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Specific Effects in Acid Catalysis by Ion Exchange Resins. I. Hydrolysis of Esters in 70% Aqueous Acetone[1]

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For a wide variety of carboxylic esters in aqueous acetone solution the hydrolysis rate is less when the catalyst is an ion exchange resin than when it is homogeneously dissolved acid in equivalent amount. There is a significant specificity with respect both to the ester and to the resin. For seven methyl esters of the composition RCO_2CH_3 the retardation observed with the resin catalyst parallels the entropy of the gaseous compound RH, and shows no relation to any other obvious property of the ester. An increase in the degree of cross linking of the resin decreases the reaction rate, in different proportions for different esters. Both of these effects are consistent with the hypothesis of Haskell and Hammett that the resin catalyst imposes a loss in entropy on the transition state whose magnitude differs from ester to ester. A variety of experiments demonstrate conclusively that these effects are in no way dependent on the diffusion rate of the ester through the resin particle.

A cross-linked and hence insoluble polymeric aromatic sulfonic acid, an ion exchange resin, has catalytic properties which are specifically dependent on the structure of the substance undergoing reaction. Defining the efficiency q of the catalyst for a particular reaction by the relation

$$q = k_R/k_H \qquad (1)$$

where k_R is the second order specific rate for the hydrolysis of an ester catalyzed by the resin and k_H the corresponding specific rate for the same reaction catalyzed by approximately 0.44 M hydrochloric acid, Haskell and Hammett[2] found that in 70% by volume aqueous acetone the efficiency dropped from 0.50 for the hydrolysis of methyl acetate to 0.049 for the hydrolysis of ethyl hexanoate. It may easily be shown that the ratio of the efficiencies for two esters 1 and 2 is given by

$$-RT \ln q_2/q_1 = (F^{\pm}_{R_2} - F^{\pm}_{H_2}) - (F^{\pm}_{R_1} - F^{\pm}_{H_1})$$

where the $F^{\pm}$'s are standard free energies of transition states and the subscript R refers to the resin, and H to the homogeneous system. The ratio depends therefore only on the properties of the four transition states, whereas if we were to study the effect of a change in solvent upon the hydrolysis rates of two esters the corresponding equation would involve the effect of the changing solvent on the standard free energies of the esters as well as on those of the transition states. Consequently the resin catalysis puts us in a position to study the effect of a particular controllable and intelligible change in environment on the free energy of the transition state and on this alone. Such information is valuable with respect to the general problem of structure and reactivity and particularly with respect to the problem of heterogeneous catalysis.

Effect of the Structure of the Reactant.—For four straight chain aliphatic esters, Haskell and Hammett found that log q was linear in the number of carbon atoms in the ester. We have now studied a number of other esters with the resin used previously (a particular sample of Rohm and Haas Amberlite IR-110 classified to 45–50 mesh) and list the data obtained together th those of Haskell and Hammett in Table I. Our new results show that there is no general relation between efficiency and the number of carbon atoms in the ester or between efficiency and any other measure of mass or bulk of the ester. In particular esters of cyclic acids like phenylacetic, naphthylacetic, cyclopentanecarboxylic and especially benzoic acid show much higher efficiencies than do straight chain esters of comparable mass.

TABLE I

HYDROLYSIS OF ESTERS BY 0.466 N HCl AND BY IR-120 RESIN (TIME IN SEC.)

Ester	Temp., °C.	$k_H \times 10^6$	$k_R \times 10^6$	k_R/k_H
Methyl acetate[2]	25.00	54.5	27.2	0.502
Ethyl acetate[2]	25.00	46.4	15.0	.326
Ethyl *n*-butyrate[2]	25.00	19.2	2.56	.134
Ethyl *n*-hexanoate[2]	25.00	15.3	0.745	.0490
Methyl *n*-octanoate	25.00	16.8	0.948	.0564
Methyl phenylacetate	25.00	21.6	2.13	.0987
Methyl α-naphthylacetate	37.50	15.5	1.27	.0819
Methyl chloroacetate	25.00	38	11	.29
Methyl benzoate	45.00	0.614	0.134	.218
Methyl cyclopentanecarboxylate	25.00	24.0	3.47	.144

The qualitative result is, however, just what would be expected from the hypothesis which Haskell and Hammett's studies of the temperature coefficient of the efficiency suggested, namely, that the difference in efficiency between different esters arises from a difference in the magnitude of the loss in internal entropy of the ester molecule which accompanies its fixation on the skeleton of the resin catalyst in the formation of the transition state. It seems reasonable that this loss in entropy should be less the smaller the entropy of the ester, *i.e.*, that the cyclic esters which possess less freedom of internal motion and hence less internal entropy should lose less entropy when subjected to strong constraints. The hypothesis turns out not merely to be qualitatively useful but also to have a surprising degree of quantitative validity as Fig. 1 shows. We have here compared the efficiency q of the hydrolysis of each of the seven methyl esters of composition $RCOOCH_3$ which we have studied with the

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(2) V. C. Haskell and L. P. Hammett, THIS JOURNAL, **71**, 1284 (1949).

entropy S at 298°K. of the gaseous compound RH,[3] assuming that the differences in entropy of the compounds RH will measure the differences in entropy of the compounds $RCOOCH_3$. In view of the wide range of structures involved, and the fact that the rates of hydrolysis of the esters either in homogeneous solution or on the resin do not at all parallel the efficiency, the correlation of Fig. 1 is striking evidence for the Haskell and Hammett hypothesis.

Effect of Resin Structure.—The most obvious way to vary the nature of the resin catalyst is to vary the degree of cross linking by altering the proportion of divinylbenzene in the styrene–divinylbenzene copolymer whose sulfonation leads to the ion exchange resin. There are enough uncertainties about the preparation of these resins to make some other characterization of the degree of cross linking than the proportion of divinylbenzene used desirable even when this proportion is known, and we have used the percentage increase in volume, the swelling, which occurs when the air-dried resin is immersed in water. For the four resins DVB-1, DVB-4, DVB-8.5, DVB-20 for which the proportion of divinylbenzene in the initial monomer mix was known to be 1, 4, 8.5 and 20%, respectively, the degree of swelling under these conditions does indeed vary in inverse fashion with the proportion of divinylbenzene.

Table II reports the specific rates k_R and the efficiencies q for the hydrolysis of the two esters for which the IR-120 resin showed the highest and the lowest efficiency. For both esters the efficiency drops with increasing degree of cross linking, but the effect is much greater with the ethyl hexanoate. The result is to be expected from our hypothesis that the resin structure imposes restraints upon the transition state which reduce its entropy and hence tend to lower the rate of reaction. The more tightly knit structure of the more highly cross-linked resin imposes more severe restraints than does the looser structure of the less cross-linked resin, and the effect is greater the greater the amount of internal entropy which the ester possesses.

TABLE II

THE EFFECT OF RESIN STRUCTURE

Resin	Swelling, %	Methyl acetate $k_R \times 10^6$	Methyl acetate q	Ethyl hexanoate $k_R \times 10^6$	Ethyl hexanoate q
DVB-1	1000	49.4	0.906	5.66	0.370
DVB-4	180	42.5	.779	2.65	.173
CLTE-fs	88	36.2	.664	1.21	.079
DVB-8.5	73	35.0	.642	1.17	.075
IR-120	40	27.2	.502	0.745	.049
DVB-20	33	21.1	.387	0.456	.030

A third ester, methyl phenylacetate, was hydrolyzed by the DVB-4 resin at a specific rate of 6.30×10^{-6} and an efficiency of 0.296. The corresponding efficiency on the IR-120 resin was 0.0987, and it seems probable the efficiency for this ester drops with increasing cross linking in much the same sort of way that it does for the other two esters, with a value always greater than that for ethyl hexanoate, and less than that for methyl acetate.

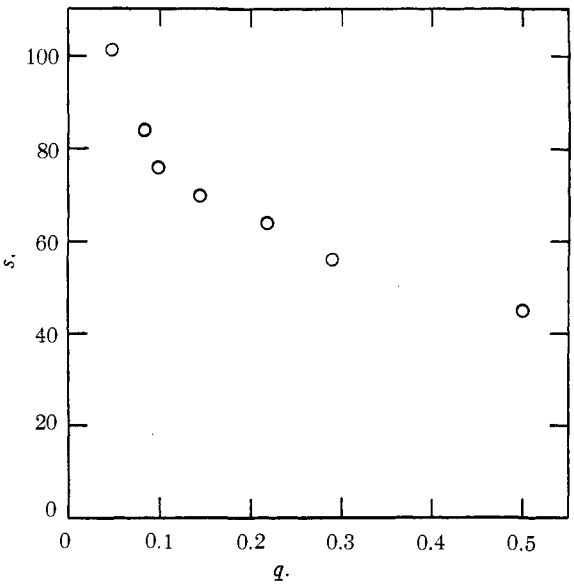

Fig. 1.

The Diffusion Question.—Haskell and Hammett concluded that diffusion within the resin particle is not a significant factor in determining the rate of the resin-catalyzed reaction from the fact that 80 to 100 mesh resin particles hydrolyzed three different esters, ethyl acetate, butyrate and hexanoate at nearly the same rate as did 40 to 45 mesh particles whose diameter is 55% greater. Reaction was, it is true, faster on the more finely divided resin, but the increase was only 4 to 6%, and was as great with the slowly diffusing hexanoate as with the more mobile acetate. There did remain a small possibility that diffusion was not completely eliminated as a factor because it happened that within this group of esters diffusibility parallels reactivity and it is the ratio of these two quantities which determines whether diffusion is a negligible factor in the over-all rate. Consequently we have determined the hydrolysis rates of methyl phenylacetate and of methyl *n*-octanoate on 80–100 mesh resin as well as with 45–50 mesh resin.

The two esters have nearly the same molecular weights, but if anything the phenyl acetate should diffuse more slowly through the resin network than the octanoate. The former hydrolyzes 1.29 times faster than the latter in homogeneous solution and 2.15 times faster on IR-120 resin. Yet we find that the change from 80–100 mesh to 45–50 mesh resin retards the reaction by only 2.5% with the phenyl acetate, and by 8% with the octanoate. It seems safe to conclude that in these systems diffusion is rapid enough so that the over-all reaction rate is completely determined by the chemical reaction.

The conclusion is supported by the relatively high efficiency shown by so bulky an ester as methyl naphthylacetate, and also by some experiments we

(3) The values of S come mostly from Selected Values of the Properties of Hydrocarbons, Natl. Bur. Standards (U. S.) Circ. C461 (1947). That for CH_3Cl is based on D. P. Stevenson and J. Y. Beach. *J. Chem. Phys.*, **6**, 25 (1938), and G. Messerly and J. G. Aston, THIS JOURNAL, **62**, 886 (1940). That for methylnaphthalene was calculated from the Southard and Brickwedde value of the entropy of solid naphthalene (*ibid.*, **55**, 4378 (1933)) and data on the heat of fusion and of vaporization from the "International Critical Tables," using the assumption that the difference between the entropies of naphthalene and methylnaphthalene is the same as that between the entropies of benzene and toluene.

have carried out on the time required to neutralize the acid resin by amines whose diffusibility should be similar to that of the esters we have studied. On the addition of a 5% excess of IR-120 resin to a solution in 70% acetone of benzylamine at a concentration corresponding to that of the ester in the rate measurements we found the neutralization to be analytically complete in 3 minutes. With tri-*n*-hexylamine the time was 5 minutes. This should be contrasted with a half-life for the hydrolysis of methyl phenylacetate of 200 hours.

The effect of the particle size of the resin is probably due to a difference in composition or structure between the surface layers and the interior of the resin particles. Through the kindness of Dr. K. W. Pepper of the Chemical Laboratory, Teddington, England, we were supplied with two samples of resins prepared from styrene–divinylbenzene polymer of identical composition. One, which we have called CLTE-fs was sulfonated completely in the usual manner, the other, CLTE-ss was superficially sulfonated. In order to get a useful capacity the latter was more finely divided ($d = 1.2 \times 10^{-2}$ cm.) than the former ($d = 4 \times 10^{-2}$ cm.). From the measured exchange capacity of the ss beads compared with that of the fs beads it could be estimated that the sulfonated layer in the former was 5×10^{-5} cm. thick, which amounts to about 1% of the diameter and would correspond to about 200 layers of the monomer unit of the resin. Our results on the hydrolysis of methyl acetate and of ethyl hexanoate on these two resins are reported in Table III. The surface layers of the resin are considerably more efficient for the hydrolysis of the hexanoate, somewhat less efficient for that of the acetate.

TABLE III

HYDROLYSIS BY CLTE-fs AND CLTE-ss RESINS

Ester	Resin	k_R	q
Methyl acetate	CLTE-fs	36.2	0.664
	CLTE-ss	33	.61
Ethyl hexanoate	CLTE-fs	1.21	.0720
	CLTE-ss	2.3	.137

Experimental

Materials.—Esters were generally prepared by esterification of the commercially available carboxylic acids. Naphthylacetic acid (m.p. 126°) was prepared according to Cambron.[4] The methyl ester boiled at 142° (6 mm.). Saponification analyses of the purified (by fractionation) esters gave the following percentage compositions: methyl acetate, 100.0; ethyl acetate, 99.6; methyl phenylacetate, 99.4; ethyl hexanoate, 99.5; methyl octanoate, 99.6; methyl benzoate, 100.1; methyl chloroacetate, 100.1; ethyl propionate, 100.2. Methyl cyclopentanecarboxylate was a highly purified sample kindly supplied by Dr. Warren Watanabe.

Acetone was refluxed with alkaline permanganate and fractionated in a 30-inch column of glass helices, b.p. 56.3°. For all reaction mixtures 70 ml. of acetone, the ester, and the acid if present, were made up to 100 ml. with water.

Styrene (Eimer and Amend) was distilled at 20 mm. in an oxygen-free system. Samples were stored at 0° under nitrogen in dark sealed bottles.

Divinylbenzene as obtained commercially was a mixture reported by the manufacturer to contain 42.5% of the isomeric monomers, an approximately equal amount of ethylvinylbenzene isomers, a residue of non-polymerizable materials and an inhibitor (*t*-butylcatechol). The mixture was washed with excess 5% sodium hydroxide, then with water, and the inhibitor-free material was dried over anhydrous potassium carbonate and stored similarly to the styrene.

Resins.—All resins reported here were sulfonated styrene–divinylbenzene copolymers. DVB-8.5 and DVB-20 were prepared according to the method of Gregor and associates.[5] The copolymers contained 8.5 and 20%, respectively, of actual divinylbenzene based on the report from the manufacturer. The resins were purified and conditioned as described in the above paper; those which were more highly cross-linked than DVB-4 were sieved after air equilibration and the 45–50 standard mesh particles were used for rate studies unless otherwise noted. DVB-1 and DVB-4 were from an industrial source. IR-120 was the same sample of Rohm and Haas resin classified to 45–50 mesh used by Haskell and Hammett.[2]

Rate of Studies.—In general, the procedure was similar to that of Haskell and Hammett. For the larger esters a water–acetone mixture was used for washing the reaction products from the resin since the insolubility in pure water caused obscuring of the end-point. In all but the slowest rates, the zero time was not used in the calculation of the rate constant. Reactions were followed to approximately half-life. Ten samples were used in each run and every run was made in duplicate. The probable error by least squares analysis was ±0.2%, and duplicates agreed to ±1% or better, except as noted below. Methyl chloroacetate hydrolysis was followed potentiometrically by titration with standard ammonium hydroxide solution using a Beckman *p*H meter. Duplicates agreed to ±3%. The exchange capacity of CLTE-ss could be measured with a precision of only ±5% thus imposing the same precision limit on the rate constant.

Swelling studies were made by placing finely divided air-equilibrated samples of resin in small calibrated cylinders and noting the resin volume before and after addition of water.

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(4) F. Cambron, *J. Can. Res.*, **17B**, 10 (1939).

(5) H. P. Gregor, J. I. Bregman, F. Gutoff, R. D. Breadley, D. E. Baldwin and C. G. Overberger, *J. Colloid Sci.*, **6**, 20 (1951).