

which conditions the remainder of the resin is a pale yellow, and is thought to be due to the action of a small amount of bromine produced from the concentrated bromide solution by air oxidation.

From this it appears, then, that with the exception of Ga(III), the anion separation of the bromide

complexes of the transition elements studied offers no advantage over the more convenient chloride complex separation, while placing an upper limit of $\sim 7 M$ on the anion concentration which can be employed in the separation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Specific Effects in Acid Catalysis by Ion Exchange Resins. III. Some Observations on the Effect of Polyvalent Cations¹

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RECEIVED SEPTEMBER 14, 1953

The catalytic effectiveness for the hydrolysis of ethyl acetate and of ethyl hexanoate of the hydrogen ions of a lightly cross linked polystyrene sulfonic acid is unaffected when the resin contains a considerable proportion of magnesium ions as well as the hydrogen ions. Replacement of part of the hydrogen ions of the sulfonic acid by ethylenediammonium ions, however, reduces the catalytic effectiveness of the remaining hydrogen ions by a factor which is twice as large for the hexanoate as for the acetate.

The ratio $r = q_1/q_2$ of the efficiencies of an ion exchange resin for the hydrolysis of two carboxylic esters 1 and 2 is in 70% aqueous acetone strongly dependent on the degree of cross linking of the resin.² This ratio, which we shall call the specificity ratio of the resin relative to the two esters, measures the difference between the standard free energies of transfer of the transition states for the two esters from homogeneous solution to the environment prevailing in the resin.² One way in which increased cross linking affects this environment is merely by squeezing out solvent, so that the environment is more like an aromatic hydrocarbon and less like an aqueous solution. But the solvent content of the resin may also be reduced by partial replacement of the hydrogen ions of the cross-linked polystyrene sulfonic acid by other cations and especially by polyvalent cations.

Thus a very lightly cross linked resin (prepared with only 0.5% of divinylbenzene in the initial polymerization mix) which in the form of the air-dry acid swells 40-fold on immersion in water shrinks by a factor of 2 when the swollen acid is converted to the fully hydrated magnesium salt and by a factor of 3 when the acid is converted to the salt of the ion $\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_3^+$. A smaller but still considerable shrinkage must be expected when only part of the hydrogen ions in the acid are replaced by the polyvalent ion.³ With these considerations in mind we have determined the effect on the catalytic properties for the hydrolysis of ethyl acetate and of ethyl hexanoate of replacing part of the hydrogen ions in this resin by magnesium ion or by the diquatery ion $\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{N}^+\text{Me}_3$. The results are reported in Table I. The column headed H^+ , % lists the percentage of the hydrogen ion of the original resin which has not been replaced by another

cation. k is a second-order specific rate with time in minutes computed by dividing the first-order specific hydrolysis rate by the number of moles of hydrogen ions available from the resin per liter of solution. The specificity ratio, r , defined in the first paragraph, ester 1 being the hexanoate, ester 2 the acetate, was calculated using the data of Haskell and Hammett⁴ on hydrolysis rates in homogeneous solution at 25° on the basis that the energy of activation for the homogeneous reaction is 16.3 kcal. for both esters.⁵

TABLE I

SPECIFIC RATES AND SPECIFICITY RATIOS IN 70% AQUEOUS ACETONE AT 40° FOR RESINS WITH PARTIAL REPLACEMENT OF HYDROGEN IONS BY POLYVALENT CATIONS. TIME IN MIN.

Replacing ion	H ⁺ , % remaining	10 ⁶ k for		r
		Ethyl acetate	Ethyl hexanoate	
None	100	12.2	2.62	0.65
Mg ⁺⁺	66	12.6	2.60	.63
$\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{N}^+\text{Me}_3$	42	9.8	1.30	.40
$\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{N}^+\text{Me}_3$	29	8.1	0.85	.32

Two features of these results are of particular interest. One is the contrast between the effects of magnesium ion and of the diquatery ion. Replacement of hydrogen ion by either of these ions shrinks the resin strongly, yet in the presence of magnesium ion the remaining hydrogen ions are unchanged in catalytic properties for both esters while the diquatery ion retards the hydrolysis of both esters and alters the specificity ratio considerably. The other is the fact that if the resin in the fully acid form had been altered by increasing the degree of cross linking to such an extent as to reduce the hydrolysis rate of ethyl acetate to 8.1×10^{-6} the specificity ratio would have been decreased to 0.19 instead of to the 0.32 observed.⁶

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

(5) (a) G. Davies and D. P. Evans, *J. Chem. Soc.*, 399 (1940); (b) H. A. Smith and J. H. Steele, *THIS JOURNAL*, **63**, 3466 (1941).

(6) This figure is based on data on the effect of cross linking on hydrolysis rates at 40° contained in a forthcoming article by Riesz and Hammett; see also paper IV, p. 992.

(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) S. A. Bernhard and L. P. Hammett, *THIS JOURNAL*, **75**, 1798 (1953).

(3) D. K. Hale, D. I. Packham and K. W. Pepper, *J. Chem. Soc.*, 844 (1953).

The implication of both these effects is that the catalytic properties of the resin can be altered in considerable degree by replacement of part of the hydrogen ions by other ions and that the effect is specifically dependent on the nature both of the replacing ion and of the ester being hydrolyzed.

We record further some measurements on the effect of replacing approximately half of the hydrogen ions of the much more highly cross linked resin IR-120² by inorganic ions. When the replacing ion is sodium we have found the specific rate at 25° for the hydrolysis of methyl acetate to be 0.85 times that for the resin in the fully acid form, for ethyl hexanoate the corresponding ratio is 0.76. When the replacing ion is barium this ratio is 1.12 for the hexanoate.

Experimental

The resin used was prepared by sulfonation of a copolymer of styrene and divinylbenzene containing 0.5% of the

latter by the method described by Gregor and co-workers.⁷ When the acid form of this resin in equilibrium with water was washed with acetone the volume of the beads dropped by a factor of about 50. After air drying of this product to constant weight it was found to swell by a factor of 40 when placed in water. The partially neutralized resins were prepared by reaction of the diquaternary hydroxide or of magnesium oxide with the acid form of the resin. In the magnesium case the temperature was raised to 75°. A solution of the diquaternary hydroxide was prepared from ethylenediammonium iodide by the addition of an aqueous suspension of silver oxide followed by filtration. The iodide was prepared by the addition of the stoichiometric amount of methyl iodide to ethylenediamine over anhydrous potassium carbonate. The product was taken up in ethanol-ether, excess carbonate was filtered off, and the solution was concentrated. Upon the addition of ether a precipitate separated, which was three times crystallized from methanol and once from ethanol. The product contained 61.37% iodine, the theoretical being 63.44%.

Rate measurements were all at 40.00° and followed procedures which have been described.

(7) H. P. Gregor, J. I. Bregman, F. Gutoff, R. D. Bradley, D. E. Baldwin and C. G. Overberger, *J. Colloid Sci.*, **6**, 20 (1951).
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Specific Effects in Acid Catalysis by Ion Exchange Resins. IV. The Effect of Quaternary Ammonium Ions on the Hydrolysis of Esters of Related Structure¹

BY PETER RIESZ AND LOUIS P. HAMMETT

RECEIVED SEPTEMBER 14, 1953

Replacement of 70% of the hydrogen ions in a cross linked polystyrenesulfonic acid by cetyltrimethylammonium ions has a specifically favorable effect on the effectiveness of the remaining hydrogen ions for the hydrolysis of ethyl *n*-hexanoate, replacement by methyltribenzylammonium ions has a specifically favorable effect on the hydrolysis of methyl phenylacetate. These effects are consistent with the hypothesis that a quaternary ammonium ion alters the environment of the transition state for the hydrolysis of the ester in such a way as to produce an especially low value of the standard free energy of the transition state when the quaternary ion and the ester have some prominent structural feature in common.

In the course of further investigation of the considerable and specific effect on the catalytic properties of a cross linked aromatic sulfonic acid which is produced by replacement of part of the hydrogen ions by other ions² we have found that the phenomenon is not limited to the case in which the replacing ion is a polyvalent cation, and that large effects can be obtained when it is a singly charged quaternary ammonium ion. The pertinent data are reported in Tables I and II. The DVB-¹/₂ resin is that used in the previous study² and was prepared with 0.5% of divinylbenzene in the initial polymerization mixture; the Amberlite IR-112 is a commercial resin whose swelling properties indicate a proportion of cross linking agent of 4.5%.³ As in the previous work² the column headed H⁺, % lists the percentage of the original hydrogen ion of the resin which has not been replaced, and *k* is a second-order constant.

Considering first the behavior of the more highly

(1) Based upon a Dissertation submitted by Peter Riesz to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work 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) S. A. Bernhard, E. Garfield and L. P. Hammett, *THIS JOURNAL*, **76**, 991 (1954).

(3) S. A. Bernhard and L. P. Hammett, *ibid.*, **75**, 1798 (1953).

TABLE I
SPECIFIC RATES FOR DVB-¹/₂ RESIN WITH PARTIAL REPLACEMENT OF HYDROGEN IONS BY QUATERNARY AMMONIUM IONS. TIME IN MIN., TEMP. 40.00°, SOLVENT 70% AQUEOUS ACETONE

Quaternary ammonium ion	H ⁺ , %	10 ⁵ <i>k</i> for		
		Ethyl acetate	Ethyl hexanoate	Methyl phenylacetate
None	100	12.2 ²	2.62 ²	4.20
Tetramethyl	31.4	8.90	1.59	
Tetra- <i>n</i> -butyl	28.4	8.75	1.95	
Cetyltrimethyl	30.4	13.1	3.53	
Methyltribenzyl	34.9	11.2	2.68	4.97

TABLE II
SPECIFIC RATES FOR IR-112 RESIN WITH PARTIAL REPLACEMENT OF HYDROGEN IONS BY QUATERNARY AMMONIUM IONS. TIME IN MIN., TEMP. 40.00°, SOLVENT 70% AQUEOUS ACETONE

Quaternary ammonium ion	H ⁺ , %	10 ⁵ <i>k</i> for		
		Ethyl acetate	Ethyl hexanoate	Methyl phenylacetate
None	100	10.4	0.925	2.07
Tetramethyl	30.1	5.76	.373	1.37
Tetra- <i>n</i> -butyl	31.0	4.06	.851	1.75
Cetyltrimethyl	31.7	5.43	1.55	2.86
Methyltribenzyl	31.9	5.54	0.76	2.67

cross linked resin IR-112 it appears: (1) that the effect of the quaternary ion may be considerable,