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-120[2] 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.

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[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).

NEW YORK, N. Y.

[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 Structure[1]

BY PETER RIESZ AND LOUIS P. HAMMETT

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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 ions[2] 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 study[2] 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 work[2] 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.

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^+, %	$10^5 k$ 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-*n*-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^+, %	$10^5 k$ for Ethyl acetate	Ethyl hexanoate	Methyl phenylacetate
None	100	10.4	0.925	2.07
Tetramethyl	30.1	5.76	.373	1.37
Tetra-*n*-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

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

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[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).

the specific rate for ethyl hexanoate being 4.2 times greater with the resin containing cetyltrimethylammonium ion than with the resin containing tetramethylammonium ion; (2) that the effect is specific to the ester, the ratio of the rate with the cetyltrimethylammonium resin to that with the tetramethylammonium resin being 0.93 for ethyl acetate, and 2.1 for methyl phenylacetate as compared with the 4.2 for ethyl hexanoate; (3) that the hydrolysis of an ester containing a phenyl group is specifically favored when the neutralizing ion contains phenyl groups, the ratio of the rate for methyl phenylacetate to that for ethyl hexanoate being 3.5 when the resin contains methyltribenzylammonium ion and 1.85 when it contains cetyltrimethylammonium ion. The general pattern of the results obtained with the DVB-$^1/_2$ resin closely resembles that obtained with the more tightly cross linked resin but the magnitude of all the effects is smaller.

The observed phenomena are consistent with the following hypothesis, which served indeed as a guide in our experiments: If E* is an ester which has a prominent structural feature, such as a long aliphatic chain or an aromatic ring, in common with a quaternary ion $NR_4{}^{*+}$ and E is an ester which lacks this feature then the ratio k^*/k of the specific rates for the hydrolysis of these esters by an ion exchange resin and hence the specificity ratio r should be increased by partial replacement of the hydrogen ions of the resin by the ion $NR_4{}^{*+}$. The only deviation we have found from the corollaries of this hypothesis is the relatively favorable effect of cetyltrimethylammonium ion on the hydrolysis of methyl phenylacetate, but even here it should be noted that this ion has a much more favorable effect on the aliphatic hexanoate than on the aromatic phenylacetate.

The effect of the quaternary ions is of an entirely different nature from that produced by a change in the degree of cross linking of the resin. To demonstrate this we have plotted as open circles in Fig. 1 the efficiency q_h for the hydrolysis of ethyl hexanoate against the efficiency q_a for the hydrolysis of ethyl acetate for three resins DVB-$^1/_2$, IR-112 and IR-120[4] which differ only in degree of cross linking. As would be expected from previous work[3] a smooth curve can be drawn through the points thus plotted. But the points represented by shaded circles which represent the corresponding data for the resins obtained from IR-112 by substituting quaternary ammonium ions for part of the hydrogen ions deviate widely from this curve.

This matter is of importance in two ways. First it emphasizes the impossibility of accounting for the catalytic specificity of the various resins in terms of a single variable, such as the degree of swelling of the resin or the relative proportions of acetone and water in the solvent imbibed by the resin.[5] Second, it offers the possibility of varying the catalytic specificity of a resin in two fundamentally different ways and holds out, therefore, the hope that the specificity can be increased beyond the limits which we have so far been able to reach.

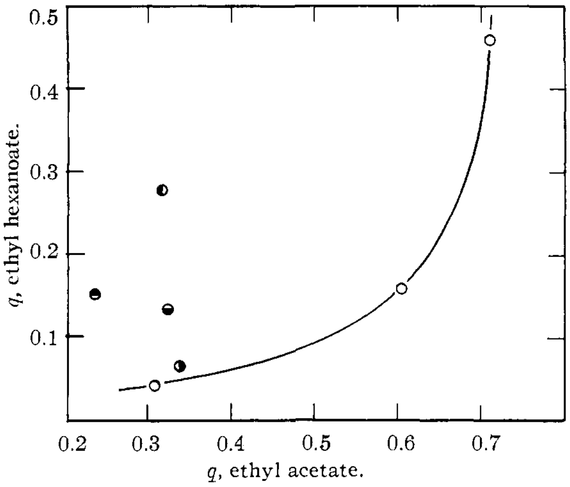

Fig. 1.—Relation between efficiencies for ethyl hexanoate and ethyl acetate: ○, resins in 100% H form; ◑, resin partially neutralized with tetramethylammonium ion; ◓, with tetrabutylammonium ion: ◐, with cetyltrimethylammonium ion: ◒, with methyltribenzylammonium ion.

The obvious interpretation of these specific catalytic effects is in terms of the old principle that like dissolves like. In the present case this is to be interpreted in the sense that increasing incorporation into the resin of long-chain aliphatic structures lowers the standard free energy of the transition state for the hydrolysis of an ester containing similar structures relative to the standard free energies of the transition states of esters of different structures, and that the incorporation of additional phenyl groups into the resin has a similar effect on the transition state of an ester containing phenyl groups.

Experimental

Materials.—Ethyl hexanoate was the sample used in previous work.[3] The other esters were commercial products which were dried, fractionated carefully, and found to give within 0.6% of the theoretical saponification value. Acetone was refluxed with alkaline permanganate and fractionated from calcium oxide powder through a good column.

Tetramethyl and tetra-*n*-butyl iodides were repeatedly recrystallized from water, and were converted to solutions of the hydroxides by treatment of a water suspension with excess of silver oxide. Cetyltrimethylammonium bromide was three times recrystallized from ethanol. Methyltribenzylammonium iodide was prepared by refluxing tribenzylamine in an equal volume of benzene with a large excess of methyl iodide for 40 hours. After evaporation of excess of methyl iodide the solid was filtered, washed with ether, and recrystallized twice from water; m.p. 186° dec.

Anal. Calcd.: C, 61.54; H, 5.59; I, 29.56. Found: C, 61.25; H, 5.75; I, 29.41.

Resins.—DVB-$^1/_2$ was the sample used in previous work.[2] Amberlite IR-112 was treated with acetone to remove any soluble impurities, then cycled five times between the hydrogen and sodium forms until the effluent liquid was colorless. The resin in the acid form was washed with distilled water until the *p*H of the effluent was over 5.2, washed with acetone and dried in vacuum at 50°. It was finally allowed to equilibrate with room air, and had then an exchange capacity of 4.06 meq. per g. The work of Pepper[6] shows

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[4] For the first two of these resins the efficiency q, which is the ratio of the specific rate for hydrolysis by the resin to the specific rate of hydrolysis in homogeneous strong acid, was calculated from data on hydrolysis rates in homogeneous solution on the same basis as in ref. 2. For IR-120 the computation assumed, on the basis of the results of Haskell and Hammett, THIS JOURNAL, **71**, 1284 (1949), that for both esters the energy of activation for the resin-catalyzed reaction is 1.3 kcal. less than it is for the homogeneous reaction.

[5] *Cf.* C. W. Davies and G. G. Thomas, *J. Chem. Soc.*, 1607 (1952).

[6] K. W. Pepper, *J. Applied Chem.*, **1**, 124 (1951).

that a completely dried resin of this type has a capacity of 5.4. The percentage swelling[3] was found to be 154% which indicates a divinylbenzene content of about 4.5% in the polymerization mix.

The preparation of the partially neutralized resins varied according to the cation involved. With tetramethyl- and tetrabutylammonium ions the calculated amount of the quaternary hydroxide solution was added to the stirred suspension of swollen resin in water over a period of 30 minutes. At the end of this period the supernatant liquid was neutral to litmus. The resin was washed with a large volume of water, then with acetone, and was dried in vacuum at 50° and then allowed to equilibrate with room air.

With cetyltrimethylammonium ion the resin suspension was stirred with a solution of the calculated amount of the quaternary bromide, and measurement of the acid titer of the supernatant liquid showed that the exchange was almost complete. The resin was washed with alcohol and water until the filtrate gave no test for bromide, and dried and air equilibrated as usual. With the sample prepared from the IR-112 four determinations each of available hydrogen and of total exchange capacity gave a figure of 31.7 ± 0.4% for the % hydrogen ion remaining. Essentially the same figure was found in samples after they had been used for the catalysis of ethyl hexanoate and of methyl phenylacetate.

With methyltribenzylammonium ion a procedure analogous to that used with cetyltrimethylammonium ion led to the replacement of only 50% of the available hydrogen ion. A second treatment of the product thus obtained with fresh quaternary iodide led to a product containing 31.7 ± 0.2% of unneutralized hydrogen ion in the IR-112 case. This value was found to be essentially unchanged after the resin had been used as catalyst with each of the three esters involved in the present study.

In determining the total exchange capacity of the resins which had been partially neutralized with cetyltrimethylammonium and with methyltribenzylammonium ions it was found to be necessary to use six successive treatments of 15 minutes each with 50 ml. of 4 N hydrochloric acid in 50% ethanol, in order to convert the sample completely to the hydrogen form.

Rate Studies.—These followed methods previously described.[3] With the IR-112 resin 1 g. of resin in the hydrogen form and correspondingly larger amounts of the partially neutralized resins were employed with 10 ml. of liquid reaction mixture. With the DVB-$^{1}/_{2}$ resin only about one-tenth of this amount of resin could be used because of the bulk of the swollen resin.

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[CONTRIBUTION FROM THE INSTITUTE FOR CHEMICAL RESEARCH, KYOTO UNIVERSITY]

Kinetics of Iodine-catalyzed Aromatic Bromination. II. Bromination of Toluene

BY TEIJI TSURUTA, KEN-ICHI SASAKI AND JUNJI FURUKAWA

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The rates of the iodine-catalyzed bromination of toluene in carbon tetrachloride were measured in the dark at 25°. The results showed that the rate expression which had previously been derived from the assumption that the rate-determining step is the loss of hydrogen bromide from a 1:1 aromatic–bromine complex still held well in this case. The dependence of the reaction rate v upon the concentration of toluene was examined. This examination has revealed the rate expression $v = k[C_6H_5Me{\cdot}Br_2][BrI]^3$ to be the most probable expression within the four possible ones. An induction period was observed in the bromination. But the nature of this induction period is still obscured in the present stage.

In the first paper[1] of this series, we suggested that the previous interpretations of data on the rate of iodine-catalyzed aromatic bromination are not satisfactory. A new rate expression for the bromination was derived under the assumption that the rate-determining step is the loss of bromoanion from a 1:1 aromatic–bromine complex

$$C_6H_6Br_2 + m\mathrm{BrI} \xrightarrow{k} C_6H_5Br + m\mathrm{BrI} \qquad (1)$$

where k is the rate constant of the reaction and m is a constant. The rate v of reaction 1 can be written as

$$v = k[C_6H_6Br_2]\,[BrI]^m \qquad (2)$$

Equation 2 was transformed into equation 3 or 4 by use of the relations between the equilibrium concentrations of the various halogen species and the total bromine and iodine in the reaction mixture

$$v = Muw^m \qquad (3)$$

or

$$\log (v/u) = \log M + m \log w \qquad (4)$$

where

$M = \{2/(1 + K_4\phi)\}^m K_2k\phi/(1 + K_2\phi)$
$u = \{X^2/(X + Y)\} + \{(L/K_1)X^2Y^2/(X + Y)^3\}$ (related to bromine)
$w = \{XY/(X + Y)\} - \{(L/K_1)X^2Y^2/(X + Y)^3\}$ (related to iodine bromide)
ϕ = mole fraction of the free aromatic hydrocarbon
X = total concentration of bromine
Y = total concentration of iodine
$L = \{4(1 + K_2\phi)(1 + K_3\phi)/(1 + K_4\phi)\} - K_1$
$L/K_1 \fallingdotseq -1$

and K_1, K_2, K_3 and K_4 are the equilibrium constants of the reactions

$$Br_2 + I_2 \overset{K_1}{\rightleftarrows} 2BrI$$
$$Br_2 + C_6H_6 \overset{K_2}{\rightleftarrows} C_6H_6Br_2$$
$$I_2 + C_6H_6 \overset{K_3}{\rightleftarrows} C_6H_6I_2$$
$$BrI + C_6H_6 \overset{K_4}{\rightleftarrows} C_6H_6BrI$$

When ϕ is constant, the straight line relationship between log (v/u) and log w was expected. This relation was confirmed by recalculating Bruner's data[2] in which ϕ might be considered as a constant because the reactions were all carried out in pure benzene. From the slope of the straight line, it was found that m was equal to 3 in the case of benzene.

This paper presents the results obtained from several series of experiments in which the rates of bromination of toluene in carbon tetrachloride were measured in the dark at 25°. In series I of the experiment, every initial concentration of total bromine was kept at a specific value, while in series

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[1] T. Tsuruta, K. Sasaki and J. Furukawa, THIS JOURNAL, **74**, 5995 (1952).

[2] L. Bruner, *Z. physik. Chem.*, **41**, 514 (1902).