Equilibria between Aliphatic Acids and a Strong Base Anion Exchanger[1]

BY SIGFRED PETERSON AND ROBERT W. JEFFERS

As part of an investigation of ion exchange behavior of carboxylic acids, we measured equilibria between a series of aliphatic acids and the hydroxide of a strong base type anion exchange resin. The resin chosen, Nalcite SAR (Dowex-2), has been described in recent papers.[2,3] Exchange equilibria between the chloride of this resin and several anions have been recently reported.[2]

Experimental

Eastman Kodak white label chloropropionic acids, Tennessee Eastman crotonic acid, C.P. Baker Analyzed formic and acetic acid, Coleman and Bell C.P. butyric acid, and Dow specially purified chloroacetic acid were used. Eimer and Amend C.P. propionic acid and Sapon Laboratories isobutyric acid were distilled, the fractions used boiling, respectively, at 141.0° (750 mm.) and 158.4° (760 mm.).

The resin, obtained as the chloride, was left in 500-g. batches in contact with distilled water for a week, with water changed once or twice daily. The resin was then placed in a large buchner funnel, washed with one liter of distilled water using gentle suction, treated with three one-liter portions of 5% sodium hydroxide and washed again with water. It was then treated with a 5% solution of hydrochloric acid without suction until sufficient acid had been run through to convert the resin to the chloride form, washed and treated as before with sodium hydroxide. This washing with sodium hydroxide was followed by washing with water and continued until the *p*H of the washings was the same as that of the water used. Full suction was then applied for one hour. The resin was then removed from the funnel and dried *in vacuo* over calcium chloride for three days. Resin was used soon after processing to avoid decomposition.

Laboratory distilled water was further demineralized by a mixed-bed ion exchange column.

To weighed samples of resin (usually about 2 g.) in Pyrex glass-stoppered bottles were added 100-ml. portions of acid of known concentration. The bottle was then agitated gently, sealed with paraffin wax and placed in a constant temperature bath at 30.3° for 72 hours, a time found to be quite sufficient for the system to reach equilibrium. The bottles were then removed and the concentration of the acid in the solution measured.

Acid concentrations were measured by titration with standardized sodium hydroxide. For acid concentrations below 0.02 *M* conductometric titrations[4] were used. From the decrease in acid concentration in the solution the concentration of acid in the resin phase is calculated in millimoles per gram of dry resin. This neglects the possibility of water transferred between the solution and the resin, a phenomenon which is known to affect cation exchange equilibria.[5] This source of error is in our work significant only at the higher concentrations, and there not sufficient to alter the qualitative significance of our results.

Results and Discussion

The equilibrium measured is presumably

$$R^+OH^- + HA \rightleftarrows R^+A^- + H_2O$$

where *R* represents one equivalent of resin cation. The anion of the acid neutralized replaces the hydroxide ion in the resin to maintain electrical neutrality of the phases. Equilibrium isotherms determined simultaneously at 30.3° are shown for six acids in Fig. 1 with the acid neutralized per gram of resin plotted against the equilibrium concentration in the solution.

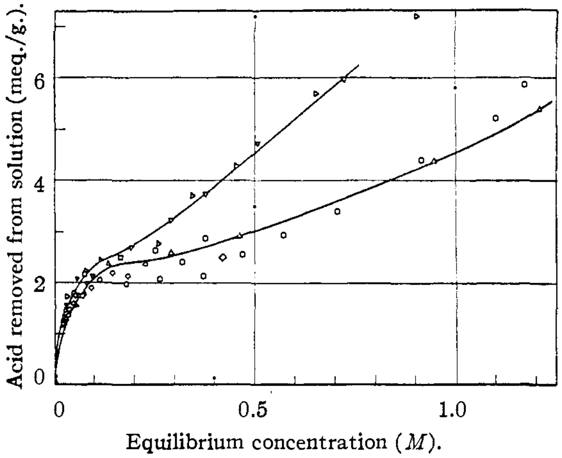

Fig. 1.—Equilibrium isotherms at 30.3° for Nalcite SAR and the acids: ○, acetic; ▷, butyric; □, chloroacetic; ◇, formic; ▽, isobutyric; △, propionic. Curves are drawn in to fit the data for propionic and isobutyric.

It can be seen from the graph that in the dilute range, in which the isotherms should be expected to be most closely related to the acid strengths the differences between the different acids are not much greater than the experimental error. For this reason, no attempt will be made at this time to give an interpretation to these data. The form of the isotherms and their high concentration behavior call for comment, however. The capacity of the resin is 2.69 milliequivalents of quaternary ammonium groups per gram of dry resin and essentially no weakly basic groups.[6] This figure should limit the acid removed from solution by the resin if no processes are occurring other than the neutralization. The isotherms appear to level off at a value somewhat lower than this capacity, probably because either our resin was not completely dry when weighed and possibly not completely in the hydroxide form. But increase of the acid concentration leads to a more or less sharp increase in the acid removed from solution to values considerably beyond the capacity of the resin. We have observed the same behavior with a weak base resin, only less prominently, probably because of the much greater capacity of that resin. That with both resins the phenomenon is greater with butyric and isobutyric acids suggests it is probably true adsorption of acid on the resin. It even appears that this must account for part of the removal of these two acids from dilute solutions by the strong base resin.

A second series of measurements, divided between two temperatures, with seven acids, including three not previously studied, is shown in Fig. 2 for the range of concentrations covered with the added acids. The form and proportions of the curves for the acids common to both series are the same in both series, including data we have beyond the range of concentrations shown in Fig. 2. The

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(1) Presented before the Southwide Chemical Conference, Wilson Dam, Alabama, Oct. 18–20, 1951.

(2) R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **43**, 1088 (1951).

(3) F. K. Lindsay and J. S. D'Amico, *ibid.*, **43**, 1085 (1951).

(4) H. H. Willard, L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis," 2nd Ed., D. Van Nostrand Co., New York, N. Y., 1951, p. 235.

(5) W. K. Lowen, R. W. Stoenner, W. J. Argersinger, Jr., A. W. Davidson and D. N. Hume, THIS JOURNAL, **73**, 2666 (1951).

(6) F. K. Lindsay, private communication.

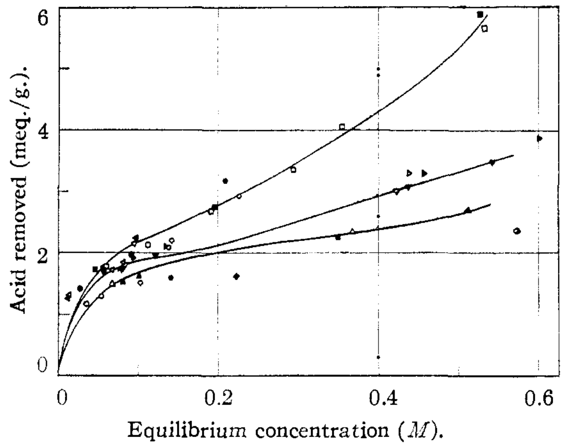

Fig. 2.—Equilibria at two temperatures for Nalcite SAR and the acids: ▷, butyric; □, α-chloropropionic; O, β-chloropropionic; △, crotonic; ◇, formic; ▽, isobutyric; △, propionic at 30.3°; corresponding symbols filled in represent the same acids at 18.0°. Curves are drawn in to fit the data for α-chloropropionic, isobutyric and propionic.

curves for the second series, obtained with resin processed in a different batch, show lower concentrations in the resin for corresponding solution concentrations, no doubt due to a less complete conversion of resin to hydroxide during the processing. That the acid removal beyond resin capacity is greater for crotonic acid and the chloropropionic acids than for butyric and isobutyric shows that acid removal beyond capacity by this resin is favored by unsaturation and substitution of chlorine for methyl groups. That the measurements at 18.0 and 30.3° for any one acid fit the same curve within the reproducibility of the measurements shows a negligible temperature coefficient for the process. The heat of neutralization of a carboxylic acid by a strong base is not small, although different energies of hydration of the ions in the resin phase than in water may make the heat of neutralization by the resin considerably different than that by aqueous hydroxide ion. It appears that the added process which contributes a large part of the equilibrium has little heat effect.

While adsorption is suggested as this added process, a perhaps more plausible process is the distribution of un-ionized acid between the water within the resin granules and the water outside the resin. This picture is consistent with the approximate linearity of the high concentration parts of the isotherms and the small temperature coefficient of the equilibrium. Adsorption, probably of this same nature, has recently been found[5] to be an important factor in some cation exchange equilibria.

It appears that our original purpose, the correlation of the equilibria of formation of resin carboxylates with anion structure, could have been served better by equilibration of the resin chloride with solutions of salts as has been done for a variety of other anions by Wheaton and Bauman.[2] The lack of sensitivity of our method at low concentrations, the instability of the resin hydroxide as indicated by darkening on standing and the removal of acid without complete neutralization by the resin prevent such a correlation. The last of these three is a new phase of the behavior of resins of this type in contact with acid solutions.

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Formation of Ether by Association of Alkyl and Alkoxy Free Radicals

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Coexisting alkoxy and alkyl free radicals undergo various reactions including alkyl–alkyl association, hydrogen atom transfer, and decomposition of the alkoxy radicals.[1-3]

A priori it might be expected that, under proper conditions, these two types of radicals would also associate to form an ether. Previous attempts in this Laboratory to isolate an ether from the decomposition products of di-*t*-alkyl peroxides have been unsuccessful. This note, however, reports the identification of methyl ethyl ether as a product of the pyrolysis of methyl *t*-amyl peroxide, a source of methoxy and ethyl radicals. The ether is believed to arise from an association process rather than from attack of either radical on the peroxide, since the latter reaction is known to result in hydrogen atom transfer.[4] It is clear from the ether yield, however, that under the stated conditions reactions of the radicals other than ether formation predominate. It is not surprising, hence, that experiments with the less thermally stable *t*-alkoxy radicals failed to produce detectable amounts of ethers.

Experimental

Methyl *t*-amyl peroxide was prepared by adding dimethyl sulfate to an aqueous solution of the potassium salt of *t*-amyl hydroperoxide. The distilled product (b.p. 32° (60 mm.), $n^{20}\mathrm{D}$ 1.3924; C, 61.5; H, 12.3; equivalent weight by reaction with HI, 65.8; theoretical values, respectively, 60.98, 11.94 and 59.09) contained no hydroxyl, carbonyl, ethylenic or aromatic groups detectable by an infrared examination.

The peroxide and nitrogen, in a molar ratio of 2:3, were passed through an unpacked Pyrex tube at 195°. Complete decomposition occurred during the two-minute residence time. The effluent was conducted through a water scrubber and traps held at about 0 and −70°. The remaining vapor, together with that evolved from the receivers upon subsequent warming to room temperature, was collected and analyzed by Orsat and mass spectrometric procedures. The combined liquid from the receivers was then distilled and the various fractions analyzed by standard procedures.

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[1] F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **72**, 338 (1950).

[2] G. K. Adams and C. E. H. Bawn, *Trans. Faraday Soc.*, **45**, 494 (1949).

[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, pp. 141-143.

[4] E. R. Bell, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **72**, 337 (1950).