**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 in-
soluble 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 Davies[5] and MacInnes[6] 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 con-
ductance blanks were obtained and subtracted as previously.[4]

The results from the conductance experiments were obtained as the products $\Lambda^P \rho_r$, where
$\Lambda^P$ 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:

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

Also $\alpha = \Lambda \rho_r/\Lambda' \rho_r$

In these expressions $a$ is the activity of a species, $\alpha$ 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 $\Lambda'$ 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. $\gamma_{HA}$ was taken as unity at all pressures for the low concentrations used. The value of $\gamma_{\pm}$ was obtained as previously [4] 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 previously [4] 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 $\eta^1/\eta^P$ are also given for water and the two pure alcohols. For sodium

### Series A at 25°: Water as solvent.

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

| $P$ (atm.) | 1 | 500 | 1000 | 2000 | 3000 |
|---|---|---|---|---|---|
| Benzoic acid | (103·4) | 1·026 | 1·042 | 1·045 | 1·028 |
| o-Nitrobenzoic acid | (104·1) | 1·025 | 1·048 | 1·053 | 1·042 |
| m-Nitrobenzoic acid | (105·2) | 1·027 | 1·043 | 1·046 | 1·035 |
| p-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) | $1·5 \times 10^{-6}$ | 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. (10⁻³m) | $P$ (atm.) | $\Delta\rho_r$ | $\Lambda'\rho_r$ | $\gamma_{\pm}$ | log $K_a{}^P/K_a{}^1$ ($K_a$ at $P = 1$) |
|---|---|---|---|---|---|
| 20·0 | 1 | 20·73 | 379 | 0·965 | $(5·9 \times 10^{-5})$ |
| ,, | 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 | $(6·1 \times 10^{-5})$ |
| ,, | 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 | $(6·4 \times 10^{-5})$ |
| ,, | 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 | $(6·4 \times 10^{-5})$ |
| ,, | 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. (10⁻³m) | $P$ (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 | $(6·1 \times 10^{-3})$ |
| ,, | 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 | $(6·0 \times 10^{-3})$ |
| ,, | 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 | $(6·2 \times 10^{-3})$ |
| ,, | 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 | $(6·2 \times 10^{-3})$ |
| ,, | 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.