196	0·0308	0·0443	0·074	0·103	0·132
100Λ	1·43	1·36	1·27	1·33	1·53	1·83	2·22

In all these solutions Λ has a minimum value. Godlewski (*J. Chim. physique*, 1905, **3**, 432) has observed a similar minimum for the case of acetic acid in amyl alcohol.

The conductivities of solutions with a higher proportion of benzene were very low, *e.g.*, 0·088*N*-hydrogen chloride in 60% benzene solution had an equivalent conductivity of $7{\cdot}1 \times 10^{-4}$ mho.

Reaction Velocity.

The rate of esterification was measured in the manner previously described (Bhide and Sudborough, *loc. cit.*) at 30° ± 0·01°. At this temperature the concentration of a 0·05*N*-solution of hydrogen chloride in *iso*amyl alcohol remained unchanged for more than 48 hours. As the reaction with suberic acid was practically complete in 7 hours, no complication was produced by reaction between the alcohol and hydrogen chloride.

According to Goldschmidt the value of r in his formula is constant for any one alcohol. It may be calculated by taking a series of readings during the course of an esterification and solving for k and r from two of the simultaneous equations so obtained. In the present case, r was determined from esterification experiments with both suberic and acetic acids, and the mean value 0·11 was found to yield values of k which were in good agreement with each other in every experiment, so that it is not necessary to give detailed results. The final values for the velocity coefficients are in all cases the mean of at least two concordant determinations.

Preliminary experiments showed that the velocity coefficient was not proportional to the concentration of catalyst but became relatively greater as the concentration increased. In all subsequent experiments the concentration of hydrogen chloride was kept as near to 0·05*N* as possible.

Table IV shows the extent of this variation for the esterification of 0·1*N*-suberic acid by *iso*amyl alcohol. The coefficients given are calculated for 0·05*N* catalyst on the assumption that the velocity coefficient is proportional to the concentration of catalyst.

TABLE IV.

Change in velocity coefficient with catalyst concentration.

HCl (*N*)	0·0045	0·012	0·050	0·100	0·220	0·464
k for 0·05*N*-HCl	0·036	0·045	0·053	0·056	0·071	0·086

Goldschmidt and Udby's formula was found not to give a constant for the highest concentration of acid, the value of k increasing with time. The figure 0·086 in the table is the initial value.

Table V shows the velocity coefficients for 0·1*N*-suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol and benzene with 0·05*N*-hydrogen chloride as catalyst.

As has been pointed out by Kailan (*loc. cit.*), the quantity k, although constant in any one experiment, is not proportional to the true velocity coefficient when the composition of the solvent is altered. The general equation for a second-order reaction may be written $dx/dt = k_1Cc$, where C and c are the concentrations of

TABLE V.

Velocity coefficients of 0·1N-suberic and n-butyric acids.

	Suberic acid.		n-Butyric acid.	
Benzene, %.	$k \times 10^4$.	$k_1 \times 10^4$.	$k \times 10^4$.	$k_1 \times 10^4$.
0	535	535	550	550
10	458	509		
20	380	475	430	537
40	381	635	446	743
60	378	945	487	1220
70	531	1770		
80	625	3130	645	3230
90	725	7250		

the reacting substances. When one of these substances is used as solvent, as in the present case, C may be regarded as constant throughout the reaction, and k_1C may be replaced by k. The latter is the velocity coefficient of Goldschmidt and Udby's equation. The true velocity coefficient $k_1 = k/C$. If C is changed by the addition of a second solvent, this fact must be taken into account when calculating k_1. In Table V, C has been taken as unity for the pure solvent.

Fig. 1 shows diagrammatically the values of k in Table V and also the results for 0·1N-n-butyric acid in mixtures of *iso*amyl alcohol and ligroin. The curves are similar in shape and appear to exhibit breaks, but this cannot be confirmed without a large number of fresh determinations. The experimental points have been joined merely to show the general trend.

Discussion of Results.

The most striking feature of these results is the large increase in the value of k_1 as the alcohol is diluted with the neutral solvent. The values of k, on the other hand, although decreasing at first and then rising, do not fluctuate to such an extent. This suggests that the method by which k_1 has been calculated from k is inaccurate, or that there is some compensating factor which has not been taken into account, for it seems unlikely that the reactivity should increase more than ten times on the addition of a second solvent.

While the assumption that the reaction velocity is proportional to the concentration of the alcohol is probably correct in the case of an uncatalysed reaction, it does not follow that the same is true in the presence of a catalyst. In the latter case, it is quite possible that the catalyst is mainly associated with the alcohol, a certain proportion of the complexes (whether ionic or molecular) being in the active condition. If a neutral solvent, particularly one in which the catalyst is comparatively insoluble, is now added, the relation between alcohol and catalyst may be only slightly changed. In other words, the velocity may depend upon the ratio of catalyst molecules to alcohol molecules.

Consider 50 c.c. of a 0·1*N*-solution of suberic acid in 0·1*N*-amyl-alcoholic hydrogen chloride. The velocity coefficient according to Table IV is 0·056 × 2, corresponding with the presence of a certain number of active complexes. If 50 c.c. of benzene, containing the necessary amount of suberic acid to keep the concentration constant, are now added, and it is supposed that the total number of these complexes does not alter, the number in 50 c.c. will be half the original number and the velocity coefficient will be 0·056, and not 0·053 as might be expected from the fact that the catalyst concentration is now 0·05*N*. Similarly for a 10% amyl alcohol solution, the velocity coefficient for 0·05*N* catalyst would be 0·1 times its value for 0·5*N* catalyst, or approximately 0·09. This is qualitatively in agreement with observation, as may be seen in Fig. 1 : curve 4 represents the figures in Table IV for the variation of velocity coefficient with acid concentration, plotted in such a way that they show the velocity coefficient calculated as above for each mixed solvent, *i.e.*, corrected so as to show the concentration with reference to the amyl alcohol. The general shape of the later part of this curve has a distinct resemblance to the corresponding portions of the esterification curves.

If this hypothesis be correct, k represents the velocity coefficient, and not k_1.

The present results show that reaction can take place rapidly in the absence of any appreciable number of ions, but they do not afford information as to the relative effect of ions and molecules.

It has so far not been possible to explain either the diminution in k on adding small quantities of benzene, or the minimum in the conductivity curves. Attempts have been made to measure the hydrogen-ion concentration, but so far they have not been successful.

It is evident that much further work is required before more definite conclusions can be drawn, and the experiments are being continued.

Summary.

1. The velocity coefficients of esterification of suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol with benzene and ligroin have been measured in the presence of hydrogen chloride as catalyst.

2. Goldschmidt and Udby's formula has been found to yield satisfactorily constant coefficients.

3. The coefficients increase very considerably on addition of

the neutral solvents, the relation between the value of the coefficient and the composition of the solution being approximately hyperbolic. A possible explanation is that the velocity depends upon the ratio of catalyst to alcohol molecules, and not upon the concentration of catalyst in the whole solution.

4. Conductivity and viscosity measurements have also been made, and it is shown that the ionisation of the catalyst is a negligible factor in determining the velocity. The conductivity of the solutions in which the reaction took place most readily was very low.

INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

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