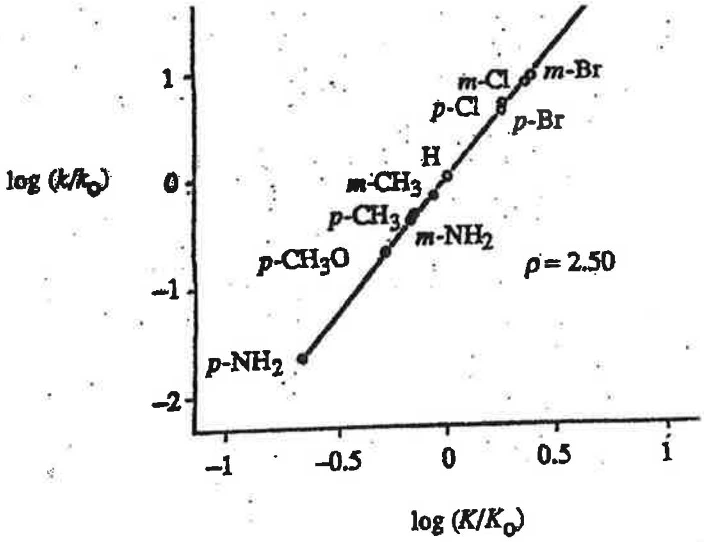

Figure 7.1. Logarithmic relationship between relative rate constants of base-catalyzed hydrolysis of substituted ethyl benzoates and relative K values of substituted benzoic acid ionizations. (Rate and equilibrium measurements were carried out in 4:1 (v/v) ethanol–water at 30°C and in water at 25°C, respectively.)

Table 7.1 Hammett substituent constants and their modified values

Group	σ_m[a]	σ_p[a]	σ_p^-[d]	σ_p^+[f]	σ_p^o[h]
H	0	0	0	0	0
Me	−0.06	−0.14		−0.31	−0.12
Et	−0.07	−0.15		−0.30	−0.13
i-Pr	−0.07	−0.15		−0.28	−0.16
t-Bu	−0.09	−0.15		−0.26[g]	−0.17
CH_2Ph	−0.08	−0.09		−0.27	
$CH{=}CH_2$	0.08	−0.08			
C≡CH	0.20	0.23	0.52	0.18[g]	
Ph	0.05	−0.01	0.08	−0.18	0.04
CHO	0.36	0.43	1.13		
COMe	0.38	0.50	0.87		0.46
COOH	0.35	0.44	0.73		
COOEt	0.35	0.44	0.64		0.46
COO^-	0.11[b]	0.02[b]			
CN	0.61	0.65	1.0		0.69
CF_3	0.43	0.54	0.74		0.53[i]
F	0.34	0.15		−0.07	0.17
Cl	0.37	0.24		0.11	0.27
Br	0.37	0.26		0.15	0.26
I	0.34	0.28		0.14	0.27
NH_2	−0.09	−0.57		−1.3	−0.38
NMe_2	−0.10	−0.63		−1.7	−0.44
NHCOMe	0.14	0.00		−0.6	0.03[j]
NH_3^+	0.86	0.60			
NMe_3^+	0.88	0.82			0.80[i]
NO_2	0.71	0.81	1.27		0.82
N_2^+	1.65[c]	1.93[c]	3.0[e]		
O^-	−0.47	−0.81			
OH	0.13	−0.38		−0.92	−0.16
OMe	0.10	−0.28		−0.78	−0.10
OCOMe	0.39	0.31			
SH	0.25	0.15			
SMe	0.14	0.00	0.04	−0.60	0.08
SMe_2^+	1.00	0.90	1.16		
SOMe	0.52	0.49	0.73		
SO_2Me	0.64	0.73	1.05		0.69[i]

values are taken from refs. 8

TABLE 5.16

Hammett ρ-values for the dissociation of aromatic acids, 25 °C

$$\mathrm{AH+S} \underset{25\,^\circ\mathrm{C}}{\overset{\mathrm{S}}{\rightleftharpoons}} \mathrm{SH^+ + A^-}$$

or

$$\mathrm{BH^+ + S} \underset{25\,^\circ\mathrm{C}}{\overset{\mathrm{S}}{\rightleftharpoons}} \mathrm{SH^+ + B}$$

Acid[a]	Solvent	ρ	Note or Ref.
$ArCO_2H$	H_2O	1.00	see text
$ArCO_2H$	C_2H_5OH	1.65	*b*
$ArCO_2H$	DMF	2.36	*c*
$ArCO_2H$	CH_3CN	2.41	*c*
$ArCO_2H$	DMSO	2.48	*c*
$ArCH_2CO_2H$	H_2O	0.49	Fig. 5.3
$ArCH_2CH_2CO_2H$	H_2O	0.21	Fig. 5.3
trans-$ArCH{=}CHCO_2H$	H_2O	0.45	ref. 31
$ArPO(OH)_2$	H_2O	0.76	ref. 31
$ArOH$	H_2O	2.11	ref. 31
$ArSO_2H$	H_2O	0.98	ref. 32
$ArNH_3^+$	H_2O	2.77	ref. 31
$ArNH_3^+$	C_2H_5OH	3.54	ref. 31
$ArCH_2NH_3^+$	H_2O	0.72	ref. 31

[a] $Ar = X\text{-}C_6H_5\text{-}$ where X = the substituent.

[b] C. D. Ritchie and R. E. Uschold, *J. Am. chem. Soc.* **90,** 2821 (1968).

[c] I. M. Kolthoff and M. K. Chantooni, *J. Am. chem. Soc.* **93,** 3843 (1971); $DMF = HCON(CH_3)_2$, $DMSO = CH_3SOCH_3$.

and

$$\sigma(p\mathrm{NO_2}) = 0.78 \text{ (Table 5.15)},$$

therefore

$$\log K_X + 11.0 = 2.48 \times 0.78$$

$$\log K_X = 1.93 - 11.0$$

$$= -9.1.$$

$$\underline{\text{The } pK_{AH} \text{ of } p\text{-nitrobenzoic acid in DMSO} = 9.1}$$

(in good agreement with the experimental value of 9.0[18]).

This example illustrates one use of the Hammett equation. If the ρ-value for a reaction type is established by measuring K_X for several (preferably, many) members of the series, the equilibrium constants for other members of the series can be easily estimated by interpolation using eqn (5.36) and σ-values for the substituents (of which well over 500 are now known[30]). The accuracy of the estimated pK_{AH} depends principally upon the quality of the correlation (which is expressed by the correlation coefficient) in the determination of ρ.[28]

Substituent	σ^*	Substituent	σ^*
CCl_3	2.65	$CH{=}CHPh$	0.41
CHF_2	2.05	$CHPh_2$	0.40
CO_2Me	2.00	CH_2CH_2Cl	0.38
$CHCl_2$	1.94	$CH{=}CHMe$	0.36
Ac	1.65	$CH_2CH_2CF_3$	0.32
$C{\equiv}CPh$	1.35	CH_2Ph	0.22
CH_2SO_2Me	1.32	$CH_2CH{=}CHMe$	0.13
CH_2CN	1.30	$(CH_2)_3CF_3$	0.12
CH_2F	1.10	CH_2CH_2Ph	0.08
CH_2Cl	1.05	Me	0.000
CH_2Br	1.00	Et	−0.10
CH_2CF_3	0.92	*n*-Pr	−0.12
CH_2I	0.85	*n*-Bu	−0.13
CH_2OPh	0.85	Cyclohexyl	−0.15
CH_2OMe	0.64[b]	CH_2Bu-*t*	−0.16
CH_2Ac	0.60	*i*-Pr	−0.19
Ph	0.60	Cyclopentyl	−0.20
CH_2OH	0.56	$CHEt_2$	−0.22
$CH_2CH_2NO_2$	0.50	CH_2SiMe_3	−0.26
H	0.49	*t*-Bu	−0.30

Taft’s Steric Substituent Constants

Group	E_s	Group	E_s
H	0.0	F	-0.46
Me	-1.24	Cl	-0.97
Et	-1.31	Br	-1.16
i-Pr	-1.71	I	-1.4
t-Bu	-2.78	NH_2	-0.61
$CH{=}CH_2$	-2.84	NMe_3^+	-2.84
Ph	-1.01/-3.79	NO_2	-1.01/-2.52
CN	-0.51	OH	-0.55
CF_3	-2.4	OMe	-0.55