[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Specific Effects in Acid Catalysis by Ion Exchange Resins. V. Resins Prepared from Styrenesulfonic Esters[1]

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Resins prepared by copolymerizing an ester of styrenesulfonic acid with divinylbenzene are difficult to hydrolyze completely to the acid, especially when the alkyl group of the ester is large. The polymeric sulfonic acids prepared by partial hydrolysis of the polymeric esters have high catalytic efficiencies for the hydrolysis of esters yet show little swelling when the air-dry resin is immersed in water. This is in marked contrast to the properties of sulfonic acid ion-exchange resins prepared in the usual way. This suggests that the local environment in these resins contains both regions of very loose cross linking and regions of very tight linking.

We have investigated the method of Spinner, Ciric and Graydon[2] for the preparation of ion-exchange resins of the cross linked polystyrenesulfonic acid type with respect to the catalytic properties of the resulting resins. In this method an ester of styrenesulfonic acid is copolymerized with divinylbenzene, and the resulting polymeric ester is then hydrolyzed to the acid. In the light of our previous experience[3] one variable of interest is the effect on the catalytic properties of the nature of the alcohol group in the ester. It soon developed from our studies that these cross linked polystyrenesulfonic esters are surprisingly difficult to hydrolyze, and that the difficulty increases rapidly with the bulk of the alcohol residue. The method thus offers an effective way of preparing ternary copolymers which are derived from styrenesulfonic acid, divinylbenzene and a styrenesulfonic ester. The catalytic effects studied involved the acid catalyzed hydrolysis of four esters of differing types, all of which have been investigated in our previous studies with other resins.

Experimental

Preparation of Styrenesulfonic Esters.—The ethyl ester was prepared by the method of Spinner, Ciric and Graydon[2] using β-(*p*-chlorosulfonylphenyl)-ethyl bromide prepared by the method of Inskeep and Deanin.[4] With higher alcohols this method, which involved reaction of the sulfonyl chloride with excess of alcohol, gave low yields because the high temperatures required for the removal of this excess even *in vacuo* tended to cause decomposition and polymerization of the product. The following method, illustrated for the *n*-butyl ester, also gave satisfactory results for the *n*-hexyl, *n*-octyl and benzyl esters.

With vigorous stirring under reflux 18 g. of powdered zinc oxide was added to a mixture of 21.5 g. (0.29 mole) of *n*-butyl alcohol, 120 g. of benzene and 100 g. (0.35 mole) of β-(*p*-chlorosulfonylphenyl)-ethyl bromide and this was followed by the addition of 1.5 g. of pyridine. All materials had been dried carefully. After cooling the mixture was extracted with ether, the ether layer was washed and dried with calcium chloride, and the solvent was removed *in vacuo;* 80–90 g. of light yellow oil was obtained. This was dissolved in an adequate amount of ethanol, the solution was heated to 50°, a little phenolphthalein was added, and a solution of potassium hydroxide in ethanol at 50° was added gradually with vigorous stirring, keeping the temperature below 60°. When a permanent pink color was obtained the mixture was cooled, ether was added, and the ether layer was washed with water, and dried over sodium sulfate after adding a trace of *p*-*t*-butylcatechol. After removal of the ether *in vacuo* a yellow to brown oil was obtained which was not further purified. The material decomposes badly when the attempt is made to distil it *in vacuo*. The yield of crude product in the dehydrobromination varied from 60 to 80%.

The β-phenylethyl ester of the bromoethylbenzenesulfonic acid could be prepared in good yield, but β-elimination occurred at both ends of the molecule in the dehydrobromination process and styrene is one of the main products instead of the phenylethyl ester of styrenesulfonic acid. The phenyl ester was prepared in the same way as the butyl ester except that the ethereal solution of the bromoethyl ester was washed successively with potassium hydroxide solution, water, hydrochloric acid and water before drying.

Polymerization.—A mixture of the styrenesulfonic ester with a sufficient proportion of commercial divinylbenzene (reported to contain 45% of actual divinylbenzene) to make the divinylbenzene content 10% of the charge was polymerized under the usual conditions for suspension polymerization to give beads, except that the temperature was 60–70° instead of the usual 90–100°. 1% of benzoyl peroxide was used as initiator, and 10% of soluble starch as emulsion stabilizer. The total time of polymerization was 30–32 hr. The lower temperature decreased considerably the loss of monomer by hydrolysis of the ester groups and also reduced the proportion of the product in which the ester groups had already been hydrolyzed at the end of the polymerization. To judge from relative weights of monomer charged and resin produced losses were small.

Two resins, designated 1x and 1y, were prepared from a polymerization mix containing a non-polymerizable additive. For 1x the batch contained the ethyl ester of styrenesulfonic acid with the usual proportion of divinylbenzene plus two moles of ethyl caproate for each mole of styrenesulfonic ester. Resin 1y contained methyl phenylacetate in the same proportion.

Hydrolysis of the Polymer Esters.—This was carried out with aqueous or with alcoholic sodium hydroxide at refluxing temperatures. To obtain the maximum degree of hydrolysis several changes of the hydroxide solution at 4 to 6 hr. intervals were used. With the higher esters, such as the phenyl and phenylethyl derivatives the aqueous hydroxide was ineffective.

Kinetic and Other Measurements.—These followed methods previously used in this Laboratory.[3] Rate measurements were usually in duplicate, the average difference between duplicates being 1.8% and the maximum difference 6.6%. Capacities, reported as milliequivalents per g. dry resin, and swelling data are for resins dried over calcium chloride. Swelling data are for water.

Results

Data on the properties of the resins and on their catalytic efficiencies for the four esters ethyl acetate, ethyl *n*-butyrate, ethyl *n*-hexanoate and methyl phenylacetate are reported in Table I. Column I lists the alcohol group of the styrenesul-

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[2] I. H. Spinner, J. Ciric and W. F. Graydon, *Canadian J. Chem.*, **32**, 143 (1954).

[3] (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); (c) **75**, 5834 (1953); (d) S. A. Bernhard, E. Garfield and L. P. Hammett, *ibid.*, **76**, 991 (1954); (e) P. Riesz and L. P. Hammett, *ibid.*, **76**, 992 (1954); (f) H. Samelson and L. P. Hammett, *ibid.*, **78**, 524 (1956).

[4] G. E. Inskeep and R. Deanin, *ibid.*, **69**, 2237 (1947).

fonic ester used in the preparation of the resin. Rates were measured at 25.00°, the solvent was 70% aqueous acetone, and the catalytic efficiency q is the ratio of the specific rate of hydrolysis of the ester on the resin to its specific rate of hydrolysis in homogeneous strong acid solution. In calculating the efficiencies the specific rate of hydrolysis in homogeneous strong acid was taken as 4.60 for ethyl acetate, 1.91 for ethyl butyrate, 1.52 for ethyl hexanoate, and 2.16 for methyl phenylacetate, all in 10^5 l. mole^{-1}-sec.$^{-1}$.

TABLE I

			Efficiency, q, for			
Resin no. and type	Capacity	Swelling, %	Ethyl acetate	Ethyl butyrate	Ethyl hexanoate	Methyl phenylacetate
1a Ethyl	3.06	81	0.661	0.521	0.316	0.447
1b Ethyl	3.43	138		.514	.300	.498
2a Butyl	3.07	90	.800	.621	.421	.514
2b Butyl	3.41	138	.778	.605	.367	
3a Hexyl	2.10	80	.821	.806	.586	.750
3b Hexyl	2.94	103	.787	.657	.465	.586
3c Hexyl	3.25	100			.435	.570
4a Octyl	2.40	100	.891	.806	.525	.561
4b Octyl	2.93	134	.793	.681	.449	.574
4c Octyl	3.35	111	.809	.660	.443	.558
5 Phenyl	3.34	100	.775	.686	.389	.491
6a Phenylethyl	2.40	75	.820	.697	.470	.578
6b Phenylethyl	3.24	90	.788	.681	.465	.559
1x Ethyl[a]	2.70	84	.613	.576	.305	.378
1y Ethyl[b]	3.09	122	.770	.733	.456	.574

[a] Ethyl caproate present during the polymerization. [b] Methyl phenylacetate present during the polymerization.

Rate measurements at 40° on resin 3a lead to an activation energy of 15.7 kcal. for ethyl acetate and 16.3 for ethyl hexanoate. The corresponding values for resin 3b were 14.0 and 14.3.

Conclusions

The group of resins which we have prepared vary considerably among themselves in catalytic efficiency for the ester hydrolysis, the extremes differing by a factor of two in the hydrolysis of methyl phenylacetate. In contrast to resins prepared in the conventional way by sulfonation of a styrenedivinylbenzene copolymer they have high catalytic efficiencies yet show relatively little swelling when the dried resin is immersed in water. Thus the least efficient of the new resins for the hydrolysis of ethyl hexanoate (1b) is more efficient in the ratio of 0.300/0.173 than a resin prepared in the conventional way from a copolymer containing 4% of divinylbenzene,[3b] yet the new resin is less swollen by water than the conventional one in the ratio of 138/180. All but four of the new resins have indeed higher efficiencies for the hydrolysis of this ester than a conventionally prepared resin with a divinylbenzene content of only 1%,[3b] yet the latter swells 1000% and none of the new resins swells more than 138%. With respect also to the ratio of the catalytic efficiency for ethyl hexanoate to that for ethyl acetate the new resins behave like very loosely cross linked resins of the conventional type.[3b,3e] For the new resins this ratio averages 0.52 with a high of 0.72 and a low of 0.47. For a conventionally prepared resin of 4.5% divinylbenzene content the ratio is 0.27, and for one with only 0.5% divinylbenzene it is 0.65.[5]

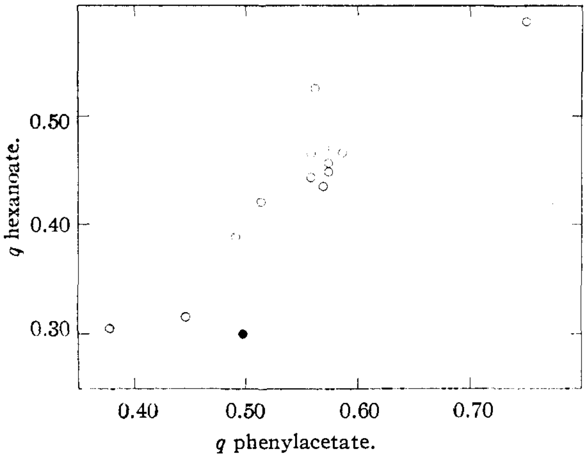

Fig. 1.

The three resins (3a, 4a, and 6a) which have the lowest exchange capacity, *i.e.*, the lowest content of free sulfonic acid groups, have notably high efficiencies for the hydrolysis of all four esters studied. These resins were prepared from the styrenesulfonic esters with the bulkiest alcohol groups, namely, hexyl, octyl and phenylethyl, and the low capacity results from the difficulty of hydrolyzing the ester groups in these resins. In each case the more complete hydrolysis obtained in the corresponding b and c resins led to decreased efficiency for ester hydrolysis as well as to increased capacity. There is however no generally valid correlation between exchange capacity and efficiency for ester hydrolysis. The exchange capacity of all the new resins is materially lower than the 5 meq./g. or so which is normal for resins prepared in the conventional fashion. Much of this difference stems from the fact that the benzene rings derived from the divinylbenzene and its polymerizable impurities bear sulfonic acid groups in the conventional resins but not in the new ones.

All of the effects cited are consistent with the hypothesis that the local environment in the new resins varies from regions in which it corresponds to very loose cross linking to others in which it corresponds to very tight cross linking. Sulfonic ester groups, especially those containing the bulkier alcohol residues, which are situated in the tightly cross linked regions are shielded against hydrolysis, consequently the sulfonic acid groups which are generated by partial hydrolysis occur predominantly in regions of loose cross linking and have therefore high efficiency for ester hydrolysis. At the same time the regions of tight cross linking hold the resin structure together in such a way that the total swelling that can be attained by the imbibition of water is relatively small. The efficiency is higher the smaller the proportion of the total ester groups in the resin which have been hydrolyzed because the ester groups which lie in the more loosely cross linked regions are those which are most rapidly hydrolyzed. When equal proportions of the ester groups have been hydrolyzed, as judged by the

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(5) These efficiencies were determined at 40° (ref. 3e) but the ratio of the efficiencies should be nearly independent of temperature (ref. 3a).

production of equal exchange capacities, efficiencies are higher with the resins prepared from the sulfonic esters with the bulkier alcohol residues (*cf.* 1a with 2a or 1b with 4c). This may be because the bulkier alcohol residues directly assist in the formation of the loosely cross linked regions or it may be because the dependence of the hydrolysis rate of resin ester on local degree of cross linking is sharper with a bulkier alcohol group, so that the groups actually hydrolyzed are more closely limited to the regions of loose cross linking.

The group of resins show among themselves some specificities in their catalytic activity toward different esters, but these are not pronounced and show no obvious pattern. Thus most of the points of a plot (Fig. 1) in which the abscissa of a point is efficiency for the hydrolysis of methyl phenylacetate and the ordinate is efficiency for ethyl hexanoate lie along a single line, which may be taken as the norm, and similar results are obtained when any other pair of esters are compared in the same way. There are however exceptions; thus the point for resin 1b (the solid circle) lies decidedly below the normal line in Fig. 1. By itself this would have little if any significance but the data for this resin also deviate in the direction of a high efficiency for phenylacetate in all the comparisons involving this ester and do not deviate from the norm in comparisons which do not involve phenylacetate. The resin may therefore be said to show a positive specificity for phenylacetate. On the same basis it may be concluded that resin 3a shows a negative specificity for ethyl acetate and butyrate, and that resin 4a shows a negative one for phenylacetate, resin 5 a negative one for butyrate, and resin 1x a positive one for butyrate.

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The Mechanism of Chemisorption: Hydrogen on Nickel at Elevated Pressures

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A volumetric method is described for gas adsorption on solids at adsorbate pressures above one atmosphere. The method is used for simultaneous measurement of hydrogen adsorption and of specific magnetization up to 140 atmospheres on a supported nickel catalyst. Some results are given in terms of magnetization–pressure and magnetization–volume isotherms, all at room temperature. At progressively higher pressures hydrogen adsorption causes a progressive though diminishing decrease of magnetization. The adsorption on particles which exhibit ferromagnetism at room temperature is essentially instantaneous and these data may be represented by a Langmuir adsorption isotherm. Chemisorption of hydrogen on nickel is essentially complete at about 100 atm. pressure.

Introduction

The purpose of this work was to extend our studies on the mechanism of chemisorption through use of the changes of magnetization which occur when hydrogen is chemisorbed on finely divided nickel.[1,2] The present paper is concerned with hydrogen adsorption at elevated pressures, and its correlation with the accompanying decrease of magnetization.

Experimental

Magnetic Measurements.—Magnetization changes as a function of hydrogen adsorption were observed on the low frequency a.c. permeameter previously described.[1] Minor modifications of the magnetization assembly included an enlarged primary solenoid of 5172 turns and a coaxial arrangement of the secondaries, of 44 turns each, as shown in Fig. 1. Convenience and precision were gained by placing a Leeds and Northrup Speedomax recorder (Type G) after the Hewlett-Packard 400-D millivoltmeter in the electrical circuit. A reverse e.m.f. was used to extend the zero of the recorder. The primary was operated at 0.70 amp., stabilized 60 cycle a.c. at *ca.* 230 v. The secondary e.m.f. produced by a typical reduced sample averaged about 1 to 2.5 mv. which was sufficient to obtain reproducible readings of the relative magnetization on the recorder within ±0.02%.

High Pressure Adsorption Measurements.—Of the common methods available, the gravimetric one has been most often used to obtain the limited available data on adsorption at high pressures. Since the present investigation was concerned with simultaneous measurement of hydrogen adsorption and of magnetization, the gravimetric method could not be utilized. On the other hand, a moderately precise volumetric method for obtaining adsorption isotherms at high pressures, such as described by Doerner,[3a] requires a large adsorbent sample.[3b] This condition could not be observed in the present work, because the accuracy of magnetic measurements requires that the sample be situated in a relatively uniform magnetic field which is, of course, near the center of the primary solenoid. Consequently, for a given length of the primary, the choice of the catalyst sample size represents a compromise between the accuracy of magnetic and adsorption measurements. In view of this situation, a new volumetric method was adopted. This may best be described with reference to the diagram of the apparatus, shown in Fig. 2, and in terms of operations to obtain the adsorption isotherms.

The adsorbent chamber, a stainless steel autoclave, is shown in Fig. 1. This autoclave a (Fig. 2) is connected to a gas pipet b of steel tubing, *via* steel tubing j, the valve e_4, and a reducing coupling (not shown in the diagram). The pipet b is connected to a constant pressure gas source *via* valve e_2 and to a glass buret c *via* valve e_3 and kovar-to-glass seal f. The pressure of the gas in c is read from a constant-volume manometer d.

The valves, fittings and tubing of the high pressure equipment were obtained from Autoclave Engineers, Inc., Erie, Pa. Two kinds of valves and fittings were tried and used during the course of this work: (1) Tube Line valves and fittings (Bulletin 255) and (2) autoclave 30,000 p.s.i. valves and fittings (Bulletin 555). While the latter kind proved to be more satisfactory with respect to gas-tight seals, the Tube Line category was used exclusively for valves e_4, e_5 and tubing j because of the availability of $^1/_{16}$ in. i.d. tubing, which was necessary to minimize the free space of the catalyst chamber.

The free spaces of a (with reduced catalyst present), b

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(1) P. W. Selwood, THIS JOURNAL, **78**, 3893 (1956).

(2) E. L. Lee, J. A. Sabatka and P. W. Selwood, *ibid.*, **79**, 5391 (1958).

(3) (a) W. A. Doerner, "Diffusion and Adsorption of Hydrogen in a Porous Nickel Catalyst," Dissertation, University of Michigan, 1952; (b) Doerner used 370 g. of $Ni–SiO_2$ catalyst.