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

By R. J. H. Clark and A. J. Ellis.

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

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[1] Cohen and Schut, " Piezochemie Kondensierter Systeme," Akademische Verlagsgesellschaft m.b.H., Leipzig, 1919.

[2] Hamann, " Physico-chemical Effects of Pressure," Butterworths, London, 1957.

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 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:

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

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

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 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 η^1/η^P are also given for water and the two pure alcohols. For sodium

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[3] Dippy, Evans, Gordon, Lewis, and Watson, *J.*, 1937, 1421.

[4] Ellis, *J.*, 1959, 3689.

[5] Davies, *J. Phys. Chem.*, 1925, **29**, 977.

[6] MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068.

Series A at 25°: Water as solvent.

TABLE 1. *Values of $\Lambda^{P}{}_{p_r}/\Lambda^1$ 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
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. $(10^{-3}$m$)$	P (atm.)	Λ_{p_r}	Λ'_{p_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. $(10^{-3}$m$)$	P (atm.)	Λ_{p_r}	Λ'_{p_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}.

TABLE 4. m-*Nitrobenzoic acid.*

Conc. $(10^{-3}$m$)$	P (atm.)	Λ_{p_r}	Λ'_{p_r}	$\gamma_\pm$	log $K_a{}^P/K_a{}^1$ (K_a at $P = 1$)
9·85	1	63·5	378	0·958	$(3·1 \times 10^{-4})$
,,	1010	81·1	413	0·958	0·155
,,	2010	99·1	437	0·957	0·292
,,	2780	112·0	450	0·956	0·384
1·97	1	126·5	380	0·972	$(3·1 \times 10^{-4})$
,,	1010	159·1	416	0·971	0·155
,,	1390	169·1	426	0·971	0·196
,,	2010	188·7	440	0·971	0·290
,,	2780	208·8	453	0·971	0·375
0·985	1	165·0	381	0·977	$(3·1 \times 10^{-4})$
,,	1010	204·6	417	0·976	0·155
,,	2010	238·6	441	0·976	0·286
,,	2780	263·5	454	0·976	0·384
0·492	1	207·8	382	0·981	$(3·1 \times 10^{-4})$
,,	1010	252·7	417	0·981	0·155
,,	2010	290·3	441	0·981	0·288
,,	2930	321·7	457	0·981	0·412

$\Delta V^1 = -8·7$ c.c. mole^{-1}; $\Delta V^{3000} = -6·2$ c.c. mole^{-1}; Average $\Delta K = -0·0008$ atm.$^{-1}$ c.c. mole^{-1}.

TABLE 5. p-*Nitrobenzoic acid.*

Concn. $(10^{-3}$m$)$	P (atm.)	Λ_{p_r}	Λ'_{p_r}	$\gamma_\pm$	log $K_a{}^P/K_a{}^1$ (K_a at $P = 1$)
1·00	1	168·2	381	0·976	$(3·3 \times 10^{-4})$
,,	1010	208·5	417	0·976	0·158
,,	2030	243·4	441	0·976	0·290
,,	2780	266·6	454	0·976	0·378
0·900	1	174·2	381	0·972	$(3·3 \times 10^{-4})$
,,	1010	218·2	417	0·972	0·173
,,	2010	249·4	441	0·972	0·281
,,	2780	274·0	454	0·972	0·377
0·500	1	217·3	382	0·981	$(3·6 \times 10^{-4})$
,,	1010	264·9	417	0·981	0·167
,,	2020	303·8	441	0·981	0·305
,,	2780	328·6	455	0·981	0·398
0·200	1	264·6	382	0·986	$(3·0 \times 10^{-4})$
,,	1010	314·6	418	0·987	0·170
,,	1700	340·6	436	0·987	0·255
,,	2440	365·9	450	0·987	0·360

$\Delta V^1 = -9·1$ c.c. mole^{-1}; $\Delta V^{3000} = -5·9$ c.c. mole^{-1}; Average $\Delta K = -0·0011$ atm.$^{-1}$ c.c. mole^{-1}.

TABLE 6. 3,5-*Dimethyl-4-nitrobenzoic acid.*

Concn. (10^{-3}m)	P (atm.)	$\Lambda\rho_r$	$\Lambda'\rho_r$	$\gamma_\pm$	log $K_a{}^P/K_a{}^1$ (K_a at $P = 1$)
0·769	1	101·6	381	0·983	($7{\cdot}2 \times 10^{-5}$)
,,	1050	131·1	417	0·983	0·173
,,	2020	155·8	441	0·983	0·299
,,	3000	180·2	457	0·982	0·422
0·769	1	106·0	381	0·983	($8{\cdot}0 \times 10^{-5}$)
,,	1010	136·0	416	0·983	0·170
,,	2030	163·2	441	0·982	0·308
,,	3000	188·7	457	0·982	0·431
1·00	1	89·7	381	0·982	($7{\cdot}0 \times 10^{-5}$)
,,	1010	116·4	416	0·982	0·176
,,	2010	139·1	441	0·981	0·303
,,	3000	160·5	457	0·981	0·418
1·15	1	86·8	381	0·982	($7{\cdot}5 \times 10^{-5}$)
,,	1010	112·6	416	0·982	0·173
,,	2010	133·8	441	0·981	0·295
,,	3000	153·5	457	0·981	0·401

$\Delta V^1 = -9{\cdot}5$ c.c. mole^{-1}; $\Delta V^{3000} = -6{\cdot}3$ c.c. mole^{-1}; Average $\Delta K = -0{\cdot}0011$ atm.$^{-1}$ c.c. mole^{-1}.

The solutions in this series of experiments contained 10% (by volume) of ethanol.

TABLE 7. *Salicylic acid.*

Concn. (10^{-3}m)	P (atm.)	$\Lambda\rho_r$	$\Lambda'\rho_r$	$\gamma_\pm$	log $K_a{}^P/K_a{}^1$ (K_a at $P = 1$)
10·81	1	103·8	376	0·948	($1{\cdot}02 \times 10^{-3}$)
,,	1010	127·8	410	0·949	0·127
,,	2010	150·2	434	0·948	0·241
,,	2780	167·5	447	0·948	0·328
5·41	1	137·1	377	0·956	($1{\cdot}03 \times 10^{-3}$)
,,	1010	167·5	412	0·956	0·127
,,	2010	195·1	436	0·957	0·243
,,	2850	217·6	451	0·957	0·337
2·16	1	189·0	379	0·966	($1{\cdot}00 \times 10^{-3}$)
,,	1010	226·6	414	0·966	0·127
,,	2030	260·6	438	0·966	0·246
,,	2850	276·0	447	0·966	0·303
1·08	1	233·5	380	0·972	($1{\cdot}00 \times 10^{-3}$)
,,	1010	275·8	415	0·973	0·130
,,	2030	310·6	439	0·973	0·241
,,	2780	335·8	453	0·974	0·339
0·541	1	275·2	381	0·978	($0{\cdot}98 \times 10^{-3}$)
,,	1010	319·5	416	0·979	0·130
,,	2010	354·5	440	0·979	0·248
,,	2780	377·0	453	0·980	0·339

$\Delta V^1 = -7{\cdot}2$ c.c. mole^{-1}; $\Delta V^{3000} = -5{\cdot}8$ c.c. mole^{-1}; Average $\Delta K = -0{\cdot}0005$ atm.$^{-1}$ c.c. mole^{-1}.

Series B at 25°; Ethanol–water as solvent.

TABLE 8. *Values of* $\Lambda^P\rho_r/\Lambda^1$ (*values of* Λ^1 *in parentheses*).

P (atm.) Solution and concn. (m)		1	1020	1700	2380	3060
0·0110	HCl	(108·1)	0·988	0·976	0·966	0·954
0·00110	HCl	(107·1)	0·980	0·967	0·951	0·937
0·0110	NaCl	(38·5)	0·874	0·804	0·738	0·702
0·00110	NaCl	(43·7)	0·862	0·787	0·719	0·663
0·00022	NaCl	(50·1)	0·862	0·784	0·710	0·659
0·110	NaOBz	(16·5)	0·859	0·778	0·708	0·649
0·0220	NaOBz	(19·4)	0·844	0·761	0·688	0·628
0·00220	NaOBz	(22·0)	0·834	0·741	0·663	0·606
0·00044	NaOBz	(23·9)	0·813	0·706	0·609	0·537
0·01456	$NaO_2C{\cdot}C_6H_4Me$-*p*	(27·6)	0·850	0·763	0·695	0·635
0·00146	,, ...	(31·5)	0·832	0·741	0·663	0·596
0·00029	,, ...	(34·3)	0·820	0·712	0·618	0·539
0·02793	$NaO_2C{\cdot}C_6H_4{\cdot}OH$-*o* ...	(23·3)	0·843	0·758	0·689	0·627
0·00279	,, ...	(25·1)	0·836	0·750	0·680	0·615
Solvent blank (specific conductance)	....	($4{\cdot}2 \times 10^{-6}$)	1·013	1·040	1·078	1·123

TABLE 9. *Benzoic acid.*

Concn. (10^{-2}m)	P (atm.)	$\Lambda\rho_r$	$\Lambda'\rho_r$	$\gamma_\pm$	log $K_a{}^P/K_a{}^1$ (K_a at $P = 1$)
11·1	1	0·503	86·2	0·940	($3{\cdot}3 \times 10^{-6}$)
,,	1020	0·696	86·0	0·928	0·272
,,	1700	0·840	85·8	0·922	0·433
,,	2380	1·004	85·2	0·913	0·588
,,	3060	1·200	84·8	0·904	0·738
2·20	1	0·991	86·7	0·959	($2{\cdot}7 \times 10^{-6}$)
,,	1020	1·380	85·8	0·953	0·294
,,	1700	1·638	85·1	0·948	0·447
,,	2380	1·947	84·2	0·943	0·601
,,	3060	2·293	83·7	0·938	0·748
0·220	1	2·73	86·7	0·978	($2{\cdot}2 \times 10^{-6}$)
,,	1020	3·65	85·6	0·974	0·265
,,	1700	4·33	84·7	0·972	0·425
,,	2380	5·09	83·6	0·969	0·580
,,	3060	5·86	83·0	0·966	0·710

$\Delta V^1 = -16{\cdot}1$ c.c. mole^{-1}; $\Delta V^{3000} = -12{\cdot}3$ c.c. mole^{-1}; Average $\Delta K = -0{\cdot}0013$ atm.$^{-1}$ c.c. mole^{-1}.

TABLE 10. p-*Methylbenzoic acid.*

Concn. (10^{-3}m)	P (atm.)	$\Lambda\rho_r$	$\Lambda'\rho_r$	$\gamma_\pm$	log $K_a{}^P/K_a{}^1$ (K_a at $P = 1$)
64·6	1	0·614	96·1	0·951	($2{\cdot}4 \times 10^{-6}$)
,,	1020	0·813	94·0	0·943	0·258
,,	1700	0·966	92·5	0·937	0·419
,,	2380	1·129	91·1	0·930	0·560
,,	3060	1·271	89·7	0·925	0·675
14·6	1	1·255	96·7	0·966	($2{\cdot}3 \times 10^{-6}$)
,,	1020	1·692	94·1	0·959	0·279
,,	1700	2·016	92·1	0·954	0·455
,,	2380	2·371	90·5	0·950	0·608
,,	3060	2·737	88·9	0·945	0·745
4·00	1	2·36	97·3	0·976	($2{\cdot}3 \times 10^{-6}$)
,,	1020	3·13	94·3	0·969	0·269
,,	1700	3·71	92·1	0·966	0·438
,,	2380	4·31	90·3	0·963	0·588
,,	3060	4·93	88·4	0·960	0·722

$\Delta V^1 = -16{\cdot}1$ c.c. mole^{-1}; $\Delta V^{3000} = -12{\cdot}3$ c.c. mole^{-1}; Average $\Delta K = -0{\cdot}0013$ atm.$^{-1}$ c.c. mole^{-1}.

TABLE 11. *Salicylic acid.*

Concn. (10^{-2}m)	P (atm.)	Λp_r	$\Lambda' p_r$	$\gamma_{\pm}$	$\log K_a{}^P/K_a{}^1$ (K_a at $P = 1$)
16·8	1	3·06	92·1	0·836	($1·4 \times 10^{-4}$)
,,	1020	3·99	92·4	0·819	0·207
,,	1700	4·59	92·5	0·810	0·328
,,	2380	5·19	92·5	0·800	0·426
,,	3060	5·79	91·5	0·795	0·526
2·79	1	7·66	90·0	0·889	($1·8 \times 10^{-4}$)
,,	1020	9·91	90·0	0·878	0·223
,,	1700	11·4	89·9	0·872	0·350
,,	2380	12·8	89·7	0·866	0·456
,,	3060	14·2	89·2	0·862	0·553

Concn. (10^{-2}m)	P (atm.)	Λp_r	$\Lambda' p_r$	γ	$\log K_a{}^P/K_a{}^1$ (K_a at $P = 1$)
0·369	1	18·9	88·5	0·937	($1·9 \times 10^{-4}$)
,,	1020	23·8	88·5	0·930	0·230
,,	1700	27·0	88·2	0·927	0·361
,,	2380	30·3	87·7	0·924	0·485
,,	3060	33·0	87·1	0·921	0·590

$\Delta V^1 = -12·7$ c.c. mole^{-1}; $\Delta V^{3000} = -9·4$ c.c. mole^{-1}; Average $\Delta K = -0·0011$ atm.$^{-1}$ c.c. mole^{-1}.

TABLE 12. *Comparison of pressure effects in water and alcohol solvents.*

P (atm.)	500	1000	2000	3000
Ratios $\Lambda^P p_r/\Lambda^1$ at 25°.				
0·001m-HCl in water [4]	1·050	1·087	1·151	1·191
0·0011m-HCl in ethanol–water	0·990	0·980	0·959	0·938
0·0028m-HBr in methanol [7]	—	0·909	0·844	0·791
0·01m-KCl in water [4]	1·031	1·052	1·068	1·058
0·011m-NaCl in ethanol–water	0·938	0·876	0·775	0·700
0·0092m-NaCl in methanol [7]	—	0·846	0·747	0·665
Viscosity ratios η^1/η^P at 30°.				
Water [9]	0·975	0·947	0·882	0·808
Methanol [9]	—	0·675	0·510	0·402
Ethanol [9]	—	0·625	0·440	0·316

and potassium benzoates in water and alcohol solutions the conductance results have a similar pattern to those of the alkali halides.

The term $\Lambda^P \rho_r/\Lambda^1$ for strong electrolyte salts in water is at first increased slightly, and then decreased with increasing pressure. This arises from the two competing factors—compression, which increases the number of ions per unit volume, and the decrease in mobility of the ions as the viscosity is increased.

However, in ethanol–water there is a steady and much larger decrease in the conductance of strong electrolyte salts over the whole pressure range. The decrease is not as great as that found for pure methanol solutions by Strauss [7] and Hamann and Strauss.[8] The marked difference in behaviour between aqueous and alcoholic solutions in this regard is ascribed to the greater relative increase in the viscosity of methanol or ethanol at high pressures.[8,9]

A further difference between the solvents water and ethanol–water is that with the latter the effect of pressure on conductance shows a significant dependence on the electrolyte concentration. The changes in the pressure effects for aqueous solutions of uni-univalent electrolytes with concentrations below about 0·1m were very slight.[4] The concentration-dependence can be predicted approximately at any pressure by the Kohlrausch expression, $\Lambda = \Lambda_0 - Bc^{\frac{1}{2}}$. Hamann [2] showed that for sodium bromide in methanol the value of B calculated from the Debye–Hückel–Onsager equation was more than halved at a pressure of 3000 atm., whereas for alkali halides in water the decrease was calculated to be only about 30%. The larger decrease in B predicted for alcohol and alcohol–water solvents is a consequence mainly of their large increase in viscosity with pressure. It was later suggested [4] that the concentration dependence of the pressure effects for conductance in aqueous solution as predicted by the Debye–Hückel–Onsager equation may be opposed by the lower structural temperature of water at increased pressures. This would explain

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[7] Strauss, *Austral. J. Chem.*, 1957, **10**, 277.

[8] Hamann and Strauss, *Discuss. Faraday Soc.*, 1956, **22**, 70.

[9] Bridgman, " The Physics of High Pressures," G. Bell & Sons, London, 1949.

the fact that the concentration effects observed for water were even less than those calculated.

Hamann[2] has also shown that the excess of conductance of the H_3O^+ and OH^- ions in water, *i.e.*, the amount by which the conductance of these ions exceeds that of similarly-sized ions which move by normal diffusion in an electric field, is increased with pressure but at a decreasing rate. He adopted Bell's[10] model for proton transfer and suggested that pressure assists proton exchange by providing some of the repulsion energy necessary to bring the oxygen atom close enough for a proton switch to occur. In the model of proton transfer by Conway, Bockris, and Linton[11] the rate-determining step is the rotation of water molecules into the hydration sheath of the H_3O^+ ions as protons are transferred through solution. In water, increased pressure increases the co-ordination number of the H_3O^+ ions by breaking down the open tetrahedral water structure and hence increases the excess of conductance owing to proton transfer ($\lambda_{H^+} - \lambda_{Na^+}$).

In the simple alcohol series the excess of proton conductance decreases with the length of the carbon chain,[11] and pressure decreases it slightly[7] owing, probably, to the higher viscosity's slowing the rotation of alcohol molecules.

At 1 atm. $\lambda_{H^+} - \lambda_{Na^+}$ in ethanol–water is slightly less than in methanol and much smaller than in water. Pressure has only a small effect. As soon as there is more than a trace of water present in ethanol, equilibrium data show that nearly all protons form H_3O^+ ions in preference to $EtOH_2^+$ ions.[11] Normal transfers between H_3O^+ and H_2O are rare at low concentrations of water, so that H_3O^+ entities are more permanent than in water and consequently diffuse in the applied field rather in the manner of salt ions. With increasing water content exchanges between H_3O^+ and H_2O occur more frequently and the anomalous conductance becomes predominant.

Ionization of Weak Electrolytes.—Table 13 gives a comparison of the values for K_a from Series *A* with those usually accepted. The present experiments were deisgned to show changes with pressure rather than give highly accurate values at 1 atm. No previous values for benzoic acids in ethanol–water were found but values are reported[12] for benzoic acid in 50% methanol–water ($5{\cdot}1 \times 10^{-6}$) and in 25% ethanol–water ($2{\cdot}3 \times 10^{-5}$).

TABLE 13. *Dissociation constants at 25°.*

Acid	10^5K_a (Mean)	Accepted value 10^5K_a	Source
Benzoic	6·2	6·29	Harned and Owen[13]
o-Nitrobenzoic	610	671	Dippy[12]
m-Nitrobenzoic	31	32·1	,,
p-Nitrobenzoic	33	37·6	,,
3,5-Dimethyl-4-nitrobenzoic	7·5 *	—	—
Salicylic	101	106	Dippy[12]

* In 10% v/v ethanol–water.

It is now established that pressure causes a large increase in the dissociation of weak acids and bases, and that this increase arises largely from the enhanced solvation of the free ions at high pressures.[2] For acids and bases of the hydrated gas type, increases in the apparent dissociation constants may be also due partly to the greater concentration of true acid or base molecules at high pressures (*e.g.*, the CO_2–H_2CO_3 equilibrium[4]). As the increase in ionization is continuous to the highest pressures measured all weak electrolytes become " strong " under sufficient pressure.[2]

Tables 2—7 and 9—11 include values for the volume change ΔV which accompanies the ionization as calculated from the slope of the plot of log K_a^P/K_a^1 against pressure. The value of ΔV is given at 3000 atm. (ΔV^{3000}) and also its limiting value at 1 atm. (ΔV^1).

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[10] Bell, *Trans. Faraday Soc.*, 1941, **37**, 493.

[11] Conway, Bockris, and Linton, *J. Chem. Phys.*, 1956, **24**, 834.

[12] Dippy, *Chem. Reviews*, 1939, **25**, 151.

[13] Harned and Owen, " The Physical Chemistry of Electrolyte Solutions," 2nd Edn., Reinhold, New York, 1950.

The average value of ΔK, the change in compressibility on ionization, was obtained approximately from the difference between ΔV^1 and ΔV^{3000}.

$$\left(\frac{\partial(\ln K_a)}{\partial P}\right)_{T,m} = \frac{-\Delta V}{RT}; \quad -\left(\frac{\partial \Delta V}{\partial P}\right)_{T,m} = \Delta K \approx \frac{\Delta V^{3000} - \Delta V^1}{3000}$$

The values of ΔV^1 and ΔK for the two solvents are compared in Table 14 for benzoic and salicylic acids.

TABLE 14.

	Ethanol–water		Water	
Acid	ΔV^1	ΔK	ΔV^1	ΔK
Benzoic	$-16{\cdot}1$	$-0{\cdot}0013$	$-10{\cdot}6$	$-0{\cdot}0011$
Salicylic	$-12{\cdot}7$	$-0{\cdot}0011$	$-7{\cdot}2$	$-0{\cdot}0005$

It is known that the solvent in the immediate neighbourhood of an ion is in a state of compression,[14] and one might therefore expect that the volume decrease accompanying the introduction of ions into a liquid should vary with the compressibility of the liquid. Hamann and Lim [15] have shown that there is a linear relation between the compressibility of several solvents ($-\partial V/V\,.\,\partial P$) and the difference between the volume change on ionization in these solvents and the volume change in water ($\Delta V^\circ_{\text{solvent}} - \Delta V^\circ_{\text{water}}$). They list the figure -14 cm.^{3} mole^{-1} as the value of ΔV° (ethanol) $-$ ΔV° (water). From Table 14, for both benzoic and salicylic acids, a value of $-5{\cdot}5$ cm.^{3} mole^{-1} is obtained for ΔV° (50 : 50 w/w ethanol–water) $-$ ΔV° (water). This figure seems to be in reasonable agreement with that obtained by Hamann.

The effect of pressure on the hydration free energies of singly charged ions can be calculated by means of the Born equation

$$\Delta G_h = \frac{Ne^2}{2r}\left(1 - \frac{1}{D}\right)$$

where ΔG_h is the free energy of hydration of a mole of ions at infinite dilution, r is the radius of the ion, and D the dielectric constant of the solvent. The increase in the true dissociation constant of a weak acid with pressure can be correlated with the increased free energy of hydration of the ions if it is assumed that the free energy of hydration of the acid molecule is small and that pressure has little effect on the H–A bond dissociation energy, the ionization potential of H, and the electron affinity of A.[2]

The change in radius of the unsolvated ion with pressure is not affected by varying the solvent. The change in dielectric constant however is much more important for methanol and ethanol solutions than for water. The greater value of log K_a^P/K_a^1 for a given pressure and acid in ethanol–water than in water is associated with the lower and more pressure-susceptible dielectric constant of the former medium. This observation has also been made for the weak base piperidine in methanol and in water.[8]

The individual benzoic acids may now be considered (Figure). The graph of log K_a^P/K_a^1 for *p*-methylbenzoic acid completely overlies that for benzoic acid. Evidently a *p*-methyl constituent has little effect on the change in ionic-solvation free energies with increased pressure.

If the compressibility of the organic acid ions does not change with molar volume the effect of pressure should increase inversely with the size of the ions.[16] The present values of K_a^P/K_a^1 for benzoic acid in water are for equal pressures rather less than Hamann and Strauss's values [16] for acetic and formic acids. The values of ΔV^1 for *m*- and *p*-nitrobenzoic acids are in turn slightly less than that for benzoic acid.

The effect of pressure on salicylic acid is less than that for any other acid on which data are available. It has been suggested [17] that an internal hydrogen bond is formed

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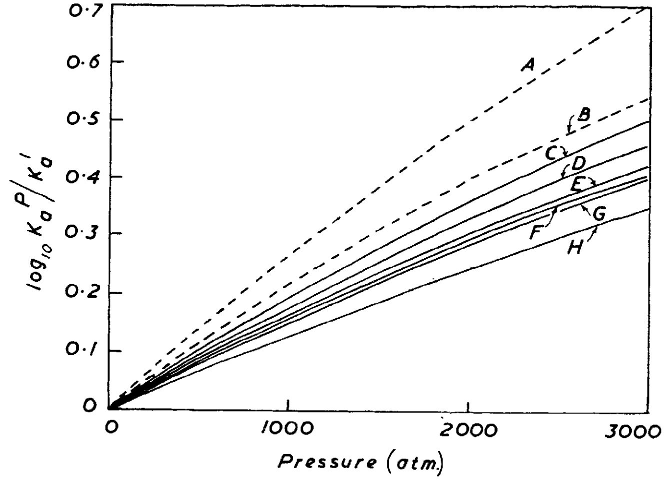
[14] Zwicky, *Phys. Z.*, 1925, **26**, 664.

[15] Hamann and Lim, *Austral. J. Chem.*, 1954, **7**, 329.

[16] Hamann and Strauss, *Trans. Faraday Soc.*, 1955, **51**, 1684.

between the carboxyl and the hydroxyl group which stabilizes the salicylate anion with respect to the free acid. This accounts for the high dissociation constant. Internal hydrogen bonding in the anion would lower the energy of hydration by drawing off part of the charge on the carboxylate group, and by hindering the access of water molecules. The low decrease in compressibility on ionization is in agreement with a low degree of hydration.

Hamann [2] estimated the volume contraction on the formation of one hydrogen bond to be —3·4 cm.^{3} mole^{-1}. Table 14 gives the difference between the volume contractions for benzoic and salicylic acids as —3·4 cm.^{3} mole^{-1} for both water and ethanol-water. Although no significance can be attached to the exact agreement in volume figures the results do support the hydrogen bond explanation for the low ΔV for salicylic acid.

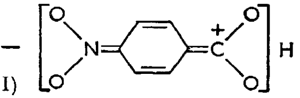


Variation in strengths of benzoic acids with increasing pressure at 25°.

A, Benzoic and *p*-methylbenzoic acid in ethanol–water.
B, Salicylic acid in ethanol–water.
C, Benzoic acid in water.
D, *o*-Nitrobenzoic acid in water.
E, 3,5-Dimethyl-4-nitrobenzoic acid in water.
F, *p*-Nitrobenzoic acid in water.
G, *m*-Nitrobenzoic acid in water.
H, Salicylic acid in water.

Newman [18] considered that the high acid dissociation constant for *o*-nitrobenzoic acid was due to the decrease in the resonance energy of the free acid form, caused by steric interaction of the nitro- and the carboxyl group. The present results suggest that high pressures increase this interaction slightly.

3,5-Dimethyl-4-nitrobenzoic acid has a dissociation constant at 25° only slightly greater than that of benzoic acid, whereas the constant for *p*-nitrobenzoic acid is greater by a factor of about 6. The use of 10% ethanol as a solvent would account for only a small part of this difference. Part of the decreased acid strength may be due to the increased positive induction effect of the two methyl groups, but a greater decrease is probably due to the steric interaction of the methyl groups with the nitro-group. The anion of *p*-nitrobenzoic acid is stabilized by the resonance structure (I) which can make a maximum contribution to the energy of the anion only if the nitro-group can become coplanar with the benzene ring.[18] The methyl groups hinder the formation of this planar arrangement. As the pressure effect for the acid is similar to that for *p*-nitrobenzoic acid the interaction between the methyl and the nitro-group cannot be altered appreciably by pressure.



(I)

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[17] Branch and Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 2568.
[18] Newman, " Steric Effects in Organic Chemistry," John Wiley and Sons, New York, 1956.