
SECTION 9

PHYSICOCHEMICAL RELATIONSHIPS

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9.1 LINEAR FREE ENERGY RELATIONSHIPS

Many equilibrium and rate processes can be systematized when the influence of each substituent on the reactivity of substrates is assigned a characteristic constant σ and the reaction parameter ρ is known or can be calculated. The Hammett equation

$$\log \frac{K}{K^\circ} = \sigma\rho$$

describes the behavior of many *meta*- and *para*-substituted aromatic species. In this equation K° is the acid dissociation constant of the reference in aqueous solution at 25°C and K is the corresponding constant for the substituted acid. Separate sigma values are defined by this reaction for *meta* and *para* substituents and provide a measure of the total electronic influence (polar, inductive, and resonance effects) in the absence of conjugation effects. Sigma constants are not valid of substituents *ortho* to the reaction center because of anomalous (mainly steric) effects. The inductive effect is transmitted about equally to the *meta* and *para* positions. Consequently, σ_m is an approximate measure of the size of the inductive effect of a given substituent and $\sigma_p - \sigma_m$ is an approximate measure of a substituent's resonance effect. Values of Hammett sigma constants are listed in Table 9.1.

Taft sigma values σ^* perform a similar function with respect to aliphatic and alicyclic systems. Values of σ^* are listed in Table 9.1.

The reaction parameter ρ depends upon the reaction series but not upon the substituents employed. Values of the reaction parameter for some aromatic and aliphatic systems are given in Tables 9.2 and 9.3.

Since substituent effects in aliphatic systems and in *meta* positions in aromatic systems are essentially inductive in character, σ^* and σ_m values are often related by the expression $\sigma_m = 0.217\sigma^* - 0.106$. Substituent effects fall off with increasing distance from the reaction center; generally a factor of 0.36 corresponds to the interposition of a $-\text{CH}_2-$ group, which enables σ^* values to be estimated for $\text{R}-\text{CH}_2-$ groups not otherwise available.

TABLE 9.1 Hammett and Taft Substituent Constants

Substituent	Hammett constants		Taft constant σ^*
	σ_m	σ_p	
$-\text{AsO}_3\text{H}^-$	-0.09	-0.02	0.06
$-\text{B}(\text{OH})_2$	0.01	0.45	
$-\text{Br}$	0.39	0.23	2.84
$-\text{CH}_2\text{Br}$			1.00
<i>m</i> - BrC_6H_4-		0.09	
<i>p</i> - BrC_6H_4-		0.08	
$-\text{CH}_3$	-0.07	-0.17	0.0
$-\text{CH}_2\text{CH}_3$	-0.07	-0.15	-0.10
$-\text{CH}_2\text{CH}_2\text{CH}_3$	-0.05	-0.15	-0.12
$-\text{CH}(\text{CH}_3)_2$	-0.07	-0.15	-0.19
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-0.07	-0.16	-0.13
$-\text{CH}_2\text{CH}(\text{CH}_3)_2$	-0.07	-0.12	-0.13
$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$		-0.12	-0.19
$-\text{C}(\text{CH}_3)_3$	-0.10	-0.20	-0.30
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$			-0.25
$-\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$			-0.17

TABLE 9.1 Hammett and Taft Substituent Constants (Continued)

Substituent	Hammett constants		Taft constant σ^*
	σ_m	σ_p	
$-\text{CH}_2\text{C}(\text{CH}_3)_3$		-0.23	-0.12
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$			-0.37
Cyclopropyl—	-0.07	-0.21	
Cyclohexyl—			-0.15
$-\text{3,4}-(\text{CH}_2)_2$ (fused)		-0.26	
$-\text{3,4}-(\text{CH}_2)_3$ — (fused ring)		-0.48	
$-\text{3,4}-(\text{CH})_4$ — (fused ring)	0.06	0.04	
$-\text{CH}=\text{CH}_2$	0.02		0.56
$-\text{CH}=\text{C}(\text{CH}_3)_2$			0.19
$-\text{CH}=\text{CHCH}_3$, <i>trans</i>			0.36
$-\text{CH}_2-\text{CH}=\text{CH}_2$			0.0
$-\text{CH}=\text{CHC}_6\text{H}_5$	0.14	-0.05	0.41
$-\text{C}\equiv\text{CH}$	0.21	0.23	2.18
$-\text{C}\equiv\text{CC}_6\text{H}_5$	0.14	0.16	1.35
$-\text{CH}_2-\text{C}\equiv\text{CH}$			0.81
$-\text{C}_6\text{H}_5$	0.06	-0.01	0.60
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$ —		-0.5	
Naphthyl— (both 1- and 2-)			0.75
$-\text{CH}_2\text{C}_6\text{H}_5$		0.46	0.22
$-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_5$			-0.06
$-\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$			0.37
$-\text{CH}(\text{C}_6\text{H}_5)_2$			0.41
$-\text{CH}_2-\text{C}_{10}\text{H}_7$			0.44
2-Furoyl—			0.25
3-Indolyl—			-0.06
2-Thienyl—			1.31
2-Thienylmethylene—			0.31
$-\text{CHO}$	0.36	0.22	
$-\text{COCH}_3$	0.38	0.50	1.65
$-\text{COCH}_2\text{CH}_2$		0.48	
$-\text{COCH}(\text{CH}_3)_2$		0.47	
$-\text{COC}(\text{CH}_3)_3$		0.32	
$-\text{COCF}_3$	0.65		3.7
$-\text{COC}_6\text{H}_5$	0.34	0.46	2.2
$-\text{CONH}_2$	0.28	0.36	1.68
$-\text{CONHC}_6\text{H}_5$			1.56
$-\text{CH}_2\text{COCH}_3$			0.60
$-\text{CH}_2\text{CONH}_2$			0.31
$-\text{CH}_2\text{CH}_2\text{CONH}_2$			0.19
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CONH}_2$			0.12
$-\text{CH}_2\text{CONHC}_6\text{H}_5$			0.0
$-\text{COO}^-$	-0.1	0.0	-1.06
$-\text{COOH}$	0.36	0.43	2.08
$-\text{CO}-\text{OCH}_3$	0.32	0.39	2.00
$-\text{CO}-\text{OCH}_2\text{CH}_3$	0.37	0.45	2.12
$-\text{CH}_2\text{CO}-\text{OCH}_3$			1.06
$-\text{CH}_2\text{CO}-\text{OCH}_2\text{CH}_3$			0.82
$-\text{CH}_2\text{COO}$			-0.06
$-\text{CH}_2\text{CH}_2\text{COOH}$	-0.03	-0.07	
$-\text{Cl}$	0.37	0.23	2.96
$-\text{CCl}_3$	0.47		2.65
$-\text{CHCl}_2$			1.94

TABLE 9.1 Hammett and Taft Substituent Constants (Continued)

Substituent	Hammett constants		Taft constant σ^*
	σ_m	σ_p	
—CH ₂ Cl	0.12	0.18	1.05
—CH ₂ CH ₂ Cl			0.38
—CH ₂ CCl ₃			0.75
—CH ₂ CH ₂ CCl ₃			0.25
—CH=CCl ₂			1.00
—CH ₂ CH=CCl ₂			0.19
<i>p</i> -ClC ₆ H ₄ —		0.08	
—F	0.34	0.06	3.21
—CF ₃	0.43	0.54	2.61
—CHF ₂			2.05
—CH ₂ F			1.10
—CH ₂ CF ₃			0.90
—CH ₂ CF ₂ CF ₂ CF ₃			0.87
—C ₆ F ₅	—0.12	—0.03	
—Ge(CH ₃) ₃		0.0	
—Ge(CH ₂ CH ₃) ₃		0.0	
—H	0.00	0.00	0.49
—I	0.35	0.28	2.46
—CH ₂ I			0.85
—IO ₂	0.70	0.76	
—N ₂ ⁺	1.76	1.91	
—N ₃ (azide)	0.33	0.08	2.62
—NH ₂	—0.16	—0.66	0.62
—NH ₃ ⁺	1.13	1.70	3.76
—CH ₂ —NH ₂			0.50
—CH ₂ —NH ₃ ⁺			2.24
—NH—CH ₃	—0.30	—0.84	
—NH—C ₂ H ₅	—0.24	—0.61	
—NH—C ₄ H ₉	—0.34	—0.51	
—NH(CH ₃) ₂ ⁺			4.36
—NH ₂ —CH ₃ ⁺	0.96		3.74
—NH ₂ —C ₂ H ₅ ⁺	0.96		3.74
—N(CH ₃) ₃ ⁺	0.88	0.82	4.55
—N(CH ₃) ₂	—0.2	—0.83	0.32
—CH ₂ —N(CH ₃) ₃ ⁺			1.90
—N(CF ₃) ₂	0.45	0.53	
<i>p</i> -H ₂ N—C ₆ H ₅ —		—0.30	
—NH—CO—CH ₃	0.21	0.00	1.40
—NH—CO—C ₂ H ₅			1.56
—NH—CO—C ₆ H ₅	0.22	0.08	1.68
—NH—CHO	0.25		1.62
—NH—CO—NH ₂	0.18		1.31
—NH—OH	—0.04	—0.34	
—NH—CO—OC ₂ H ₅	0.33		1.99
—CH ₂ —NH—CO—CH ₃			0.43
—NH—SO ₂ —C ₆ H ₅			1.99
—NH—NH ₂	—0.02	—0.55	
—CN	0.56	0.66	3.30
—CH ₂ —CN	0.17	0.01	1.30
—NO		0.12	
—NO ₂	0.71	0.78	4.0
—CH ₂ —NO ₂			1.40

TABLE 9.1 Hammett and Taft Substituent Constants (Continued)

Substituent	Hammett constants		Taft constant σ^*
	σ_m	σ_p	
$-\text{CH}_2-\text{CH}_2-\text{NO}_2$			0.50
$-\text{CH}=\text{CHNO}_2$	0.33	0.26	
$m\text{-O}_2\text{N}-\text{C}_6\text{H}_4$		0.18	
$p\text{-O}_2\text{N}-\text{C}_6\text{H}_4$		0.24	
$(\text{NO}_2)_2\text{C}_6\text{H}_2$ — (picryl)	0.43	0.41	
$-\text{N}(\text{CO}-\text{CH}_3)(\text{CO}-\text{C}_6\text{H}_5)$			1.37
$-\text{N}(\text{CO}-\text{CH}_3)(\text{naphthyl})$			1.65
$-\text{O}^-$	-0.71	-0.52	
$-\text{OH}$	0.12	-0.37	1.34
$-\text{O}-\text{CH}_3$	0.12	-0.27	1.81
$-\text{O}-\text{C}_2\text{H}_5$	0.10	-0.24	1.68
$-\text{O}-\text{C}_3\text{H}_7$	0.00	-0.25	1.68
$-\text{O}-\text{CH}(\text{CH}_3)_2$	0.05	-0.45	1.62
$-\text{O}-\text{C}_4\text{H}_9$	-0.05	-0.32	1.68
$-\text{O}-\text{cyclopentyl}$			1.62
$-\text{O}-\text{cyclohexyl}$	0.29		1.81
$-\text{O}-\text{CH}_2-\text{cyclohexyl}$	0.18		1.31
$-\text{O}-\text{C}_6\text{H}_5$	0.25	-0.32	2.43
$-\text{O}-\text{CH}_2-\text{C}_6\text{H}_5$		-0.42	
$-\text{OCF}_3$	0.40	0.35	
$3,4\text{-O}-\text{CH}_2-\text{O}-$		-0.27	
$3,4\text{-O}-(\text{CH}_2-)_2\text{O}-$		-0.12	
$-\text{O}-\text{CO}-\text{CH}_3$	0.39	0.31	
$-\text{ONO}_2$			3.86
$-\text{O}-\text{N}=\text{C}(\text{CH}_3)_2$			1.81
$-\text{ONH}_3^+$			2.92
$-\text{CH}_2-\text{O}^-$			0.27
$-\text{CH}_2-\text{OH}$	0.08	0.08	0.31
$-\text{CH}_2-\text{O}-\text{CH}_3$			0.52
$-\text{CH}(\text{OH})-\text{CH}_3$			0.12
$-\text{CH}(\text{OH})-\text{C}_6\text{H}_5$			0.50
$p\text{-HO}-\text{C}_6\text{H}_4-$		-0.24	
$p\text{-CH}_3\text{O}-\text{C}_6\text{H}_4-$		-0.10	
$-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$			-0.06
$-\text{CH}_2-\text{C}(\text{OH})(\text{CH}_3)_2$			-0.25
$-\text{P}(\text{CH}_3)_2$	0.1	0.05	
$-\text{P}(\text{CH}_3)_3^+$	0.8	0.9	
$-\text{P}(\text{CF}_3)_2$	0.6	0.7	
$-\text{PO}_3\text{H}^-$	0.2	0.26	
$-\text{PO}(\text{OC}_2\text{H}_5)_2$	0.55	0.60	
$-\text{SH}$	0.25	0.15	1.68
$-\text{SCH}_3$	0.15	0.00	1.56
$-\text{S}(\text{CH}_3)_2^+$	1.0	0.9	
$-\text{SCH}_2\text{CH}_3$	0.23	0.03	1.56
$-\text{SCH}_2\text{CH}_2\text{CH}_3$			1.49
$-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$			1.44
$-\text{S}-\text{cyclohexyl}$			1.93
$-\text{SC}_6\text{H}_5$	0.30		1.87
$-\text{SC}(\text{C}_6\text{H}_5)_3$			0.69
$-\text{SCH}_2\text{C}_6\text{H}_5$			1.56
$-\text{SCH}_2\text{CH}_2\text{C}_6\text{H}_5$			1.44
$-\text{CH}_2\text{SH}$	0.03		0.62

TABLE 9.1 Hammett and Taft Substituent Constants (Continued)

Substituent	Hammett constants		Taft constant σ^*
	σ_m	σ_p	
—CH ₂ SCH ₂ C ₆ H ₅			0.37
—SCF ₃	0.40	0.50	
—SCN	0.63	0.52	3.43
—S—CO—CH ₃	0.39	0.44	
—S—CONH ₂	0.34		2.07
—SO—CH ₃	0.52	0.49	
—SO—C ₆ H ₅			3.24
—CH ₂ —SO—CH ₃			1.33
—SO ₂ —CH ₃	0.60	0.68	3.68
—SO ₂ —CH ₂ CH ₃			3.74
—SO ₂ —CH ₂ CH ₂ CH ₃			3.68
—SO ₂ —C ₆ H ₅	0.67		3.55
—SO ₂ —CF ₃	0.79	0.93	
—SO ₂ —NH ₂	0.46	0.57	
—CH ₂ —SO ₂ —CH ₃			1.38
—SO ₃ ⁻	0.05	0.09	0.81
—SO ₃ H		0.50	
—SeCH ₃	0.1	0.0	
—Se—cyclohexyl			2.37
—SeCN	0.67	0.66	3.61
—Si(CH ₃) ₃	-0.04	-0.07	-0.81
—Si(CH ₂ CH ₃) ₃		0.0	
—Si(CH ₃) ₂ C ₆ H ₅			-0.87
—Si(CH ₃) ₂ —O—Si(CH ₃) ₃			-0.81
—CH ₂ Si(CH ₃) ₃	-0.16	-0.22	-0.25
—CH ₂ CH ₂ Si(CH ₃) ₃			-0.25
—Sn(CH ₃) ₃		0.0	
—Sn(CH ₂ CH ₃) ₃		0.0	

TABLE 9.2 pK_a° and Rho Values for Hammett Equation

Acid	pK_a°	ρ
Arenearsonic acids		
pK_1	3.54	1.05
pK_2	8.49	0.87
Areneboronic acids (in aqueous 25% ethanol)		
	9.70	2.15
Arenephosphonic acids		
pK_1	1.84	0.76
pK_2	6.97	0.95
α -Aryladoximes	10.70	0.86
Benzeneseleninic acids	4.78	1.03
Benzenesulfonamides (20°C)	10.00	1.06
Benzenesulfonanilides (20°C)		
X—C ₆ H ₄ —SO ₂ —NH—C ₆ H ₅	8.31	1.16
C ₆ H ₅ —SO ₂ —NH—C ₆ H ₄ —X	8.31	1.74
Benzoic acids	4.21	1.00
Cinnamic acids	4.45	0.47
Phenols	9.92	2.23

TABLE 9.2 pK_a° and Rho Values for Hammett Equation (*Continued*)

Acid	pK_a°	ρ
Phenylacetic acids	4.30	0.49
Phenylpropionic acids (in aqueous 35% dioxane)	3.24	0.81
Phenylpropionic acids	4.45	0.21
Phenyltrifluoromethylcarbinols	11.90	1.01
Pyridine-1-oxides	0.94	2.09
2-Pyridones	11.65	4.28
4-Pyridones	11.12	4.28
Pyrroles	17.00	4.28
5-Substituted pyrrole-2-carboxylic acids	2.82	1.40
Thiobenzoic acids	2.61	1.0
Thiophenols	6.50	2.2
Trifluoroacetophenone hydrates	10.00	1.11
5-Substituted topolones	6.42	3.10
Protonated cations of		
Acetophenones	-6.0	2.6
Anilines	4.60	2.90
C-Aryl-N-dibutylamidines (in aqueous 50% ethanol)	11.14	1.41
N,N-Dimethylanilines	5.07	3.46
Isoquinolines	5.32	5.90
1-Naphthylamines	3.85	2.81
2-Naphthylamines	4.29	2.81
Pyridines	5.18	5.90
Quinolines	4.88	5.90

TABLE 9.3 pK_a° and Rho Values for Taft Equation

Acid	pK_a°	ρ
RCOOH	4.66	1.62
RCH ₂ COOH	4.76	0.67
RC≡C—COOH	2.39	1.89
H ₂ C=C(R)—COOH	4.39	0.64
(CH ₃) ₂ C=C(R)—COOH	4.65	0.47
<i>cis</i> -C ₆ H ₅ —CH=C(R)—COOH	3.77	0.63
<i>trans</i> -C ₆ H ₅ —CH=C(R)—COOH	4.61	0.47
R—CO—CH ₂ —COOH	4.12	0.43
HON=C(R)—COOH	4.84	0.34
RCH ₂ OH	15.9	1.42
RCH(OH) ₂	14.4	1.42
R ₁ CO—NHR ₂	22.0	3.1*
CH ₃ CO—C(R)=C(OH)CH ₃	9.25	1.78
CH ₃ CO—CH(R)—CO—OC ₂ H ₅	12.59	3.44
R—CO—NHOH	9.48	0.98
R ₁ R ₂ C=NOH (R ₁ , R ₂ not acyl groups)	12.35	1.18
(R)(CH ₃ CO)C=NOH	9.00	0.94
RC(NO ₂) ₂ H	5.24	3.60
RSH	10.22	3.50
RCH ₂ SH	10.54	1.47
R—CO—SH	3.52	1.62

TABLE 9.3 pK_a° and Rho Values for Taft Equation (*Continued*)

Acid	pK_a°	ρ
Protonated cations of		
RNH ₂	10.15	3.14
R ₁ R ₂ NH	10.59	3.23
R ₁ R ₂ R ₃ N	9.61	3.30
R ₁ R ₂ PH	3.59	2.61
R ₁ R ₂ R ₃ P	7.85	2.67

* σ^* for R₁CO and R₂.

Two modified sigma constants have been formulated for situations in which the substituent enters into resonance with the reaction center in an electron-demanding transition state (σ^+) or for an electron-rich transition state (σ^-). σ^- constants give better correlations in reactions involving phenols, anilines, and pyridines and in nucleophilic substitutions. Values of some modified sigma constants are given in Table 9.4.

TABLE 9.4 Special Hammett Sigma Constants

Substituent	σ_m^+	σ_p^+	σ_p^-
—CH ₃	-0.07	-0.31	-0.17
—C(CH ₃) ₃	-0.06	-0.26	
—C ₆ H ₅	0.11	-0.18	
—CF ₃	0.52	0.61	0.74
—F	0.35	-0.07	0.02
—Cl	0.40	0.11	0.23
—Br	0.41	0.15	0.26
—I	0.36	0.14	
—CN	0.56	0.66	0.88
—CHO			1.13
—CONH ₂			0.63
—COCH ₃			0.85
—COOH	0.32	0.42	0.73
—CO—OCH ₃	0.37	0.49	0.66
—CO—OCH ₂ CH ₃	0.37	0.48	0.68
—N ₂ ⁺			3.2
—NH ₂	0.16	-1.3	-0.66
—N(CH ₃) ₂		-1.7	
—N(CH ₃) ₃ ⁺	0.36	0.41	
—NH—CO—CH ₃		-0.60	
—NO ₂	0.67	0.79	1.25
—OH		-0.92	
—O ⁻			-0.81
—OCH ₃	0.05	-0.78	-0.27
—SF ₅			0.70
—SCF ₃			0.57
—SO ₂ CH ₃			1.05
—SO ₂ CF ₃			1.36