

48. The Effect of Pressure on the Ionization of Some Benzoic Acids.

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By means of conductivity measurements the dissociation constants in water of benzoic, *o*-, *m*-, and *p*-nitrobenzoic, salicylic, and 3,5-dimethyl-4-nitrobenzoic acid have been determined at 25° and at pressures up to 3000 atm. Benzoic, *p*-methylbenzoic, and salicylic acid have been studied in 50% ethyl alcohol-water (w/w) under the same conditions.

The increases in ionization of the weak acids can be broadly correlated with the changes in dielectric constant of the solvents with pressure, and the variation in conduction of strong electrolytes is related primarily to the viscosity changes of the solvents.

Pressure has an unusually small effect on the ionization of salicylic acid, probably owing to the internal hydrogen bonding in the salicylate anion.

INFORMATION is available on the variation with pressure of the dissociation constants of many weak acids and bases, both in water and in alcohol solutions.^{1,2} The ionization of a series of benzoic acids under high pressures has, however, not been studied.

It was hoped to study a series of *para*-substituted benzoic acids to show how a graded series of substituents affected the changes in dissociation constants with pressure, but many of the acids, in particular the chloro-, bromo-, and iodo-derivatives, were too insoluble in water to give reliable results with the present conductivity apparatus. Although the solubilities are increased in ethanol-water, the consequent decrease in dissociation constants still rendered their measurement doubtful. Results were obtained at 25° for six substituted benzoic acids in water, and for three in 50% ethanol-water (w/w), at pressures up to 3000 atm.

The conductivities of hydrochloric acid, sodium chloride, or potassium chloride, and the sodium or potassium benzoates, were determined in the course of obtaining the acid dissociation constants. The information on ionic conduction and acid dissociation from the studies in mixed solvent is a useful supplement to that already available on the variation of pressure effects between pure solvents.

EXPERIMENTAL

Materials and Apparatus.—Sodium and potassium chlorides and hydrochloric acid were of "AnalaR" quality and not purified further. The benzoic acids were all recrystallized from alcohol-water and carefully dried, and their m. p.s were checked with standard values. 3,5-Dimethyl-4-nitrobenzoic acid had m. p. 218°. Standard solutions of the acids were made up by weight.

Solutions of the sodium or potassium benzoates were prepared in either solvent by titrating solutions of the acids to pH 8.5 with hydroxide, and diluting to the required concentrations. Dippy *et al.*³ found it impossible to isolate the nitrobenzoates.

Since 3,5-dimethyl-4-nitrobenzoates was almost insoluble in water, a 10% ethanol solution was used to obtain sufficient concentration for conductance measurements.

The pressure apparatus and conductance cell were similar to those used to study the ionization of carbonic acid.⁴ For the series of solutions in water the Teflon cell had a cell constant of 0.365 cm.⁻¹, and for the ethanol-water series the cell constant was 0.338 cm.⁻¹.

Method.—The methods of Davies⁵ and MacInnes⁶ were used to determine the acid dissociation constants. The required conductances of the various solutions of acids and salts at suitable concentrations were determined at pressures up to 3000 atm. The solvent conductance blanks were obtained and subtracted as previously.⁴

The results from the conductance experiments were obtained as the products $\Lambda^P \rho_r$, where Λ^P is the molar conductance of a solution at the pressure P , and $\rho_r = \rho^P / \rho^1$ is the ratio of densities of the solution (*ca.* that for solvent) at high pressure and at 1 atm.

The molal acid dissociation constants were obtained at any pressure and concentration from the following relationships:

$$K_a = a_{H^+}a_{A^-}/a_{HA} = \alpha^2 m \gamma_{\pm}^2 / (1 - \alpha) \gamma_{HA}$$

$$\text{Also } \alpha = \Delta \rho_r / \Lambda' \rho_r$$

In these expressions a is the activity of a species, α is the degree of dissociation of the weak acid HA into the ions H^+ and A^- , m the molality of the weak acid, $\gamma_{\pm}$ the mean molal activity coefficient for the ions, and Λ' the sum of the molar conductances of the ions H^+ and A^- at the same pressure and ionic strength as those of the weak acid solution. γ_{HA} was taken as unity at all pressures for the low concentrations used. The value of $\gamma_{\pm}$ was obtained as previously⁴ by the Debye-Hückel equation, consideration being taken of the change with pressure in the molar concentrations and dielectric constants.

RESULTS

The conductances in water at high pressures and 25° reported previously⁴ for hydrochloric acid and potassium chloride were used in conjunction with those given below in Series A for various weak acids and their potassium salts. The derived values of K_a in water are shown in Tables 2—7. For the ethanol-water solutions a complete set of conductance data is given under Series B for hydrochloric acid, sodium chloride, sodium benzoates, and benzoic acids. The acid dissociation constants are in Tables 9—11.

DISCUSSION

Electrolyte Conductance.—Table 12 compares the changes in conductance with pressure for halogen acids and alkali halides in the solvents water, methanol, and ethanol-water. The viscosity ratios η^1/η^P are also given for water and the two pure alcohols. For sodium

Series A at 25°: Water as solvent.

TABLE 1. Values of $\Delta^P \rho_r / \Lambda^1$ for the potassium benzoates (values of Λ^1 in parentheses).

P (atm.)	1	500	1000	2000	3000
Benzoic acid	(103.4)	1.026	1.042	1.045	1.028
<i>o</i> -Nitrobenzoic acid	(104.1)	1.025	1.048	1.053	1.042
<i>m</i> -Nitrobenzoic acid	(105.2)	1.027	1.043	1.046	1.035
<i>p</i> -Nitrobenzoic acid	(105.2)	1.026	1.044	1.046	1.034
3,5-Dimethyl-4-nitrobenzoic acid	(104.7)	1.025	1.043	1.044	1.035
Salicylic acid	(104.4)	1.023	1.039	1.044	1.033
Water (specific conductance)	1.5×10^{-6}	1.2	1.4	1.8	2.0

Results are for 0.001M-solutions but the same ratio results within experimental error were obtained for 0.01M-solutions.

TABLE 2. Benzoic acid.

Concn. (10 ⁻³ m)	<i>P</i> (atm.)	$\Delta\rho_r$	$\Delta'\rho_r$	$\gamma_{\pm}$	$\log K_a^P/K_a^1$ (K_a at $P=1$)
20.0	1	20.73	379	0.965	(5.9 × 10 ⁻⁵)
„	1030	28.31	413	0.963	0.199
„	2030	35.96	437	0.962	0.365
„	2780	41.89	450	0.961	0.477
2.00	1	61.86	379	0.980	(6.1 × 10 ⁻⁵)
„	1020	83.03	415	0.979	0.196
„	2100	104.9	440	0.978	0.365
„	2780	118.4	452	0.977	0.462
0.500	1	115.0	379	0.985	(6.4 × 10 ⁻⁵)
„	1030	151.1	415	0.985	0.199
„	2010	186.5	439	0.985	0.377
„	2780	210.7	452	0.984	0.487
0.200	1	162.9	379	0.989	(6.4 × 10 ⁻⁵)
„	1390	226.5	425	0.989	0.272
„	2910	282.6	454	0.988	0.498

$\Delta V^1 = -10.6$ c.c. mole⁻¹; $\Delta V^{3000} = -7.4$ c.c. mole⁻¹; Average $\Delta K = -0.0011$ atm.⁻¹ c.c. mole⁻¹.

TABLE 3. *o*-Nitrobenzoic acid.

Concn. (10 ⁻³ m)	<i>P</i> (atm.)	$\Delta\rho_r$	$\Lambda'\rho_r$	$\gamma_{\pm}$	$\log K_a^P/K_a^1$ (K_a at $P=1$)
11.0	1	202.0	373	0.931	(6.1 × 10 ⁻³)
„	1020	251.9	408	0.930	0.190
„	2010	290.8	432	0.930	0.335
„	2780	317.0	445	0.931	0.438
5.05	1	244.5	375	0.946	(6.0 × 10 ⁻³)
„	1010	297.1	410	0.947	0.193
„	2030	336.2	435	0.947	0.337
„	2800	361.1	448	0.947	0.438
3.00	1	283.3	377	0.956	(6.2 × 10 ⁻³)
„	1010	334.3	413	0.957	0.182
„	2010	372.3	437	0.958	0.335
„	2780	393.2	451	0.959	0.422
1.26	1	326.0	379	0.968	(6.2 × 10 ⁻³)
„	1010	372.9	415	0.969	0.188
„	2010	405.2	440	0.970	0.320
„	2790	424.8	453	0.971	0.433
„	2930	428.4	455	0.971	0.467

$\Delta V^1 = -10.2$ c.c. mole⁻¹; $\Delta V^{3000} = -6.9$ c.c. mole⁻¹; Average $\Delta K = -0.0011$ atm.⁻¹ c.c. mole⁻¹.