295. *Ion-exchange Resins as Catalysts in the Hydrolysis of Esters.*

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Rate constants and apparent activation energies are reported for the hydrolysis of a number of esters, catalysed in aqueous solution by ion-exchange resins in the hydrogen form. For equivalent amounts, the resins are more effective catalysts than hydrochloric acid, and increasingly so as the molecular weight of the ester increases. An explanation is offered for the apparent conflict between these results and those of Haskell and Hammett.

The catalysts of ester hydrolysis by exchange resins was the subject of a note by us some years ago (*Nature*, 1947, **159**, 732). Since then Haskell and Hammett (*J. Amer. Chem. Soc.*, 1949, **71**, 1284) have published the results of some studies in the same field which, at first sight, seem to lead to conclusions almost diametrically opposed to ours. The object of the present paper is to place our data on record, and to put forward an explanation of the apparent discrepancy.

EXPERIMENTAL

Materials.—Two resins were used, Amberlite IR-100 (20—60 mesh) and Wofatit C. Two particle sizes were employed with the latter, 20—40 mesh and 40—60 mesh. The resins were regenerated with 2N-hydrochloric acid, thoroughly washed, and air-dried. Their moisture contents were determined by heating samples for two days at 130°. The esters were purified by storage over sodium carbonate and then over anhydrous calcium chloride, followed by distillation.

Method.—In a few experiments the proportions of resin, ester, and water were varied. Usually, however, 50 ml. of water and 2 ml. of ester were employed, with 1 g. of Amberlite IR-100 or 2 g. of the weakly acid Wofatit. The reaction mixtures were contained in 100-ml. glass-stoppered bottles which were suspended in a thermostat controlled to within 0·05° (0·10° at 55°), and agitated by a device similar to that described by Willcocks (*J. Soc. Chem. Ind.*, 1938, **57**, 249). The resin–water mixture was allowed to come to temperature equilibrium, and the ester (at the same temperature) was added. After measured times, bottles were opened, 25 ml. (usually) of the aqueous phase were withdrawn, and the liberated acetic acid was titrated against standard barium hydroxide (phenolphthalein). The titre corresponding to complete hydrolysis was checked by control experiments, and preliminary experiments showed that the adsorption of acetic acid by the resin was negligible.

Where the ester was completely soluble at the concentrations used, the volume of solution was taken to be the sum of the volumes of the added water and ester plus the water originally present in the resin. First-order constants were calculated from the expression

$$k_1 = (2{\cdot}303/wt) \log T_\infty/(T_\infty - T_t)$$

where w is the weight (in g.) of dry resin, t the time (in seconds), T_t the titre at time t, and T_∞ that corresponding to total hydrolysis of the sample withdrawn (assuming uniform distribution, *i.e.*, negligible adsorption by the resin of the ester). Table 1 shows the course of a typical series of experiments.

TABLE 1. *Hydrolysis of ethyl acetate with Amberlite* IR-100 *at* 25°.

Wt. of dry resin, 0·6635 g. Initial ester concn., 0·3925M. 10-Ml. samples titrated. T_∞ = 66·24 ml.

t, hours	10·52	18·93	42·53	47·45	53·73	64·48	71·38	74·53	94·60	116·0	360
T_t	13·41	22·80	40·75	43·42	46·41	50·79	52·84	53·70	57·90	60·20	63·13
$k_1 \times 10^6$	9·02	9·33	9·40	9·40	9·40	9·45	9·38	9·35	9·18	8·65	—

With the less soluble esters a separate ester phase was visible during the greater part of the reaction, and in these cases zero-order constants were calculated : k_0 = moles hydrolysed per g. of dry resin per second. Blank experiments in which aqueous acetic acid solutions were shaken with the appropriate ester provided small corrections for the volume change resulting from ester passing into the aqueous phase, and from acetic acid being retained in the ester phase. Table 2 gives details of a typical experiment.

TABLE 2. *Hydrolysis of* n-*amyl acetate with Amberlite* IR-100 *at* 25°.

Wt. of dry resin, 0·6640 g. 25-Ml. samples titrated with 0·1192N-barium hydroxide.

t, hours	8·80	13·93	24·58	36·87	46·18	69·05	86·65	109·23
T_t	3·91	6·54	11·50	16·78	21·17	30·00	35·93	42·10
$k_0 \times 10^8$	4·52	4·77	4·75	4·63	4·66	4·41	3·20	3·01

RESULTS AND DISCUSSION

In earlier work (Davies and Thomas, *J.*, 1951, 2624) we had found that organic acids are positively adsorbed on the resins used here. With acids of low molecular weight, however, the extent of adsorption was relatively slight, and at moderate concentrations the amount of acid at the resin surface was almost proportional to its concentration in the outer solution. We expected that simple ester molecules would show similar behaviour, so that the amount undergoing hydrolysis at the resin surface would show an approximately linear dependence on the concentration of ester in solution. That this is so is shown by the satisfactory first-order constant in the typical series recorded in Table 1. Where the added ester was not wholly soluble in the aqueous phase, a zero-order constant such as that shown in Table 2 was obtained, expressing the rate of hydrolysis in a surface layer which was in equilibrium with a saturated aqueous solution of the ester; the resin was without influence on the excess of undissolved ester.

In some experiments the amount of resin was varied. 2 Ml. of methyl acetate and 50 ml. of water being used with Amberlite IR-100 at 25°, the first-order constants (per g. of resin) obtained with 0·5, 1·0, and 2·0 g. of air-dried resin were, respectively, 7·56, 7·38, and 6·90 × 10^{-6}. This decrease in reaction rate would be consistent with an adsorption of approximately 1 milli-equiv. of ester per g. of resin. With *n*-butyl acetate, when a separate ester phase was present, the rate constant was unaffected by change in the amount of resin.

When the amount of ester was varied, the rate constant was again affected. For example, on doubling of the concentration of methyl acetate the value 7·38 × 10^{-6}, just quoted, fell to 6·33 × 10^{-6}. This decrease would be expected on the basis of an adsorption isotherm of the type found for organic acids (Davies and Thomas, *loc. cit.*), the concentration in the adsorbed layer being less than doubled. In accordance with expectation, the zero-order constants for *n*-butyl and *n*-amyl acetates were unaffected by varying the amount of ester.

The effect of particle size was studied in the hydrolysis of *n*-butyl acetate by Wofatit C. The zero-order constant was 6% higher for 40—60 mesh resin than for the 20—40 mesh size. Similar data have been reported by Haskell and Hammett (*loc. cit.*). The results suggest that the outer layers of the resin granules are responsible for much of the catalytic effect, the diffusion of non-electrolytes towards or away from the centre of the particles being a slow process. The same conclusion was reached in our earlier paper on adsorption and desorption rates. It will be noticed in Table 1 that the rate constant falls off towards the end of the reaction. This was a general phenomenon, and suggests that the reaction is somewhat retarded, as might be expected, by its products. This probably applies particularly to the interior of the granules as acid and alcohol molecules accumulate.

Our results are collected in Tables 3 and 4. The constants given here are comparable, in so far as uniform amounts of ester, water, and resin were used and the resin samples were taken from a common stock.

The values of r in Table 4 give the ratio of the constant found for Amberlite IR-100 (20—60 mesh) to that for Wofatit C (20—40 mesh). The figures are reasonably constant, and show that Amberlite IR-100, containing 2 milli-equivs. of sulphonic groups per g., is about 11 times more efficient as a catalyst than the Wofatit C, which contained approximately 4 milli-equivs. of carboxyl groups per g. Strong acid Amberlites possessing both higher capacity and greater stability than the IR-100 resin are now, of course, available.

The rate constants of Table 3 may be compared with the constants previously obtained for homogeneous catalysis by hydrochloric acid at similar ester concentrations. For methyl acetate at 25° we used the data of Griffiths and Lewis (*J.*, 1916, **109**, 67) and for ethyl acetate those of Harned and Pfanstiel (*J. Amer. Chem. Soc.*, 1922, **44**, 2193). For the sparingly soluble esters our results were compared with calculated rates for the homogeneous catalysis of saturated aqueous solutions, the velocity data of Palomaa (*Chem. Z.*, 1913, **84**, 1950) being used for butyl acetate and those of Smith and Paterson (*J.*, 1926, 940) for benzoyl acetate. The solubility of butyl acetate was taken from Hodgman ("Handbook of Chemistry and Physics," 32nd edn., p. 666). The comparison shows that the resin is more effective than hydrochloric acid by factors of 1·8 for methyl acetate, 2·3 for ethyl acetate, 10 for *n*-butyl acetate, and 20 for benzyl acetate. These results are reasonable in view of the other evidence that the esters are positively adsorbed at the active surface, and the probability that the amount adsorbed, for the esters as for the organic acids, increases rapidly with increasing molecular weight.

TABLE 3. *Amberlite* IR-100 *as catalyst.*

	$k_1 \times 10^6$		$k_0 \times 10^8$		
Temp.	MeOAc	EtOAc	BuOAc	AmOAc	$CH_2Ph{\cdot}OAc$
15°	2·87	3·50	4·11	2·15	—
25	7·38	9·40	9·47	4·72	5·28
35	18·3	22·7	19·6	9·20	—
45	—	49·2	38·6	—	—
55	—	97·8	—	—	—

TABLE 4. *Wofatit C as catalyst.*

	$k_1 \times 10^6$		$k_0 \times 10^8$			$k_1 \times 10^6$		$k_0 \times 10^8$	
Temp.	EtOAc	r	BuOAc	r	Temp.	EtOAc	r	BuOAc	r
15°	—	—	0·356	11·6	35°	2·05	11·1	1·85	10·6
25	0·860	10·9	0·861	11·0					

The results of Haskell and Hammett (*loc. cit.*) appear, at first sight, to be almost exactly the reverse of ours. These authors studied the hydrolysis of methyl and ethyl acetates, ethyl *n*-butyrate, and ethyl *n*-hexanoate dissolved in 70% acetone (*a*) in the presence of Amberlite IR-120, and (*b*) with an equivalent amount of hydrochloric acid. They found that hydrochloric acid was catalytically more efficient than the resin by factors of approximately 2 for methyl acetate, 3 for ethyl acetate, 7·5 for ethyl butyrate, and 20 for ethyl hexanoate. The two sets of results, though apparently so divergent, can both find a simple common explanation, along the lines we have used in discussing our own, if it is supposed that in 70% acetone the esters are negatively adsorbed by the resin: that is, the ester concentration is *less* in the resin than in the body of the solution, and increasingly so with increasing molecular weight. Evidence for this supposition is supplied by Haskell and Hammett's Table 6, in which they show that solvent is adsorbed by the resin in preference to hexanoic or acetic acid, and that the effect is greater for the former.

The opposite effects, both in catalytic efficiency and in adsorbability, revealed by the two sets of results are clearly due to the change of solvent from water to 70% acetone, and an insight into the striking effect of this change is provided by some results recently obtained in these laboratories. B. D. R. Owen (unpublished) has found that when 10% divinylbenzene cross-linked polystyrene resin in the hydrogen form is equilibrated with a 70% acetone in water mixture, in the proportions used by Haskell and Hammett, the liquid absorbed by the resin has the composition 72% water, 28% acetone, the composition of the outer solution now being 75% acetone, 25% water. The distribution of the organic substrate between these two phases will be greatly in favour of the outer solution—especially for long-chain esters which are sparingly soluble in water—and thus provides an explanation both for the negative adsorptions and for the low catalytic activities found by Haskell and Hammett.

When the rate constants of Tables 3 and 4 are plotted against the reciprocal of the absolute temperature straight lines are obtained, and the slopes of these give the values of apparent activation energies (in cal.) recorded below. There is a marked drop in the apparent activation energy as the chain length increases. The temperature influence is not easy to interpret quantitatively, however, as not only the reaction mechanism itself but also the adsorption energy and, to a lesser degree, swelling and diffusion effects are involved.

Ester	Amberlite IR-100	Wofatit C	HCl	Ester	Amberlite IR-100	Wofatit C	HCl
Methyl acetate	16,600	—	16,920	*n*-Butyl acetate	13,180	13,960	—
Ethyl acetate	15,540	15,810	16,830	*n*-Amyl acetate	12,280	—	—

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