[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Specific Effects in Acid Catalysis by Ion Exchange Resins. II. Hydrolysis of Esters in Water Solution[1]

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In water solution a lightly cross-linked ion exchange resin of the polystyrenesulfonic acid type is a better catalyst for the hydrolysis of aliphatic esters of low molecular weight than is dilute hydrochloric acid, and the effectiveness is somewhat greater for ethyl acetate than for methyl acetate. A tightly cross-linked resin, however, behaves in water solution in the same way as all such resins do in aqueous acetone solution, namely, the resin is less effective than the homogeneous strong acid, and the relative effectiveness of the resin decreases with increasing chain length of the ester. Within the experimental error both energy and entropy of activation are the same for all resin catalysts as for hydrochloric acid and are identical for methyl and ethyl acetates.

In the hydrolysis of straight chain aliphatic esters catalyzed by a cross-linked polystyrenesulfonic acid in 70% aqueous acetone the efficiency q, defined as the ratio of the specific rate of hydrolysis catalyzed by the resin to that catalyzed by homogeneous strong acid, has been found to be less than unity and to decrease with increasing chain length of the ester.[2] With a different type of ion exchange resin, a sulfonated coal, and in a different medium, water, Thomas and Davies[3] have found efficiencies greater than unity and increasing with increasing chain length. We have therefore investigated the catalysis by the polystyrenesulfonic acid resin in water solution with the results shown in Table I. The catalysts are those used in previous work.[2b]

TABLE I

SPECIFIC RATES (L./MOLE-SEC.) AND EFFICIENCIES FOR ESTER HYDROLYSIS IN WATER SOLUTION

Ester		10^5k	q
Methyl acetate	HCl	10.6	
	DVB-4	13.0	1.23
	IR-120	10.6	1.00
	DVB-20	9.08	0.86
Ethyl acetate	HCl	11.1	
	DVB-4	14.3	1.29
	IR-120	11.2	1.01
	DVB-20	8.57	0.77
Ethyl propionate	HCl	12.0	
	IR-120	12.5	1.04

With the lightly cross-linked resin DVB-4 the effects qualitatively resemble those of Thomas and Davies, with one of intermediate cross linking (IR-120) the efficiencies are nearly unity and are nearly independent of chain length of ester, and with the strongly cross linked DVB-20 the efficiencies behave like those which we have previously observed at all degrees of cross linking in aqueous acetone, being less than unity and decreasing with increasing chain length.

In view of the importance of entropy effects in the ion exchange catalysis[2] and of the clearly demonstrated possibility that similar substances may undergo analogous reactions at nearly identical rates and yet with very different temperature coefficients of rate, we have determined the temperature coefficients of the hydrolysis rates in water solution of methyl and of ethyl acetate using hydrochloric acid and two different resins as catalysts. The results are shown in Table II. The Dowex-50 resin is a commercial product with, to judge from its swelling behavior, a degree of cross linking intermediate between IR-120 and DVB-20. Both resins were used in an amount corresponding to 4.25 meq. of acid per 10 ml. of solution, and the hydrochloric acid was 0.466 N. E_a is the Arrhenius energy of activation in kcal., $\Delta\Delta S^{\ddagger}$ is the difference $\Delta S_r^{\ddagger} - \Delta S_h^{\ddagger}$ in cal./deg., where $\Delta S_r^{\ddagger}$ is the entropy of activation for the resin-catalyzed reaction and $\Delta S_h^{\ddagger}$ is that for the reaction catalyzed by hydrochloric acid.

TABLE II

TEMPERATURE COEFFICIENTS IN THE HYDROLYSIS OF METHYL AND ETHYL ACETATES

	10^5k				
Catalyst	10°	20°	30°	E_a	$\Delta\Delta S^{\ddagger}$
			Methyl acetate		
HCl	2.28	6.54	17.0	17.1 ± 0.2	
DVB-4	2.76	7.80	21.6	17.5 ± .4	1.7 ± 1.0
Dowex-50	2.14	5.85	15.8	17.1 ± .4	0 ± 1.0
			Ethyl acetate		
HCl	2.32	6.60	17.2	17.1 ± 0.2	
DVB-4	3.20	9.21	24.0	17.3 ± .3	1.3 ± 1.0
Dowex-50	2.09	5.99	16.0	17.4 ± .2	0 ± 1.0

Within the limits of experimental error both energies and entropies of activation are the same for all resin catalysts as for hydrochloric acid and are identical for methyl and ethyl acetates. This is in decided contrast to the results obtained in aqueous acetone solution[2a] in which both energy and entropy are appreciably lower for the resin than for the hydrochloric acid catalyst.

Even with respect to homogeneous systems, water solutions appear to occupy a special position in the acid-catalyzed hydrolysis of esters. For a variety of mixed solvents, hydrolysis rates decrease with increasing chain length in simple aliphatic esters[4] and the same is true for esterification in alcohol solution.[5] Specifically the rates

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[1] The work reported herewith was carried out as project NR 056-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] (a) V. C. Haskell and L. P. Hammett, THIS JOURNAL, **71**, 1284 (1949); (b) S. A. Bernhard and L. P. Hammett, *ibid.*, **75**, 1798 (1953).

[3] (a) G. G. Thomas and C. W. Davies, *Nature*, **159**, 732 (1947); (b) C. W. Davies and G. G. Thomas, *J. Chem. Soc.*, 1607 (1952).

[4] (a) H. A. Smith and J. H. Steele, THIS JOURNAL, **63**, 3466 (1941); (b) H. A. Smith and R. R. Meyers, *ibid.*, **64**, 2362 (1942); (c) G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940).

[5] (a) H. A. Smith and C. H. Reichardt, THIS JOURNAL, **63**, 605 (1941); (b) H. A. Smith and J. Burn, *ibid.*, **66**, 1494 (1944).

in l./mole-sec. at 25° for the hydrochloric acid catalyzed hydrolysis in 70% aqueous acetone are for methyl acetate 5.45,[2b] for ethyl acetate 4.64,[2b] for ethyl propionate 3.95.[4b] In contrast to this 28% decrease, the rates in water increase by 13% from methyl acetate to ethyl propionate (*cf.* Table I). For the esters of lower molecular weight the effect in alcohol-water solvent appears to arise chiefly or entirely from a decrease in entropy of activation with increasing chain length.[4a] It is therefore of a kind which may be attributed to a hampering of the internal motions of the ester molecule when it is converted to the transition state for the hydrolysis with a resultant decrease in entropy which parallels the entropy of the reactant ester.[6] We would suggest that all the effects here considered are consistent with the following hypothesis. In the mixed solvents the electrically charged transition state is subjected to restraints arising from solvation, which are stronger than those acting on the ester. These lead to a decrease in entropy of activation which is greater the greater the chain length of the ester. Still greater restraints imposed by the resin network lead to still greater decreases in entropy of activation with increasing chain length in the resin-catalyzed reaction. In water solution, however, the solvation of the polar groups in the ester itself is so powerful that no further important restraints are imposed on the internal motions of the ester by the solvation of the charged transition state or by the resin network (except in the most highly cross linked resins). Consequently the entropy change involved in the conversion of ester to transition state is no longer more negative for esters of greater chain length.

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Experimental

The experimental methods were those described previously.[2b] All runs were made at least in duplicate, those used in the temperature coefficient studies being in triplicate. Agreement was better than 1% in all cases except those involving ethyl propionate. Plus and minus values for the energies of activation listed in Table II refer to mean deviations between high and low temperature range calculations, except when these agreed to better than 200 cal. In such cases a minimum error of 200 cal. was assumed, this being the value arising from the estimated probable error in the specific rates derived from least squares analysis of concentration-time plots.

Commercial Dowex-50 was purified by the methods of Gregor and associates,[7] and 45-50 mesh particles were used in the rate measurements. The other resins have been described previously.[3]

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[6] F. P. Price and L. P. Hammett, THIS JOURNAL, **63**, 2387 (1941).

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

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Acid-Base Levels in Methanol-Water and 1,4-Dioxane-Water Solutions

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The apparent acid-base levels of 3.077×10^{-3} *M* sodium hydroxide solutions in methanol-water and dioxane-water have been studied at approximately 25° by means of an indicator method. Complete absorption spectra were determined for both acid and base forms of Alizarin Yellow R in the range 220-600 mμ in water, in methanol and in methanol-water and dioxane-water solutions of various compositions; and extinction coefficients were determined at 375 and 495 mμ in the various solvents both for the acid and for the base forms of the indicator. A knowledge of these values allowed analyses to be made for the concentrations of the base and of the acid form, and thence the "indicator ratio," R = [base form]/[acid form], in any of the solvents or solvent combinations. Values for R were determined in water solutions in which there was a constant concentration of sodium hydroxide but in which the ionic strength was varied by adding potassium chloride. Extrapolation of the log R values to zero ionic strength gave a limiting ratio from which pK for the Alizarin Yellow R indicator was calculated to be 11.17. The slope of the log R *vs.* $\sqrt{\mu}$ curves at low ionic strengths supported the assumption that the indicator base is a doubly charged anion and the acid a singly charged anion. Similar log R extrapolations to zero ionic strength were made for 3.077×10^{-3} *M* solutions of sodium hydroxide in methanol-water and in dioxane-water. The relative order of these limiting log R values was shown to be the same as that of the p_{a}H values, and the experimental observations indicated that sodium hydroxide solutions in methanol-water have lower p_{a}H values than isodielectric dioxane-water solutions of the same sodium hydroxide concentration. Apparent p_{a}H values for these solutions were calculated from the indicator pK, the limiting log R values, and activity coefficient ratios computed by assuming 2 and 3 Å. indicator ion radii. These calculations showed that p_{a}H increases with decreasing dielectric constant in dioxane-water solutions, but that methanol-water solutions show the opposite behavior. The dielectric constant effect in dioxane-water solutions is normal; therefore the base levelling effect in methanol-water gives rise to the postulate that methanol is a stronger acid than water.

A critical evaluation of all previous investigations directed toward a comparison of the acid-base properties of water with those of the lower aliphatic alcohols and toward determining the extent to which hydroxyl ion is levelled by methanol has led us to the following conclusion: Although a recent investigation[2] has provided quantitative evidence indicating that methanol is a stronger acid than water in isopropyl alcohol solution, and although there are many other lines of evidence which indicate that methanol is a stronger acid than water, no unambiguous quantitative results are available for methanol-water solutions. In the study described in this paper, evidence bearing on the question of the comparative acid strengths of methanol and water was provided by determining the apparent hydrogen ion activities in methanol-water and in 1,4-dioxane-water solutions containing identical concen-

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[1] Abstracted from a thesis submitted by W. C. Woodland to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the D.Sc. degree.

[2] J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).