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 and the reaction parameter is known or can be calculated. The Hammett equation

$$\log \frac{K}{K}$$

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, $_m$ is an approximate measure of the size of the inductive effect of a given substituent and $_p$ $_m$ is an approximate measure of a substituent's resonance effect. Values of Hammett sigma constants are listed in Table 9.1.

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

The reaction parameter 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, * and $_m$ values are often related by the expression $_m$ 0.217 * — 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 CH_2 group, which enables * values to be estimated for RCH_2 groups not otherwise available.

TABLE 9.1 Hammett and Taft Substituent Constants

Substituent	Hammett constants		Taft constant
	$_m$	$_p$	*
AsO_3H	0.09	0.02	0.06
$B(OH)_2$	0.01	0.45	
Br	0.39	0.23	2.84
CH_2Br			1.00
m-BrC_6H_4		0.09	
p-BrC_6H_4		0.08	
CH_3	0.07	0.17	0.0
CH_2CH_3	0.07	0.15	0.10
$CH_2CH_2CH_3$	0.05	0.15	0.12
$CH(CH_3)_2$	0.07	0.15	0.19
$CH_2CH_2CH_2CH_3$	0.07	0.16	0.13
$CH_2CH(CH_3)_2$	0.07	0.12	0.13
$CH(CH_3)CH_2CH_3$		0.12	0.19
$C(CH_3)_3$	0.10	0.20	0.30
$CH_2CH_2CH_2CH_2CH_3$			0.25
$CH_2CH_2CH(CH_3)_2$			0.17

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PHYSICOCHEMICAL RELATIONSHIPS

TABLE 9.1 Hammett and Taft Substituent Constants (*Continued*)

Substituent	Hammett constants		Taft constant
	m	*p*	*
9 $CH_2C(CH_3)_3$		0.23	0.12
9 $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$			0.37
Cyclopropyl9	0.07	0.21	
Cyclohexyl9			0.15
93,4-$(CH_2)_2$ (fused)		0.26	
93,4-$(CH_2)_3$9 (fused ring)		0.48	
93,4-$(CH)_4$9 (fused ring)	0.06	0.04	
9CH''CH_2	0.02		0.56
9CH''$C(CH_3)_2$			0.19
9CH''$CHCH_3$, *trans*			0.36
9$CH_2$9CH''CH_2			0.0
9CH''CHC_6H_5	0.14	0.05	0.41
9C#CH	0.21	0.23	2.18
9C#CC_6H_5	0.14	0.16	1.35
9$CH_2$9C#CH			0.81
9C_6H_5	0.06	0.01	0.60
p-$CH_3C_6H_4$9		0.5	
Naphthyl9 (both 1- and 2-)			0.75
9$CH_2C_6H_5$		0.46	0.22
9$CH_2CH_2$9C_6H_5			0.06
9$CH(CH_3)C_6H_5$			0.37
9$CH(C_6H_5)_2$			0.41
9$CH_2$9$C_{10}H_7$			0.44
2-Furoyl 9			0.25
3-Indolyl 9			0.06
2-Thienyl 9			1.31
2-Thienylmethylene9			0.31
9CHO	0.36	0.22	
9$COCH_3$	0.38	0.50	1.65
9$COCH_2CH_2$		0.48	
9$COCH(CH_3)_2$		0.47	
9$COC(CH_3)_3$		0.32	
9$COCF_3$	0.65		3.7
9COC_6H_5	0.34	0.46	2.2
9$CONH_2$	0.28	0.36	1.68
9$CONHC_6H_5$			1.56
9CH_2COCH_3			0.60
9CH_2CONH_2			0.31
9$CH_2CH_2CONH_2$			0.19
9$CH_2CH_2CH_2CONH_2$			0.12
9$CH_2CONHC_6H_5$			0.0
9COO	0.1	0.0	1.06
9COOH	0.36	0.43	2.08
9CO9OCH_3	0.32	0.39	2.00
9CO9OCH_2CH_3	0.37	0.45	2.12
9CH_2CO9OCH_3			1.06
9CH_2CO9OCH_2CH_3			0.82
9CH_2COO			0.06
9CH_2CH_2COOH			
9Cl	0.03	0.07	
9CCl_3	0.37	0.23	2.96
9$CHCl_2$	0.47		2.65
			1.94

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 $—CH_2—$ group, which enables σ^* values to be estimated for $R—CH_2—$ groups not otherwise available.

TABLE 9.1 Hammett and Taft Substituent Constants

Substituent	Hammett constants		Taft constant
	σ_m	σ_p	σ^*
$—AsO_3H^-$	−0.09	−0.02	0.06
$—B(OH)_2$	0.01	0.45	
—Br	0.39	0.23	2.84
$—CH_2Br$			1.00
m-$BrC_6H_4—$		0.09	
p-$BrC_6H_4—$		0.08	
$—CH_3$	−0.07	−0.17	0.0
$—CH_2CH_3$	−0.07	−0.15	−0.10
$—CH_2CH_2CH_3$	−0.05	−0.15	−0.12
$—CH(CH_3)_2$	−0.07	−0.15	−0.19
$—CH_2CH_2CH_2CH_3$	−0.07	−0.16	−0.13
$—CH_2CH(CH_3)_2$	−0.07	−0.12	−0.13
$—CH(CH_3)CH_2CH_3$		−0.12	−0.19
$—C(CH_3)_3$	−0.10	−0.20	−0.30
$—CH_2CH_2CH_2CH_2CH_3$			−0.25
$—CH_2CH_2CH(CH_3)_2$			−0.17

TABLE 9.1 Hammett and Taft Substituent Constants (*Continued*)

Substituent	Hammett constants		Taft constant
	m	*p*	*
9 CH_2Cl	0.12	0.18	1.05
9 CH_2CH_2Cl			0.38
9 CH_2CCl_3			0.75
9 $CH_2CH_2CCl_3$			0.25
9 CH '' CCl_2			1.00
9 CH_2CH '' CCl_2			0.19
p-$ClC_6H_4$9		0.08	
9F	0.34	0.06	3.21
9 CF_3	0.43	0.54	2.61
9 CHF_2			2.05
9 CH_2F			1.10
9 CH_2CF_3			0.90
9 $CH_2CF_2CF_2CF_3$			0.87
9 C_6F_5	0.12	0.03	
9 $Ge(CH_3)_3$		0.0	
9 $Ge(CH_2CH_3)_3$		0.0	
9H	0.00	0.00	0.49
9I	0.35	0.28	2.46
9 CH_2I			0.85
9 IO_2	0.70	0.76	
9 N_2	1.76	1.91	
9 N_3 (azide)	0.33	0.08	2.62
9 NH_2	0.16	0.66	0.62
9 NH_3	1.13	1.70	3.76
9 $CH_2$9 NH_2			0.50
9 $CH_2$9 NH_3			2.24
9NH9 CH_3	0.30	0.84	
9NH9 C_2H_5	0.24	0.61	
9NH9 C_4H_9	0.34	0.51	
9NH(CH_3)$_2$			4.36
9 $NH_2$9 CH_3	0.96		3.74
9 $NH_2$9 C_2H_5	0.96		3.74
9N(CH_3)$_3$	0.88	0.82	4.55
9 $N(CH_3)_2$	0.2	0.83	0.32
9 $CH_2$9 $N(CH_3)_3$			1.90
9 $N(CF_3)_2$	0.45	0.53	
p-H_2N9 $C_6H_5$9		0.30	
9NH9 CO9 CH_3	0.21	0.00	1.40
9NH9 CO9 C_2H_5			1.56
9NH9 CO9 C_6H_5	0.22	0.08	1.68
9NH9 CHO	0.25		1.62
9NH9 CO9 NH_2	0.18		1.31
9NH9 OH	0.04	0.34	
9NH9 CO9 OC_2H_5	0.33		1.99
9 $CH_2$9 NH9 CO9 CH_3			0.43
9NH9 $SO_2$9 C_6H_5			1.99
9NH9 NH_2	0.02	0.55	
9 CN	0.56	0.66	3.30
9 $CH_2$9 CN	0.17	0.01	1.30
9 NO		0.12	
9 NO_2	0.71	0.78	4.0
9 $CH_2$9 NO_2			1.40

TABLE 9.1 Hammett and Taft Substituent Constants (*Continued*)

Substituent	Hammett constants		Taft constant
	σ_m	σ_p	σ^*
—$CH_2C(CH_3)_3$		−0.23	−0.12
—$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$			−0.37
Cyclopropyl—	−0.07	−0.21	
Cyclohexyl—			−0.15
—3,4-$(CH_2)_2$ (fused)		−0.26	
—3,4-$(CH_2)_3$— (fused ring)		−0.48	
—3,4-$(CH)_4$— (fused ring)	0.06	0.04	
—$CH{=}CH_2$	0.02		0.56
—$CH{=}C(CH_3)_2$			0.19
—$CH{=}CHCH_3$, *trans*			0.36
—CH_2—$CH{=}CH_2$			0.0
—$CH{=}CHC_6H_5$	0.14	−0.05	0.41
—$C{\equiv}CH$	0.21	0.23	2.18
—$C{\equiv}CC_6H_5$	0.14	0.16	1.35
—CH_2—$C{\equiv}CH$			0.81
—C_6H_5	0.06	−0.01	0.60
p-$CH_3C_6H_4$—		−0.5	
Naphthyl— (both 1- and 2-)			0.75
—$CH_2C_6H_5$		0.46	0.22
—CH_2CH_2—C_6H_5			−0.06
—$CH(CH_3)C_6H_5$			0.37
—$CH(C_6H_5)_2$			0.41
—CH_2—$C_{10}H_7$			0.44
2-Furoyl—			0.25
3-Indolyl—			−0.06
2-Thienyl—			1.31
2-Thienylmethylene—			0.31
—CHO	0.36	0.22	
—$COCH_3$	0.38	0.50	1.65
—$COCH_2CH_2$		0.48	
—$COCH(CH_3)_2$		0.47	
—$COC(CH_3)_3$		0.32	
—$COCF_3$	0.65		3.7
—COC_6H_5	0.34	0.46	2.2
—$CONH_2$	0.28	0.36	1.68
—$CONHC_6H_5$			1.56
—CH_2COCH_3			0.60
—CH_2CONH_2			0.31
—$CH_2CH_2CONH_2$			0.19
—$CH_2CH_2CH_2CONH_2$			0.12
—$CH_2CONHC_6H_5$			0.0
—COO^-	−0.1	0.0	−1.06
—COOH	0.36	0.43	2.08
—CO—OCH_3	0.32	0.39	2.00
—CO—OCH_2CH_3	0.37	0.45	2.12
—CH_2CO—OCH_3			1.06
—CH_2CO—OCH_2CH_3			0.82
—CH_2COO			−0.06
—CH_2CH_2COOH	−0.03	−0.07	
—Cl	0.37	0.23	2.96
—CCl_3	0.47		2.65
—$CHCl_2$			1.94

TABLE 9.1 Hammett and Taft Substituent Constants (*Continued*)

Substituent	Hammett constants		Taft constant
	m	*p*	*
—CH_2—CH_2—NO_2			0.50
—CH''$CHNO_2$	0.33	0.26	
m-O_2N—C_6H_4		0.18	
p-O_2N—C_6H_4		0.24	
$(NO_2)_3C_6H_2$— (picryl)	0.43	0.41	
—N(CO—CH_3)(CO—C_6H_5)			1.37
—N(CO—CH_3)(naphthyl)			1.65
—O	0.71	0.52	
—OH	0.12	0.37	1.34
—O—CH_3	0.12	0.27	1.81
—O—C_2H_5	0.10	0.24	1.68
—O—C_3H_7	0.00	0.25	1.68
—O—$CH(CH_3)_2$	0.05	0.45	1.62
—O—C_4H_9	0.05	0.32	1.68
—O—cyclopentyl			1.62
—O—cyclohexyl	0.29		1.81
—O—CH_2—cyclohexyl	0.18		1.31
—O—C_6H_5	0.25	0.32	2.43
—O—CH_2—C_6H_5		0.42	
—OCF_3	0.40	0.35	
3,4-O—CH_2—O—		0.27	
3,4-O—(CH_2—)$_2$O—		0.12	
—O—CO—CH_3	0.39	0.31	
—ONO_2			3.86
—O—N''$C(CH_3)_2$			1.81
—ONH_3			2.92
—CH_2—O			0.27
—CH_2—OH	0.08	0.08	0.31
—CH_2—O—CH_3			0.52
—CH(OH)—CH_3			0.12
—CH(OH)—C_6H_5			0.50
p-HO—C_6H_4—		0.24	
p-CH_3O — C_6H_4 —		0.10	
—CH_2—CH(OH)—CH_3			0.06
—CH_2—C(OH)$(CH_3)_2$			0.25
—$P(CH_3)_2$	0.1	0.05	
—$P(CH_3)_3$	0.8	0.9	
—$P(CF_3)_2$	0.6	0.7	
—PO_3H	0.2	0.26	
—$PO(OC_2H_5)_2$	0.55	0.60	
—SH	0.25	0.15	1.68
—SCH_3	0.15	0.00	1.56
—$S(CH_3)_2$	1.0	0.9	
—SCH_2CH_3	0.23	0.03	1.56
—$SCH_2CH_2CH_3$			1.49
—$SCH_2CH_2CH_2CH_3$			1.44
—S—cyclohexyl			1.93
—SC_6H_5	0.30		1.87
—$SC(C_6H_5)_3$			0.69
—$SCH_2C_6H_5$			1.56
—$SCH_2CH_2C_6H_5$			1.44
—CH_2SH	0.03		0.62

TABLE 9.1 Hammett and Taft Substituent Constants (*Continued*)

Substituent	Hammett constants		Taft constant
	σ_m	σ_p	σ^*
—CH_2Cl	0.12	0.18	1.05
—CH_2CH_2Cl			0.38
—CH_2CCl_3			0.75
—$CH_2CH_2CCl_3$			0.25
—$CH{=}CCl_2$			1.00
—$CH_2CH{=}CCl_2$			0.19
p-ClC_6H_4—		0.08	
—F	0.34	0.06	3.21
—CF_3	0.43	0.54	2.61
—CHF_2			2.05
—CH_2F			1.10
—CH_2CF_3			0.90
—$CH_2CF_2CF_2CF_3$			0.87
—C_6F_5	−0.12	−0.03	
—$Ge(CH_3)_3$		0.0	
—$Ge(CH_2CH_3)_3$		0.0	
—H	0.00	0.00	0.49
—I	0.35	0.28	2.46
—CH_2I			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_2H_5	−0.24	−0.61	
—NH—C_4H_9	−0.34	−0.51	
—$NH(CH_3)_2^+$			4.36
—NH_2—CH_3^+	0.96		3.74
—NH_2—$C_2H_5^+$	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	
p-H_2N—C_6H_5—		−0.30	
—NH—CO—CH_3	0.21	0.00	1.40
—NH—CO—C_2H_5			1.56
—NH—CO—C_6H_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_2H_5	0.33		1.99
—CH_2—NH—CO—CH_3			0.43
—NH—SO_2—C_6H_5			1.99
—NH—NH_2	−0.02	−0.55	
—CN	0.56	0.66	3.30
	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
	m	*p*	*
9 $CH_2SCH_2C_6H_5$			0.37
9 SCF_3	0.40	0.50	
9 SCN	0.63	0.52	3.43
9 S 9 $CO9CH_3$	0.39	0.44	
9 S 9 $CONH_2$	0.34		2.07
9 $SO9CH_3$	0.52	0.49	
9 $SO9C_6H_5$			3.24
9 $CH_2 9 SO9CH_3$			1.33
9 $SO_2 9 CH_3$	0.60	0.68	3.68
9 $SO_2 9 CH_2CH_3$			3.74
9 $SO_2 9 CH_2CH_2CH_3$			3.68
9 $SO_2 9 C_6H_5$	0.67		3.55
9 $SO_2 9 CF_3$	0.79	0.93	
9 $SO_2 9 NH_2$	0.46	0.57	
9 $CH_2 9 SO_2 9 CH_3$			1.38
9 SO_3	0.05	0.09	0.81
9 SO_3H		0.50	
9 $SeCH_3$	0.1	0.0	
9 Se 9 cyclohexyl			2.37
9	0.67	0.66	3.61
9 $Si(CH_3)_3$	0.04	0.07	0.81
9 $Si(CH_2CH_3)_3$		0.0	
9 $Si(CH_3)_2C_6H_5$			0.87
9 $Si(CH_3)_2 9 O 9 Si(CH_3)_3$			0.81
9 $CH_2Si(CH_3)_3$	0.16	0.22	0.25
9 $CH_2CH_2Si(CH_3)_3$			0.25
9 $Sn(CH_3)_3$		0.0	
9 $Sn(CH_2CH_3)_3$		0.0	

TABLE 9.2 pK_a and Rho Values for Hammett Equation

Acid	pK_a	
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
-Aryladoximes	10.70	0.86
Benzeneselenic acids	4.78	1.03
Benzenesulfonamides (20 C)	10.00	1.06
Benzenesulfonanilides (20 C)		
X 9 $C_6H_4 9 SO_2 9 NH 9 C_6H_5$	8.31	1.16
$C_6H_5 9 SO_2 9 NH 9 C_6H_4 9$ X	8.31	1.74
Benzoic acids	4.21	1.00
Cinnamic acids	4.45	0.47
Phenols	9.92	2.23

TABLE 9.1 Hammett and Taft Substituent Constants (*Continued*)

Substituent	Hammett constants		Taft constant
	σ_m	σ_p	σ^*
—CH_2—CH_2—NO_2			0.50
—CH═$CHNO_2$	0.33	0.26	
m-O_2N—C_6H_4		0.18	
p-O_2N—C_6H_4		0.24	
$(NO_2)_3C_6H_2$— (picryl)	0.43	0.41	
—N(CO—CH_3)(CO—C_6H_5)			1.37
—N(CO—CH_3)(naphthyl)			1.65
—O^-	−0.71	−0.52	
—OH	0.12	−0.37	1.34
—O—CH_3	0.12	−0.27	1.81
—O—C_2H_5	0.10	−0.24	1.68
—O—C_3H_7	0.00	−0.25	1.68
—O—$CH(CH_3)_2$	0.05	−0.45	1.62
—O—C_4H_9	−0.05	−0.32	1.68
—O—cyclopentyl			1.62
—O—cyclohexyl	0.29		1.81
—O—CH_2—cyclohexyl	0.18		1.31
—O—C_6H_5	0.25	−0.32	2.43
—O—CH_2—C_6H_5		−0.42	
—OCF_3	0.40	0.35	
3,4-O—CH_2—O—		−0.27	
3,4-O—(CH_2—)$_2$O—		−0.12	
—O—CO—CH_3	0.39	0.31	
—ONO_2			3.86
—O—N═$C(CH_3)_2$			1.81
—ONH_3^+			2.92
—CH_2—O^-			0.27
—CH_2—OH	0.08	0.08	0.31
—CH_2—O—CH_3			0.52
—CH(OH)—CH_3			0.12
—CH(OH)—C_6H_5			0.50
p-HO—C_6H_4—		−0.24	
p-CH_3O—C_6H_4—		−0.10	
—CH_2—CH(OH)—CH_3			−0.06
—CH_2—$C(OH)(CH_3)_2$			−0.25
—$P(CH_3)_2$	0.1	0.05	
—$P(CH_3)_3^+$	0.8	0.9	
—$P(CF_3)_2$	0.6	0.7	
—PO_3H^-	0.2	0.26	
—$PO(OC_2H_5)_2$	0.55	0.60	
—SH	0.25	0.15	1.68
—SCH_3	0.15	0.00	1.56
—$S(CH_3)_2^+$	1.0	0.9	
—SCH_2CH_3	0.23	0.03	1.56
—$SCH_2CH_2CH_3$			1.49
—$SCH_2CH_2CH_2CH_3$			1.44
—S—cyclohexyl			1.93
—SC_6H_5	0.30		1.87
—$SC(C_6H_5)_3$			0.69
—$SCH_2C_6H_5$			1.56
—$SCH_2CH_2C_6H_5$			1.44
—CH_2SH	0.03		0.62