[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA AND THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Dissociation Constants of Acids in Salt Solutions. IV. Cyclohexanecarboxylic Acid

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RECEIVED AUGUST 22, 1952

By measurement of cells with liquid junction the dissociation constant of cyclohexanecarboxylic acid has been determined in solutions of alkali chlorides in hydroxylic solvents and the results extrapolated to infinite dilution to give the thermodynamic dissociation constant.

The equilibrium constant for the isoelectric reaction

$$HC_y + B_0^- \rightleftarrows A_0 + C_y^- \qquad (1)$$

where HC_y represents cyclohexanecarboxylic acid and A_0 benzoic or acetic acid, has been determined in salt solutions as given earlier[2,3] and the results are summarized in columns two and four of Table I. There is very little change in the ratio of the dissociation constants with equivalent salt concentration up to 0.5 molar. This result appears surprising when one considers the difference in structure of the acids. The above observation applies to 25° and would not be expected to hold at other temperatures.[4]

TABLE I

DISSOCIATION CONSTANT OF CYCLOHEXANECARBOXYLIC ACID AT 25°

Electrolyte moles/liter Ref. acid	$K_{A_xB_0}$ Benzoic	$K_a \times 10^5$ Benzoic	$K_{A_xB_0}$ Acetic	$K_c \times 10^5$ Acetic	$K_c \times 10^5$ Hydrochloric	K_c/K_a
			Lithium chloride			
0.05	0.195	1.79[a]	0.693	1.82[b]	1.80	1.46[c]
.10	.195	2.16	.695	2.20	2.12	1.76
.20	.205	2.35	.693	2.27	2.33	1.82
.30	.208	2.47	.693	2.35	2.46	1.88
.40	.200	2.59	.690	2.53	2.61	2.02
.50	.195	2.53	.682	2.48	2.52	1.98
.60	...	..	.682	2.46	..	1.97
.70	...	..	.684	2.46	..	1.97
.80	...	..	.672	2.41	..	1.93
.90	...	..	.665	2.41	..	1.93
1.00	0.191	2.46	.657	2.38	2.42	1.90
1.50	.179	2.26	.652	2.31	2.24	1.85
2.00	.188	2.12	.645	2.05	2.09	1.64
2.50	.179	1.69	.635	1.71	1.69	1.37
3.00	...	..	.615	1.59	..	1.27
			Sodium chloride			
0.05	...	..	0.699	1.78	..	1.42
.10	.198	1.99	.702	1.96	1.96	1.57
.20	.198	2.14	.705	2.10	2.17	1.68
.30	.198	2.25	.699	2.19	2.28	1.75
.40	.198	2.36	.702	2.27	2.32	1.82
.50	.198	2.36	.702	2.30	2.35	1.84
.60			.702	2.27		1.82
.70			.699	2.24		1.79
.80			.696	2.17		1.74
.90			.696	2.13		1.70
1.00			.696	2.08		1.66
1.50			.702	1.92		1.54
2.00			.710	1.64		1.31
2.50			.722	1.34		1.07
3.00			.724	1.14		0.91
			Potassium chloride			
0.05			0.695	1.80		1.44
.10			.695	1.96		1.57
.20			.703	2.03		1.62
.30			.698	2.09		1.67
.40			.698	2.13		1.70
.50			.698	2.13		1.70
.60			.703	2.14		1.71
.70			.703	2.06		1.65
.80			.697	2.01		1.61
.90			.709	2.02		1.62
1.00			.717	1.97		1.58
1.50			.723	1.77		1.42
2.00			.728	1.53		1.22
2.50			.736	1.27		1.02
3.00			.742	1.06		0.85

[a] Based on K_c values from paper I.[2] [b] Based on K_c values from paper II.[3] [c] K_c from column 5, $K_a = 1.25 \times 10^{-5}$.

From a knowledge of the dissociation constants of benzoic acid and acetic acid in the same salt solutions the values of the dissociation constant of cyclohexanecarboxylic acid are calculated and presented in columns three and five of Table I. These results are in good agreement with the direct measurements against hydrochloric acid shown in column six. The small dependence of the equilibrium constant of equation (1) on ionic strength makes possible a more accurate extrapolation to infinite dilution in accordance with the equation

$$K_{A_xB_0} = [K_{A_xB_0}]^0 + BC \qquad (2)$$

The intercept $[K_{A_xB_0}]^0$ and the slopes B are given in Table II.

TABLE II

Reference acid	Range electrolyte	0.05–0.5 *M* Intercept	0.05–0.5 *M* Slope	0.05–3.0 *M* Intercept	0.05–3.0 *M* Slope
Benzoic	LiCl	0.199	0.00471	0.201	0.0091
	NaCl	.198	.000	...	......
Acetic	LiCl	.700	−.0339	0.702	−0.0329
	NaCl	.695	.00247	.696	.0084
	KCl	.696	.00564	.690	.0206

The ratios multiplied by the dissociation constant of benzoic acid 6.32×10^{-5} and acetic acid 1.754×10^{-5} yield values for the dissociation constant of

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(1) This paper was abstracted from the dissertation presented by Jerome Gilbert Morse to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1952.

(2) M. Kilpatrick, THIS JOURNAL, **75**, 584 (1953).

(3) M. Kilpatrick and R. D. Eanes, *ibid.*, **75**, 586 (1953).

(4) D. H. Everett and B. R. W. Pinsett, *J. Chem. Soc.*, 1029 (1948).

HC_y of 1.26 and 1.22 × 10^{-5} which are to be compared with literature values from conductance data of 1.26,[5] 1.34[6] and 1.32 × 10^{-5}.[7]

Similar measurements in the solvents methyl and ethyl alcohol and ethylene glycol, for the solvent salt lithium chloride are summarized in Table III. In these cases there are no literature values for comparison and the thermodynamic dissociation constant is based on the values for benzoic acid.

TABLE III

THE DISSOCIATION CONSTANT OF CYCLOHEXANECARBOXYLIC ACID IN ALCOHOLS

T, 25°; solvent salt, LiCl

Electrolyte mole/liter	CH_3OH $K_{A_xB_0}$[a]	CH_3OH 10^{10} K_c	CH_3OH K_c/K_a	C_2H_5OH $K_{A_xB_0}$[a]	C_2H_5OH 10^{10} K_c	C_2H_5OH K_c/K_a	$(CH_2OH)_2$ $K_{A_xB_0}$	$(CH_2OH)_2$ 10^{10} K_c
0		0.923			0.170			
0.10	0.220	8.32	9.0	0.195	7.61	44.8	0.213	94.0

[a] Reference acid, benzoic acid.

Justification for the assumption that the ratio of the dissociation constants is independent of the lithium chloride concentration is given in Table IV.

TABLE IV

$K_{A_xB_0}$ for HC_y/HB in the solvent ethanol

μ[a]	0.103	0.196	0.279	0.382	0.475
$K_{A_xB_0}$	.193	.195	.193	.195	.195

[a] Mainly LiCl.

Further evidence for the independence of the ratio of dissociation constants on electrolyte concentration in alcohols will be presented in another paper.

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[5] J. S. Lumsden, *J. Chem. Soc.*, **87**, 90 (1905).

[6] N. Zelinsky and N. Izgaruisher, *J. Russ. Phys. Chem. Soc.*, **40**, 1379 (1908).

[7] C. H. Spiers and J. F. Thorpe, *J. Chem. Soc.*, **127**, 538 (1925).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH]

Properties of Ion-Exchange Resins in Relation to their Structure. III. Kinetics of Exchange

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RECEIVED MAY 28, 1952

A study has been made of the kinetics of sodium-hydrogen exchange on sulfonated cross-linked polystyrenes in bead form. Resins of 5 and 17% (nominal) divinylbenzene content were fractionated by wet elutriation and matched according to swollen particle diameter. The rates of exchange were measured by an "indicator" method. For both resins, the kinetics at high sodium ion concentrations in solution (>1 N) are clearly distinct from those at low concentrations (<0.05 N). At high concentrations, the rate is independent of the sodium ion concentration and inversely proportional to the square of the particle radius. At low concentrations, the rate is proportional to the sodium ion concentration and inversely proportional to the particle radius. These results support the view that at low concentrations, the rate is controlled by "film" diffusion, and at high concentrations by "particle" diffusion. Equations of the type derived by Boyd, Adamson and Myers on the basis of these mechanisms are obeyed. In further confirmation, when close fractions of the same mean particle diameter were compared it was found that the two resins exchange initially at the same rate *per particle* at low concentrations (film diffusion) but at markedly different rates at high concentrations (particle diffusion).

Although there had been previous experimental studies of the rates of ion-exchange reactions[1] the first serious attempt to elucidate the rate-controlling mechanism was made by Nachod and Wood.[2] They studied the rates of exchange of the pairs of ions hydrogen–calcium, calcium–hydrogen and sodium–calcium with a number of commercial cation-exchange resins in dilute (0.001 to 0.01 N) solutions. They concluded that the "rate of bringing dissolved ions up to and away from the surface of the exchange granules" (or what is now known as "film-diffusion") "is rate determining in the case of sulfonated coal between 27 and 60°." However, since other resins under identical agitation conditions showed widely different rates, other factors were considered to play some role. Anion-exchange (chloride–hydroxide) on weak base resins was found to be 1/400 to 1/4000 as fast, "suggesting a different reaction mechanism for this class of exchanger." In a later paper[3] they showed that in cation exchange in dilute solution the nature of the anion had no effect on the rate.

Kunin and Myers[4] studied the kinetics of anion-exchange on four weak-base resins using a number of anion-pairs and concluded that "diffusion" (or what is now called "particle diffusion") was the rate-controlling process in all cases.

A great clarification of the field was made by Boyd, Adamson and Myers.[5] Although a chemical process, film diffusion and particle diffusion had previously all been separately postulated as possible rate-determining mechanisms, they gave for the first time a clear analysis of the kinetics corresponding to each hypothesis. The equations that they derived were found to assume a particularly simple and readily verifiable form if the composition of the exchanger remained virtually unaltered by the exchange, *i.e.*, if the "in-going" ion was present in solution in minute concentration compared with that of the displaced ion. This necessitated radiotracer technique, an important point since in other studies (the present one included) in which radiotracer technique has not been used, it has been necessary to violate the above condition. In most other work, the resin is changed largely or entirely from one cationic form to the other. In these circumstances, while the equation derived by Boyd, Adamson and Myers for a particle diffusion

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[1] See reference (2).

[2] F. C. Nachod and W. Wood, THIS JOURNAL, **66**, 1380 (1944).

[3] F. C. Nachod and W. Wood, *ibid.*, **67**, 629 (1945).

[4] R. Kunin and R. J. Myers, *J. Phys. Colloid Chem.*, **51**, 1111 (1947).

[5] G. E. Boyd, A. W. Adamson and L. S. Myers, THIS JOURNAL, **69**, 2836 (1947).