220. *Influence of Pressure on the Hammett Reaction Constant: Dissociation of Benzoic Acids and Phenylacetic Acids.*

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The thermodynamic p*K* values, in water at 25°, of a number of substituted benzoic and phenylacetic acids have been measured over the pressure range 1—3000 bars. For each series the Hammett reaction constant ρ decreases with increase in pressure, a result expected for this type of reaction. It is clear also that, for a given reaction series at a given pressure, a plot of ΔV against σ (substituent constant) reveals any dependence of ρ on pressure.

THE probable effect of pressure on the Hammett reaction constant ρ has been discussed, and predictions have been made for heterolytic and homolytic reactions in polar and non-polar solvents.[1] For some sets of conditions, the conclusion reached was that ρ should be unaltered by pressure changes. This should not be so, however, for a reaction producing ions in a polar solvent, a case for which it was predicted that an increase in pressure should result in a decrease in the magnitude of ρ. At present there are no results available for full reaction series studied at a variety of pressures, and the only relevant data which can be used are p*K* values for benzoic and *m*-nitrobenzoic acids.[2] From this limited information it was tentatively concluded that ρ for the benzoic acid series is, in fact, influenced by pressure and diminishes with increasing pressure. We now report the thermodynamic p*K* values, in water, of benzoic acid and *m*-fluoro-, *p*-fluoro-, *m*-methoxy-, *p*-methoxy-, *m*-nitro-, and *p*-nitro-benzoic acids at 25° and at pressures from 1 to 3000 bars. The phenylacetic acid series, with *m*-chloro-, *p*-chloro-, *m*-fluoro-, *p*-fluoro-, *p*-methoxy-, *m*-nitro-, *p*-nitro-, and *p*-methyl substituents, was similarly examined.

EXPERIMENTAL

Materials.—"AnalaR" potassium chloride was dried at 120° for 2 hr. and "AnalaR" hydrochloric acid was standardised against recrystallised borax. Of the organic acids, phenylacetic acid, *p*-methyl-, *m*-fluoro- and *p*-fluoro-phenylacetic acids were recrystallised from heptane and all other acids from ethanol–water. All m. p.s were within a degree of the accepted values. *m*-Fluorophenylacetic acid was prepared by refluxing the nitrile (40·2 g.) with water (40 ml.), sulphuric acid (40 ml.), and acetic acid (40 ml.) for 2¼ hr. The mixture was poured on cracked ice (250 g.), and the crude acid, after filtration, was dissolved in sodium carbonate solution (3%; 600 ml.). After extraction with chloroform (100 ml.) and ether (100 ml.), the solution was acidified with concentrated hydrochloric acid, and the liberated *m*-fluorophenylacetic acid was extracted with ether (3 × 50 ml.). Ether was removed and the acid distilled at 100—120°/0·5 mm. and crystallised from heptane (150 ml.), giving white crystals (27 g.), m. p. 44·5—45·5° (Found: C, 62·6; H, 4·7. $C_8H_7FO_2$ requires C, 62·6; H, 4·55%). Standard solutions of the organic acids were made up by weight, each solution usually being used for one run only, although in a few instances standard solutions were progressively diluted for a series of runs. Water free from carbon dioxide was used for all solutions. Solutions of potassium salts were prepared by adding the calculated volume of standard, carbonate-free potassium hydroxide solution to the weighed acid. Checks with a pH meter confirmed that all salt solutions had pH values within the range 7·5—8·5.

Apparatus.—Pressures were generated by means of a simple hand-operated hydraulic intensifier and the conductance cell was enclosed in a stainless steel bomb[3] sealed by an O-ring.[4] The conductance cell was one designed after consultation with Dr. A. J. Ellis. The glass cell (*ca.* 2 ml. capacity) was pear-shaped, the narrow end having a small orifice (*ca.* 0·25 mm. diam.) at its extremity. This end of the cell was ground to fit a B14 socket. To the neck of the

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[1] Ellis, Fyfe, Rutherford, Fischer, and Vaughan, *J. Chem. Phys.*, 1959, **31**, 176.
[2] See Clark and Ellis, *J.*, 1960, 247, for full details of these measurements.
[3] Ellis, *J.*, 1959, 3689.
[4] Gugan, *J. Sci. Instr.*, 1956, **33**, 160.

ground-glass socket was attached a flexible Teflon bag of capacity similar to that of the cell. The electrodes were small platinum balls and the links to the external circuit were of fine platinum wire passing through the glass wall of the cell. Earlier difficulties (at high pressures) caused by cracking at the platinum-glass seals were not experienced when the diameter of the wire was reduced to 0·04 mm. When the whole unit (cell plus bag) was filled with solution, and suspended in the steel bomb, the cell contents were isolated from the hydraulic fluid. The flexible bag still allowed pressure to be transmitted to the cell liquid *via* the small orifice. With this unit the variation with pressure of the cell constant depended only upon the compressibilities of glass and platinum, and this small variation could readily be calculated from Bridgman's figures.[5] The cell constant at 1 bar was 0·639 ± 0·005 cm.$^{-1}$.

Pressures were measured with a Bourdon gauge calibrated with a Harwood standard manganin coil resistance. In practice, accuracy was limited by dial readings but recorded pressures were considered accurate to within 0·5%. The conductivity bridge has been described previously,[6] and its high sensitivity proved of great advantage when studying the organic acids of low solubility.

Dissociation Constants.—The p*K* values were obtained by using the general approach due to Davies [7a] and MacInnes.[7b] The thermodynamic dissociation constant for the ionisation of an acid HA is given by

$$K_a = a_{\mathrm{H}^+} \,.\, a_{\mathrm{A}^-}/a_{\mathrm{HA}} = \frac{c_{\mathrm{H}^+} \,.\, c_{\mathrm{A}^-}}{c_{\mathrm{HA}}} \,.\, \frac{f_{\mathrm{H}^+} \,.\, f_{\mathrm{A}^-}}{f_{\mathrm{HA}}}$$

The activity of undissociated molecules is taken as unity and it is also assumed that $f_{\mathrm{H}^+} = f_{\mathrm{A}^-} = f_{\pm}$. Since $c_{\mathrm{H}^+} = c_{\mathrm{A}^-} = c_{\mathrm{i}}$, $K = f_{\pm}{}^2c_{\mathrm{i}}{}^2/c_{\mathrm{HA}}$.

If α is the degree of dissociation and m is the original molal concentration of the acid solution, then $c_{\mathrm{i}} = \alpha m$ and $c_{\mathrm{HA}} = m(1 - \alpha)$. Then $K_a = f_{\pm}{}^2\alpha^2m/(1 - \alpha)$.

If λ is the molal conductance of the acid solution and λ' is the molal conductance of the constituent ions at the ionic concentration of the acid solution, then $\alpha = \lambda/\lambda'$. α can be obtained by a series of successive approximations (see example below).

In water, and at the concentrations used, the molal activity coefficient $\gamma_{\pm}$ = the molar activity coefficient $f_{\pm}$, which can be obtained at all concentrations and pressures from the Debye–Hückel equation expressed as:

$$-\log f_{\pm} = \{1{\cdot}8123 \times 10^6(DT)^{-3/2}c^{\frac{1}{2}}\}/\{1 + 50{\cdot}29 \times 10^8(DT)^{-\frac{1}{2}}ac^{\frac{1}{2}}\}$$

In this expression, T is the absolute temperature, c is the ionic concentration, and a is the ionic radius, taken as 5×10^{-8} cm. D is the dielectric constant, and its pressure dependence can be found by using Owen and Brinkley's formula.[8]

The following example illustrates the general procedure followed for the determination of K_a at a specific pressure: *m*-Chlorophenylacetic acid, m = 0·001787 at 1000 bars. Resistance of acid solution at 1000 bars = 3650·85 ohms ± 0·1%. Resistance corrected for water blank = 3689·00 ohms ± 0·2%. λ = (1000 × 0·639)/(3689·00 × 0·001787) = 96·98 ohm^{-1} cm.^{2} ± 0·7%.

Conductance of constituent ions at infinite dilution, λ_0 = 404·3 ohm^{-1} cm.^{2} ± 0·2%. α_1, the first of a series of approximations to α, is given by λ/λ_0 = 0·240. Thus c_1, the first approximation to the ionic concentration, = 0·000429 g.-ion/1000 g.

By interpolation in the plots of (concentration)$^{\frac{1}{2}}$ against the conductances of hydrochloric acid, of potassium chloride, and of potassium *m*-chlorophenylacetate, λ is obtained for these electrolytes at 1 bar at the above concentration. For each of these electrolytes, the mean pressure variation is given in Table 1. The term " λ × mean pressure variation at 1000 bars " is evaluated for each of the three electrolytes and the sum of these terms gives λ'_1, the first approximation to λ'.

$$\lambda'_1 = 414{\cdot}60. \quad \alpha_2 = \lambda/\lambda'_1 = 0{\cdot}234$$

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[5] Bridgman, (*a*) *Amer. J. Sci.*, 1925, **10**, 359; (*b*) *Proc. Amer. Acad.*, 1923, **58**, 166.

[6] Fischer, Murdoch, Packer, Topsom, and Vaughan, *J.*, 1957, 4358.

[7a] Davies, *J. Phys. Chem.*, 1925, **29**, 977.

[7b] MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068.

[8] Hamann, " Physico-chemical effects of pressure," Butterworths, London, 1957, p. 104.

Thus $c_2 = 0{\cdot}000418$ g. ion/1000 g.; $\lambda'_2 = 414{\cdot}15$;

$$\alpha_3 = 0{\cdot}234 \pm 0{\cdot}9\%; \text{ and } 1 - \alpha_3 = 0{\cdot}766.$$

From the Debye–Hückel approximation, $-\log \gamma_{\pm} = 0{\cdot}00925$. Thus $K_a = \gamma_{\pm}^2\alpha^2 m/(1 - \alpha) = 1{\cdot}224 \times 10^{-4} \pm 2{\cdot}7\%$, and the p$K$ value is $3{\cdot}912 \pm 0{\cdot}01$.

Results.—Table 1 gives, for general interest, the measured variation of conductance with pressure for the strong electrolytes relevant to the present work. In this Table, λ_0 = molal conductance at infinite dilution and λ_P/λ_1, is the ratio of molal conductances at pressures P and 1 bar. An omission from the Table is potassium *p*-nitrophenylacetate, which was not sufficiently soluble to allow conductance measurements to be made. For the calculation of the pK of the acid, conductance values for this salt were taken as approximately the mean values for the other phenylacetates.

In Tables 2 and 3 are the mean derived pK values for benzoic acids and phenylacetic acids, at 25° ± 0·01°, over the pressure range 1—3000 bars. The standard deviation (s) with the number of pK determinations (n) are also given for each acid. In Table 4 are values, for all acids, of ΔV_1, the volume change on ionisation at 1 bar (calculated from the variation of K with P).

TABLE 1. *Conductances of strong electrolytes.*

P (bars)	1	500	1000	1500	2000	2500	3000
	λ_0	λ_P/λ_1					
Hydrochloric acid	426·16	1·051	1·093	1·127	1·155	1·177	1·195
Potassium chloride	149·86	1·034	1·056	1·068	1·074	1·073	1·067
Potassium benzoates:							
Unsubstituted	115·0	1·022	1·034	1·036	1·035	1·027	1·016
p-nitro-	106·2	1·023	1·037	1·041	1·041	1·036	1·027
p-methoxy-	108·2	1·024	1·037	1·041	1·039	1·032	1·021
m-methoxy-	105·4	1·023	1·035	1·038	1·036	1·028	1·016
m-fluoro-	110·4	1·022	1·034	1·038	1·035	1·026	1·015
m-nitro-	109·9	1·022	1·035	1·037	1·036	1·028	1·017
p-fluoro-	108·4	1·023	1·035	1·039	1·037	1·028	1·017
Potassium phenylacetates:							
Unsubstituted	107·4		1·038		1·037		1·018
m-nitro-	106·7		1·034		1·034		1·014
m-chloro-	103·5		1·035		1·036		1·016
p-chloro-	108·7		1·036		1·038		1·019
p-methoxy-	107·4		1·036		1·040		1·021
p-methyl-	106·6		1·037		1·042		1·024
m-fluoro-	109·2		1·037		1·041		1·024
p-fluoro-	109·9		1·036		1·037		1·017

TABLE 2. *Benzoic acids, mean p*K *values.*

P (bars)	1	500	1000	1500	2000	2500	3000
Substituent:							
H	4·205	4·107	4·021	3·943	3·865	3·795	3·726
$n = 3$, s	0·003	0·003	0·003	0·003	0·003	0·003	0·004
m-F	3·862	3·776	3·694	3·620	3·546	3·477	3·412
$n = 4$, s	0·006	0·006	0·005	0·007	0·007	0·007	0·007
p-F	4·153	4·061	3·976	3·900	3·822	3·753	3·687
$n = 4$, s	0·004	0·003	0·003	0·003	0·003	0·004	0·004
m-NO_2	3·473	3·397	3·328	3·258	3·192	3·130	3·070
$n = 4$, s	0·006	0·006	0·007	0·007	0·007	0·007	0·008
p-NO_2	3·422	3·347	3·275	3·209	3·142	3·081	3·022
$n = 4$, s	0·014	0·014	0·016	0·017	0·018	0·020	0·022
m-OMe	4·086	3·995	3·911	3·834	3·759	3·691	3·625
$n = 3$, s	0·006	0·008	0·008	0·007	0·007	0·008	0·007
p-OMe	4·511	4·411	4·320	4·237	4·156	4·083	4·013
$n = 5$, s	0·005	0·005	0·005	0·005	0·005	0·006	0·007

TABLE 3. *Phenylacetic acids, mean pK values.*

P (bars)	1	1000	2000	3000
Substituent:				
H	4·311	4·095	3·917	3·762
$n = 4$, s	0·005	0·005	0·005	0·009
p-Me	4·361	4·147	3·965	3·808
$n = 5$, s	0·003	0·004	0·003	0·004
m-NO_2	3·953	3·766	3·605	3·466
$n = 6$, s	0·015	0·016	0·016	0·017
p-NO_2	3·924	3·740	3·580	3·437
$n = 3$, s	0·013	0·009	0·016	0·017
p-Cl	4·177	3·971	3·799	3·649
$n = 5$, s	0·006	0·004	0·003	0·005
p-OMe	4·356	4·146	3·967	3·811
$n = 5$, s	0·003	0·002	0·003	0·004
m-Cl	4·110	3·911	3·738	3·585
$n = 5$, s	0·013	0·016	0·016	0·013
m-F	4·130	3·927	3·754	3·603
$n = 5$, s	0·004	0·006	0·006	0·006
p-F	4·218	4·007	3·829	3·676
$n = 5$, s	0·003	0·003	0·004	0·003

TABLE 4. *ΔV values (c.c. mole^{-1}) at one bar.*

(*a*) Benzoic acids

Substituent	H	m-F	p-F	m-NO_2	p-NO_2	m-OMe	p-OMe
$-\Delta V_1$	11·09	9·85	10·47	8·84	8·56	10·30	11·32

(*b*) Phenylacetic acids

Substituent	H	m-NO_2	p-NO_2	m-Cl	p-Cl	m-F	p-F	p-Me	p-OMe
$-\Delta V_1$	12·73	11·09	10·92	11·77	12·16	11·99	12·44	12·61	12·39

DISCUSSION

p*K and V Values.*—The dissociation constants, at atmospheric pressure, are in good agreement with those recorded by Dippy and his co-workers.[9] The ΔV_1 values lie within the same range as those found by Hamann and Strauss for formic, acetic, and propionic acids (—8·8, —12·2, and —12·9 cm.^{3} mole^{-1}, respectively). Clark and Ellis [2] have recently reported ΔV_1 values for three of the acids studied in the present work. They are benzoic ($\Delta V_1 = -10{\cdot}6$ cm.^{3} mole^{-1}), *m*-nitrobenzoic (—8·7), and *p*-nitrobenzoic (—9·1) acids.

Hammett Plots.—In obtaining the reaction constant (ρ) from the Hammett equation, all substituent constants (σ) used for the benzoic acid series were those recommended by McDaniel and Brown.[10] Jaffé's method [11] was followed and the relevant data are in Table 5(*a*). The probable error in ρ is $\pm 0{\cdot}01$. Briegleb and Bieber,[12] who studied seven benzoic acids at 25° and 1 bar, obtained $\rho = 0{\cdot}958$, with $r = 0{\cdot}996$ and $s = 0{\cdot}027$.

In the phenylacetic acids, resonance involving substituent and carboxyl side-chain is inhibited by the methylene group. Wepster's σ_N values [13] were used in calculations of ρ. At 1 bar, all substituents were included except the *p*-fluoro-substituent, which was fitted to the line to obtain $\sigma_N = 0{\cdot}167$. This value was used in subsequent determinations of ρ at 1000, 2000, and 3000 bars. Results are in Table 5(*b*), and the probable error in ρ values is $\pm 0{\cdot}006$. The ρ value from Dippy's results at 25° is 0·519, with $r = 0{\cdot}988$ and $s = 0{\cdot}026$ for 12 substituents.

Variation of ρ *with Pressure.*—It is clear from Table 5 that, in accord with prediction,

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[9] Dippy and Lewis, *J.*, 1936, 644; Dippy and Page, *J.*, 1938, 357; Dippy and Williams, *J.*, 1934, 161; Dippy and Williams, *J.*, 1924, 1888.

[10] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

[11] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[12] Briegleb and Bieber, *Z. Electrochem.*, 1951, **55**, 250.

[13] Van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

ρ diminishes with increase in pressure. It may be assumed that, as P increases and the solvent becomes more compressed, the contraction produced on ionisation becomes smaller.

TABLE 5. *Application of Hammett equation.*

(*a*) Benzoic acids ($n = 7$)

P (bars)	ρ	r	s	s_ρ	pK_0 (calc.)
1	1·039	1·000	0·013	0·014	4·217
500	1·013	1·000	0·013	0·014	4·122
1000	0·996	1·000	0·013	0·014	4·036
1500	0·979	1·000	0·013	0·014	3·957
2000	0·965	1·000	0·013	0·014	3·880
2500	0·954	0·999	0·014	0·015	3·810
3000	0·943	0·999	0·014	0·015	3·742

(*b*) Phenylacetic acids

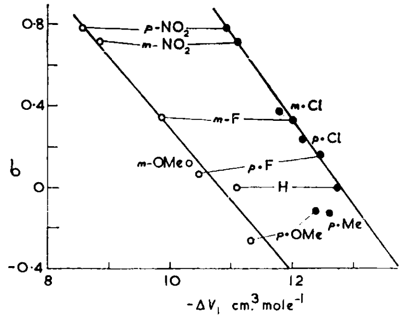
P (bars)	ρ	r	s	s_ρ	n	pK_0 (calc.)
1	0·491	0·999	0·007	0·008	8	4·300
1000	0·457	0·999	0·008	0·009	9	4·088
2000	0·434	0·998	0·009	0·010	9	3·909
3000	0·417	0·998	0·009	0·010	9	3·754

Hence $-\Delta V$ and, consequently, $|\Delta\Delta V|$ decrease (*e.g.*, see Table 6), and, from $\partial\rho/\partial P = -\Delta\Delta V/2{\cdot}303\boldsymbol{R}T\sigma$, $-\partial\rho/\partial P$ decreases also. At sufficiently high pressures, $\Delta\Delta V$ should approach zero and ρ should approach a constant value.

TABLE 6. *Variation of* ΔVp *with pressure for* p-*methoxybenzoic acid.*

P (bars)	1	500	1000	1500	2000	2500	3000
$-\Delta V$	11·32	10·25	9·35	9·12	8·22	7·89	7·66

It is to be noted that, for a given reaction, values of ΔV can be used to check whether or not ρ depends on P. From the above equation, since $\Delta\Delta V/\sigma$ is independent of σ, if ρ is a function of P, then ΔV is a linear function of σ at constant (T, P). If ρ is independent of P, then $\Delta\Delta V/\sigma = 0$ and ΔV is independent of σ. Thus, at any given pressure, a plot of ΔV against σ should be linear, and a slope other than zero reveals a dependence of ρ on P. Zero slope indicates that ρ remains constant at different pressures. The plots of ΔV_1 against σ for benzoic and phenylacetic acids are given in the Figure.



The variation of ΔV_1 *with Hammett substituent constant.*

○ *Benzoic acids.* ● *Phenylacetic acids.*

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