Field and Resonance Components of Substituent Effects

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Abstract: $\mathcal{F}$ and $\mathcal{R}$, field and resonance constants, are calculated for 42 substituents from Hammett σ_m and σ_p values by assuming that any set of substituent constants (σ_m, σ_p, σ', etc.) may be expressed as $f\mathcal{F} + r\mathcal{R}$, that $r = 0$ for σ' (from ionization of 4-substituted bicyclo[2.2.2]octanecarboxylic acids), and that $\mathcal{R} = 0$ for the $(CH_3)_3N^+$ substituent. $\mathcal{F}$ and $\mathcal{R}$ are proposed as more accurately defined and more physically significant independent variables for correlating or predicting substituent effects on all kinds of rates, equilibria, and physical properties than any other pair out of 43 sets (reaction series) considered, including σ_m, σ_p, σ_p^-, σ_p^+, $\sigma_p - \sigma_m$, σ^*, σ_I, and σ_R^0. For all 43 sets, the weighting factors f and r are evaluated, the average correlation coefficient is 0.967 (and not significantly increased by the use of the three independent variables $\mathcal{F}$, σ_p^-, σ_p^+ instead of the two $\mathcal{F}$ and $\mathcal{R}$), and the importance of resonance, % $\mathcal{R}$, is calculated from f and r, *e.g.*, as 22% for σ_m, 53% for σ_p, 66% for σ_p^+, and 92% for $\sigma_p - \sigma_m$.

Since the original proposal of the Hammett equation, many phenomena have been found that follow an equation of the form $\log (k/k^0) = \rho\sigma$ or $P - P^0 = \rho\sigma$, but are not correlated well using the original substituent constants of Hammett. The resulting proliferation of alternate sets of σ values for special systems or applications has now reached the point of absurdity, and tends to destroy the convenience of, as well as confidence in the validity of, this equation. This paper will demonstrate that not more than two σ sets are significantly independent, and will express 43 sets as linear combinations of two σ sets ($\mathcal{F}$ and $\mathcal{R}$).

The $\rho\sigma$ equation summarizes a remarkably wide range of data using only two sets of reaction-independent substituent constants (σ_m and σ_p, Table I) with derived, substituent-independent reaction constants ρ to express the effect of each substituent on equilibrium constants, rate constants, and other properties of benzene derivatives.[3-8] Nevertheless, Hammett recognized in 1938[3] that a discrepancy appears when a nitro substituent is combined with a reaction center or group having a much stronger tendency than the carboxylate ion (CO_2^-) group to supply electrons. He proposed the use of a special *para* constant (σ_p^-) for the nitro substituent, over 60% larger than its normal (σ_p) value, for reactions of phenoxide ions or anilines (O^- or NH_2 groups).[9] Accurate σ_p^- values have now been determined for 21 substituents.[7,10,11] Brown and Okamoto likewise determined σ_p^+ values for 23 substituents in systems of the other extreme sort, ones with much more electron demand than a CO_2H group, based on relative rates of solvolysis of substituted cumyl (α,α-dimethylbenzyl) chlorides in 90% acetone–10% water solution at 25°, reactions which have highly electron-deficient, carbonium ion-like, transition states.[12] These alternative plots *vs.* σ_p^- and σ_p^+ (experimental values given in Table II) have proved to be extremely useful in assessing the magnitude of electron excess or deficiency at a reaction center in a transition state.

The origin of the discrepancy that is corrected for by the use of such a special set appears to be increased importance of resonance effects relative to nonresonance effects, at least for the numerous reaction series which give more nearly linear Hammett plots *vs.* σ_p^+ than *vs.* σ_p. On the other hand, resonance factors are clearly less important for σ_m than for σ_p because conjugation is not as complete for a *meta* substituent. The σ_m, σ_p, and σ_p^+ values for a given substituent are often considerably different (*e.g.*, +0.12, −0.27, and −0.78 for methoxy), with σ_m emphasizing its nonresonance capability and σ_p^+ emphasizing its resonance capability.

As a shorter designation for nonresonance effects, we lump pure field and inductive effects together under the name field effect. Unfortunately, there are not just two or three levels for the relative importance of field *vs.* resonance effects, but a broad continuum for equilibria, rates, and other properties of interest. This has led gradually to the proposal of numerous additional σ scales (types or sets of σ values), each based experimentally on a different single reaction series or occasionally on a pair or larger number of reaction series, and each representing a different blend of field and resonance effects, with the proportion uncertain. More than 20 σ sets are now in use, including σ_m, σ_p, σ_p^-, σ_p^+, σ_m^+, I, σ^n, σ_G, σ', σ'', σ^0, σ^*, σ_0, σ_0^- (σ^{-*}), σ_I, σ_R, σ_R^0, F, M, F', and M'.[13-28] With the number

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Table I. Substituents and Substituent Constants

No.	Substituent	Formula	$\sigma_m{}^a$	$\sigma_p{}^a$	$\sigma_p{}^{+\,c}$	$\mathcal{F}^c$	$\mathcal{R}^c$
1	Acetylamino	$NHCOCH_3$	0.210	−0.010	−0.249	0.470	−0.274
2	Acetoxy	$OCOCH_3$	0.390	0.310	0.178	0.679	−0.071
3	Acetyl	$COCH_3$	0.376^b	0.502^b	0.567	0.534	0.202
4	Acetylthio	$SCOCH_3$	0.390	0.440	0.431	0.602	0.102
5	Amino	NH_2	−0.160	−0.660	−1.111	0.037	−0,681
6	Bromo	Br	0.391^b	0.232^b	0.025	0.727	−0.176
7	*n*-Butoxy	$O(CH_2)_3CH_3$	0.100	−0.320	−0.733	0.411	−0.551
8	*t*-Butyl	$C(CH_3)_3$	−0.100	−0.197^b	−0.275	−0.104	−0.138
9	Carboxy	CO_2H	0.370	0.450	0.472	0.552	0.140
10	Carboxylate anion	CO_2^-	−0.100	0.000	0.109	−0.221	0.124
11	Chloro	Cl	0.373^b	0.227^b	0.035	0.690	−0.161
12	Cyano	CN	0.560^b	0.660^b	0.674	0.847	0.184
13	Diazonium cation	N_2^+	1.760	1.910	1.797	2.760	0.360
14	Dimethyl S^+ cation	$S(CH_3)_2^+$	1.000	0.900	0.660	1.678	−0.042
15	Ethoxy	OC_2H_5	0.100	−0.240	−0.577	0.363	−0.444
16	Ethoxycarbonyl	$CO_2C_2H_5$	0.370	0.450	0.472	0.552	0.140
17	Ethyl	C_2H_5	−0.070	−0.151^b	−0.218	−0.065	−0.114
18	Fluoro	F	0.337^b	0.062^b	−0.247	0.708	−0.336
19	Hydrogen (unsubst)	H	0.000^b	0.000^b	0.000	0.000	0.000
20	Hydroxy	OH	0.121^b	−0.370^b	−0.853	0.487	−0.643
21	Iodo	I	0.352^b	0.180^b	−0.034	0.672	−0.197
22	Iodoxy	IO_2	0.700	0.760	0.716	1.098	0.144
23	Mercapto	SH	0.250	0.150	0.019	0.464	−0.111
24	Methoxy	OCH_3	0.115^b	−0.268^b	−0.648	0.413	−0.500
25	Methyl	CH_3	−0.069^b	−0.170^b	−0.256	−0.052	−0.141
26	Methylseleno	$SeCH_3$	0.100	0.000	−0.109	0.221	−0.124
27	Methylsulfinyl	$SOCH_3$	0.520	0.490	0.386	0.860	0.007
28	Methylsulfonyl	SO_2CH_3	0.600	0.720	0.747	0.900	0.215
29	Methylthio	SCH_3	0.150	0.000	−0.164	0.332	−0.186
30	Nitro	NO_2	0.710^b	0.778^b	0.740	1.109	0.155
31	*n*-Pentoxy	$O(CH_2)_4CH_3$	0.100	−0.340	−0.771	0.423	−0.577
32	Phenoxy	OC_6H_5	0.252^b	−0.320^b	−0.899	0.747	−0.740
33	Phenyl	C_6H_5	0.060	−0.010	−0.085	0.139	−0.088
34	Phosphonate anion	PO_3H^-	0.200	0.260	0.288	0.288	0.098
35	Isopropoxy	$OCH(CH_3)_2$	0.100	−0.450	−0.986	0.488	−0.724
36	*n*-Propoxy	$O(CH_2)_2CH_3$	0.100	−0.250	−0.596	0.369	−0.457
37	2-Siliconeopentyl	$CH_2Si(CH_3)_3$	−0.160	−0.210	−0.234	−0.229	−0.081
38	Sulfamoyl	SO_2NH_2	0.460	0.570	0.608	0.679	0.188
39	Sulfonate anion	SO_3^-	0.050	0.090	0.121	0.057	0.058
40	Trifluoromethyl	CF_3	0.430	0.540	0.582	0.631	0.186
41	Trimethyl N^+ cation	$N(CH_3)_3^+$	0.880	0.820	0.636	1.460	0.000
42	Trimethylsilyl	$Si(CH_3)_3$	−0.040	−0.070	−0.093	−0.047	−0.044

[a] Experimental data.[6,7] [b] Based on thermodynamic equilibrium constants for benzoic acids in water at 25°; values of σ_m or σ_p without superscript estimated from other data on ionization of benzoic acids at 25°. [c] Calculated values derived by least squares as described in the text.

of sets of substituent constants now exceeding the average number of substituents in a set, and with different authors using the same sub- or superscripts for different sets, some simplification seems highly desirable.

Yukawa and Tsuno[29] pointed the way to a solution to this problem by representing substituent effects as a linear combination of two terms, using the original Hammett substituent constant (σ_m or σ_p) and the Brown and Okamoto constant ($\sigma_p{}^+$) as independent variables. This greatly improves the fit to many series of data, but it does not fully resolve the observed effects into their basic field and resonance components, because each independent variable is itself a mixture.[30] We have attempted to make a resolution, using as few arbitrary assumptions as possible and, in particular, avoiding the often made assumption that *meta* and *para* field effects are equal for the same substituent,

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Table II. Reaction Series and Input Data

			Values of σ for substituents[b]					
	Symbol	Reaction[a]	24 CH_3O	25 CH_3	11 Cl	30 NO_2	Other	Ref
			Natural Series					
1	σ_m	E for m-XC_6H_4COOH	0.115	−0.069	0.373	0.710	*t*	6, 7
2	σ_p	E for p-XC_6H_4COOH	−0.268	−0.170	0.227	0.778	*t*	6, 7
3	σ_p^-	E for p-XC_6H_4OH	−0.130	−0.150		1.240	*u*	7, 10, 11
4	σ_p^+	R for p-$XC_6H_4C(CH_3)_2Cl$[c]	−0.778	−0.311	0.114	0.790	*u*	12
5	σ'	E for 4-$XC_8H_{12}COOH$[d]	0.472	−0.013	0.739	1.058	*u*	17
6	σ'	E for 4-$XC_8H_{12}COOH$[e]					*u*	16
7	σ''	E for 4-$XC_6H_{10}COOH$[f]	0.255		0.335		*u*	18
8	σ_m^+	R for m-$XC_6H_4C(CH_3)_2Cl$[c]	0.047	−0.066	0.399	0.674	*u*	12
9	σ_3	E for 3-$XC_{10}H_8COOH$[g]				0.610	*u*	24
10	σ_4	E for 4-$XC_{10}H_8COOH$[g]	−0.360	−0.140	0.260	0.860	*u*	24
11	σ_5	E for 5-$XC_{10}H_8COOH$[g]	−0.010	0.010	0.290	0.540	*u*	24
12	σ_6	E for 6-$XC_{10}H_8COOH$[g]	−0.060	−0.050	0.170	0.410	*u*	24
13	σ_7	E for 7-$XC_{10}H_8COOH$[g]	−0.080	−0.070		0.360	*u*	24
14	σ^0	R for $HO^- + XC_6H_4CH_2COOEt$	−0.100	−0.124	0.281	0.792	*u*	30
15	σ_m^I	Ionization potential, $XC_6H_4CH_2$[h]		7.650		8.560	*u*	25
16	σ_p^I	Ionization potential, $XC_6H_4CH_2$[h]	6.820	7.460	7.950		*u*	25
17	σ_m^Q	^{35}Cl quadrupole resonance[i]			34.936	35.457	*u*	26
18	σ_m^F	^{19}F nmr shift, XC_6H_4F[j]	−1.100	1.200	−2.000	−3.500	*u*	20
19	σ_p^F	^{19}F nmr shift, XC_6H_4F[j]	11.500	5.400	3.100	−9.300	*u*	20
20	σ_p^C	^{13}C nmr shift, XC_6H_5[k]	8.100	2.800	2.000	−6.000	*u*	27
21	σ^R	Infrared resonance standard[l]	−57.700	−16.600	−30.500	25.200	*u*	28
			Synthetic Series					
22	I	E for acids[m]				12.100	*u*	13
23	σ_p^n	E and R "normal" values[n]	−0.175	−0.129	0.238	0.778	*u*	14
24	σ_m^0	E and R "normal" values[o,p]	0.130	−0.070	0.370	0.700	*u*	20
25	σ_p^0	E and R "normal" values[o,p]	−0.120	−0.150	0.270	0.820	*u*	20
26	σ^*	R for XCH_2COOR'[p]	0.520	−0.100	1.050	1.400	*u*	19
27	σ^*	R for $XCOOR'$[p]		0.000			*u*	19
28	σ^*	R for $X_2CHCOOR'$[p]		−0.190	1.940		*u*	19
29	σ^*	R for XCH_2CH_2COOR'[p]		−0.115	0.385	0.500	*u*	19
30	σ^*	R for $XCH_2CH_2CH_2COOR'$[p]		0.130			*u*	19
31	σ^*	R for o-XC_6H_4COOR'[p]	−0.390	−0.170	0.200	0.800	*u*	19
32	σ_I	Inductive constant[q]	0.250	−0.050	0.470	0.630	*u*	19
33	σ_R^m	Resonance constant[r]	−0.190	−0.020	−0.100	0.070	*u*	21
34	σ_R^0	Resonance constant[r]	−0.410	−0.100	−0.200		*u*	21
35	σ^0	Defined as $\sigma_R^0 + \sigma_I$	−0.120	−0.150	0.270		*u*	21
36	F_{Dewar}	Calcd from σ_m and σ_p	0.200	−0.120	0.650	1.230	*u*	24
37	M	Calcd from σ_m and σ_p	−2.580	−0.770	−0.700	1.140	*u*	24
38	F'	Calcd from σ_m and σ_p	0.130	−0.140	0.630	1.260	*u*	24
39	M'	Calcd from σ_m and σ_p	−3.360	−1.000	−0.910	1.480	*u*	24
40	σ_p^+	Calcd from σ_m and σ_p	−0.648	−0.256	0.035	0.740	*t*	2
41	$\mathfrak{F}$	Calcd from σ_m and σ_p[s]	0.413	−0.052	0.690	1.109	*t*	2
42	$\mathcal{R}$	Calcd from σ' and σ_p	−0.500	−0.141	−0.161	0.155	*t*	2
43	$\sigma_p - \sigma_m$		−0.383	−0.101	−0.146	0.068	*t*	6, 7

[a] Based on acid dissociation constants (K_A) in water at 25° except where otherwise indicated. E = equilibrium $(1/\rho)\log(K/K^H)$ values. R = kinetic $(1/\rho)\log(k/k^H)$ values. Superscript H refers to the unsubstituted compound (X = H). Reaction constant ρ assumed to be 1.00 unless otherwise noted. For series **3**, $\rho = 2.23$; for series **14,** $\rho = 0.98$.

[b] Value for H = 0.000 except for series **15–17, 27, 29,** and **30.** See footnote *u*.

[c] Solvolysis in 90% acetone–10% water by volume, $\rho = -4.54$.

[d] Bicyclo[2.2.2]octane-1-carboxylic acids in 50% C_2H_5OH by weight, $\rho = 1.65$.

[e] Bicyclo[2.2.2]octane-1-carboxylic acids in 50% C_2H_5OH by volume, $\rho = 1.46$.

[f] *trans*-4-X-Cyclohexanecarboxylic acids.

[g] 1-Naphthoic acids in 50% C_2H_5OH by volume, $\rho = 1.46$.

[h] Benzyl free radicals, ionized in gas phase by electron impact, volts.

[i] Chlorobenzenes, chlorine nuclear quadrupole resonance frequency for crystals, megahertz.

[j] Fluorobenzenes, chemical shift in CCl_4 solution, parts per million.

[k] Benzenes, chemical shifts as neat liquids, parts per million, ^{13}C *para* to substituent.

[l] Benzenes, square root of absorbance of ring stretching band near 1600 cm^{-1}, $M^{-1/2}$ cm^{-1}.

[m] Inductive constants calculated from acid dissociation constants.

[n] Average value excluding reactions where substituents show abnormally strong resonance effects.

[o] Based on phenylacetic acids and esters.

[p] $\sigma^* = [\log(k/k^H)_B - \log(k/k^H)_A]/\rho$, second-order rate constants for basic or acidic hydrolysis, various esters, solvents, and temperatures. For series **26–30**, $\rho = 2.48$; for **31,** ρ same as for m- and p-X.

[q] σ_I for X = $0.45\sigma^*$ for XCH_2COOR'[p] for most of the values tabulated.

[r] Based on calculated σ_I values,[q] and on the assumption that the field effect is same for *para* as for *meta* substitution.

[s] See ref 31.

[t] See Table I for other values.

[u] Series **3** data are based on ionization of phenols in water at 25° except for substituents *9* and *40*, which are estimated from data on other reactions of phenols or anilines. Series **4** data are based on solvolysis of cumyl chlorides[c] except for substituents *1*, *5*, *20*, and *32*, which are estimated from data on other electrophilic reactions. Series **5** includes points for cyano and trimethylammonium substituents measured in a slightly different solvent (ref 16 and J. S. McIntyre, Ph.D. Thesis, Cornell University, 1962; C. F. Wilcox, Jr., and J. S. McIntyre, *J. Org. Chem.*, **30,** 777 (1965), but corrected to 50% ethanol by weight.[17] Value for substituent *19* (H) is 0.00 unless given below; other values used in calculations follow (**reaction series number**, *substituent number*, σ value); **3,** *3*, 0.840; *6*, 0.250; *8*, −0.140; *9*, 0.728; *10*, 0.240; *12*, 0.880; *13*, 3.040; *14*, 1.160; *16*, 0.640; *27*, 0.730; *28*, 0.980; *39*, 0.400; *40*, 0.740; *41*, 0.770; **4,** *1*, −0.600; *5*, −1.300; *6*, 0.150; *8*, −0.256; *9*, 0.421; *10*, −0.023; *12*, 0.659; *16*, 0.482; *17*, −0.295; *18*, −0.073; *20*, −0.920; *21*, 0.135; *29*, −0.604; *32*, −0.500; *33*, −0.179; *40*, 0.612; *41*, 0.408; *42*, 0.021; **5,** *6*, 0.736; *9*, 0.468; *10*, −0.298; *12*, 0.930; *16*, 0.473; *17*, −0.020; *20*, 0.370; *40*, 0.627; *41*, 1.500; **6,** *6*, 0.454; *12*, 0.579; *16*, 0.297; *20*, 0.283; **7,** *12*, 0.440; *20*, 0.227; **8,** *5*, −0.160; *6*, 0.405; *8*, −0.059; *9*, 0.322; *10*, −0.028; *12*, 0.562; *16*, 0.366; *17*, −0.064; *18*, 0.352; *21*, 0.359; *29*, 0.158; *33*, 0.109; *40*, 0.520; *41*, 0.359; *42*, 0.011; **9,** *6*, 0.340; *12*, 0.590; *20*, 0.060; **10,** *5*, −0.720; *6*, 0.300; *12*, 0.790; *20*, −0.520; **11,** *5*, −0.130; *6*, 0.300; *12*, 0.460; *20*, −0.060; **12,** *6*, 0.180; *12*, 0.340; *20*, −0.080; **13,** *6*, 0.070; *12*, 0.310; *20*, −0.100; **14,** *3*, 0.481; *6*, 0.300; *8*, −0.174; *17*, −0.131; *18*, 0.212; *29*, 0.083; *32*, 0.076; *33*, 0.039; **15,** *12*, 8.580; *18*, 8.180; *19*, 7.760; **16,** *12*, 8.360; *18*, 7.780; *19*, 7.760; **17,** *1*, 34.735; *5*, 34.428; *9*, 35.227; *19*, 34.622; *20*, 34.796; *40*, 35.073; **18,** *2*, −1.500; *5*, 0.400; *6*, −2.300; *9*, −0.900; *12*, −2.800; *18*, −3.000; *20*, −1.300; *21*, −2.400; *32*, −2.000; *40*, −2.100;

19, *3*, −6.600; *5*, 14.200; *6*, 2.500; *12*, −9.200; *18*, 6.800; *20*, 10.800; *21*, 1.500; *32*, 7.400; *33*, 2.900; *40*, −5.100; **20,** *1*, 5.600; *2*, 2.300; *3*, −4.200; *5*, 9.500; *6*, 1.000; *18*, 4.400; *20*, 7.300; *21*, 0.400; *32*, 5.100; **21,** *2*, −32.700; *3*, 30.700; *6*, −32.300; *12*, 15.100; *14*, 15.700; *16*, 25.900; *17*, −17.000; *18*, −46.400; *20*, −54.200; *40*, 17.800; **22**, *3*, 5.000; *9*, 6.500; *10*, −1.900; *12*, 10.000; *18*, 9.000; *32*, 6.500; *33*, 1.500; *41*, 13.600; **23,** *3*, 0.502; *5*, −0.297; *6*, 0.265; *9*, 0.406; *12*, 0.674; *18*, 0.056; *20*, −0.201; *21*, 0.299; *28*, 0.686; *40*, 0.532; *41*, 0.800; **24,** *3*, 0.340; *5*, −0.140; *6*, 0.380; *12*, 0.620; *16*, 0.360; *18*, 0.350; *20*, 0.040; *21*, 0.350; **25,** *3*, 0.460; *5*, −0.580; *6*, 0.260; *12*, 0.690; *16*, 0.460; *18*, 0.170; *20*, −0.130; *21*, 0.270; **26,** *3*, 0.600; *6*, 1.000; *8*, −0.165; *9*, 1.050; *12*, 1.300; *16*, 0.710; *17*, −0.115; *18*, 1.100; *20*, 0.555; *21*, 0.850; *28*, 1.320; *32*, 0.850; *33*, 0.215; *40*, 0.920; *41*, 1.900; *42*, −0.260; **27**, *3*, 1.650; *8*, −0.300; *17*, −0.100; *19*, 0.490; *33*, 0.600; *37*, −0.260; **28,** *17*, −0.225; *18*, 2.050; *33*, 0.405; **29,** *17*, −0.130; *19*, −0.100; *33*, 0.080; *40*, 0.320; **30,** *19*, −0.115; *33*, 0.020; *40*, 0.120; **31,** *6*, 0.210; *15*, −0.350; *18*, 0.240; *21*, 0.210; **32,** *1*, 0.280; *3*, 0.280; *5*, 0.100; *6*, 0.450; *8*, −0.070; *9*, 0.300; *12*, 0.580; *16*, 0.300; *17*, −0.050; *18*, 0.520; *20*, 0.250; *21*, 0.390; *23*, 0.250; *27*, 0.520; *28*, 0.590; *29*, 0.250; *32*, 0.380; *33*, 0.100; *40*, 0.410; **33**, *3*, 0.060; *6*, −0.070; *12*, 0.040; *18*, −0.170; *21*, −0.040; *27*, 0.000; *28*, 0.070; *40*, 0.010; **34,** *1*, −0.250; *5*, −0.480; *6*, −0.190; *18*, −0.350; *20*, −0.400; *21*, −0.120; *29*, −0.240; *33*, −0.100; **35**, *1*, 0.030; *5*, −0.380; *6*, 0.260; *18*, 0.170; *20*, −0.150; *21*, 0.270; *33*, 0.000; **36**, *1*, 0.360; *2*, 0.680; *3*, 0.650; *4*, 0.680; *5*, −0.280; *6*, 0.680; *7*, 0.170; *8*, −0.170; *9*, 0.640; *10*, −0.170; *12*, 0.970; *14*, 1.730; *15*, 0.170; *16*, 0.640; *17*, −0.120; *18*, 0.580; *20*, 0.210; *21*, 0.610; *22*, 1.210; *23*, 0.430; *26*, 0.170; *27*, 0.900; *28*, 1.040; *29*, 0.260; *31*, 0.170; *32*, 0.440; *33*, 0.100; *34*, 0.350; *35*, 0.170; *36*, 0.170; *37*, −0.280; *38*, 0.800; *39*, 0.090; *40*, 0.740; *41*, 1.520; *42*, −0.070; **37**, *1*, −1.260; *2*, −4.550; *3*, 1.240; *4*, 0.700; *5*, −3.640; *6*, −0.770; *7*, −2.840; *8*, −0.780; *9*, 0.910; *10*, 0.600; *12*, 1.230; *14*, 0.200; *15*, −2.280; *16*, 0.910; *17*, −0.640; *18*, −1.610; *20*, −3.360; *21*, −0.840; *22*, 1.050; *23*, −0.490; *26*, −0.560; *27*, 0.280; *28*, 1.400; *29*, −0.910; *31*, −3.010; *32*, −3.780; *33*, −0.420; *34*, 0.600; *35*, −3.750; *36*, −2.350; *37*, −1.370; *38*, 1.190; *39*, 0.280; *40*, 1.120; *41*, 0.390; *42*, −0.250; **38,** *1*, −0.330; *2*, 0.560; *3*, 0.680; *4*, 0.700; *5*, −0.380; *6*, 0.660; *7*, 0.100; *8*, −0.190; *9*, 0.660; *10*, −0.150; *12*, 1.000; *14*, 1.740; *15*, 0.110; *16*, 0.660; *17*, −0.130; *18*, 0.560; *20*, 0.120; *21*, 0.590; *22*, 1.240; *23*, 0.420; *26*, 0.160; *27*, 0.970; *28*, 1.080; *29*, 0.240; *31*, 0.090; *32*, 0.340; *33*, −0.110; *34*, 0.370; *35*, 0.070; *36*, 0.110; *37*, −0.320; *38*, 0.830; *39*, 0.100; *40*, 0.770; *41*, 1.530; *42*, −0.080; **39**, *1*, −1.640; *2*, −5.930; *3*, 1.620; *4*, 0.910; *5*, −4.750; *6*, −1.000; *7*, −3.700; *8*, −1.020; *9*, 1.190; *10*, 0.780; *12*, 1.600; *14*, 0.250; *15*, −2.970; *16*, 1.190; *17*, −0.830; *18*, −2.100; *20*, −4.380; *21*, −1.100; *22*, 1.370; *23*, −0.640; *26*, −0.730; *27*, 0.370; *28*, 1.830; *29*, −1.190; *31*, −3.920; *32*, −4.920; *33*, −0.550; *34*, 0.780; *35*, −4.890; *36*, −3.060; *37*, −1.780; *38*, 1.550; *39*, 0.370; *40*, 1.460; *41*, 0.510; *42*, −0.330.

which we shall show to be incorrect. We shall retain the idea of a practical distinction between field and resonance effects and show that the numerous σ sets are not independent, but that each is a linear combination of two basic σ sets, $\mathcal{F}$ and $\mathcal{R}$, which measure field and resonance capabilities of the substituents. This will provide, as a useful by-product, the field and resonance weighting factors, f and r, in $\sigma = f\mathcal{F} + r\mathcal{R}$, for 43 σ sets or reaction series. Field and resonance components of substituent effects are thus equated to $\rho f\mathcal{F}$ and $\rho r\mathcal{R}$, respectively, with the reaction constant ρ and the weighting factors f and r independent of substituent, and with $\mathcal{F}$ and $\mathcal{R}$ independent of reaction, solvent, and temperature.

The Relationship between Different Sets of Substituent Constants. As did Dewar and Grisdale,[24] we assume that we can neglect terms other than field and resonance terms in any σ for any substituent kept remote from the reaction center by three or more interposed atoms. Therefore, any substituent constant is

$$\sigma = f\mathcal{F} + r\mathcal{R} \tag{1}$$

where $\mathcal{F}$ and $\mathcal{R}$ are field and resonance constants, different for each substituent (CH_3, Cl, NO_2), and f and r are empirical sensitivities or weighting factors, independent of substituent but different for each set of substituent constants (σ_m, σ_p, σ_p^+, σ').[31]

From (1) it follows that any substituent constant for a given substituent S should be a linear combination of any other two for the same substituent

$$\sigma_{3S} = c_{31}\sigma_{1S} + c_{32}\sigma_{2S} \tag{2}$$

where numerical subscripts refer to reactions (sets or types of σ), and c_{31} and c_{32} are constants independent of the particular substituent S. For example, the 23 experimental σ_p^+ values in Table II may be used to evaluate a and b in $\sigma_p^+ = a\sigma_m + b\sigma_p$, and these may then be used to calculate σ_p^+ values for all substituents, yielding the calculated σ_p^+ set given in Table I, which is in satisfactory agreement with the 23 experimental data.

In practice, most fitting was done, instead, with eq 3

$$\sigma_{3S} = c_{31}\sigma_{1S} + c_{32}\sigma_{2S} + c_{312}$$

or

$$Z = aX + bY + i \tag{3}$$

e.g.

$$\sigma_p^+ = a\sigma_m + b\sigma_p + i$$

with a third constant or intercept, $i = c_{312}$, added to avoid giving the unsubstituted compound infinite weight, to avoid forcing the line to go through the origin, since measurements on the unsubstituted compound are in general no more accurate than those on substituted ones.

A computerized general-purpose linear least-squares multiple correlation analysis was used to determine the best values of a, b, and i, standard deviations, and correlation coefficients. To facilitate future reevaluations as more data become available, and for the simpler task of calculating $\mathcal{F}$ and $\mathcal{R}$ for a few additional substituents, or f and r for more reaction series, and for other quite different kinds of linear least-squares multiple correlation analyses, we are submitting elsewhere our FORTRAN IV program, which contains instructions about the form of input and output for a wide variety of applications.[32]

The Experimental Data. Table I lists alphabetically 42 substituents for which both σ_m and σ_p values have been measured, along with their σ_m and σ_p values.

Table II lists 43 different sets of substituent constants (39 taken from the literature plus 4 that we have added). We have separated out the first 21 as "natural series," each based experimentally on a *single* kind of reaction, to distinguish them from the 22 following "synthetic series" for average or hypothetical (imaginary) reactions. For beginning or basis sets, the

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(31) This $\mathcal{F}$ is not numerically identical with the F of Dewar and Grisdale,[24] nor is $\mathcal{R}$ the same as their M. We considered the alternate notation $\sigma = \phi\Phi + \psi\Psi$, but decided that it is not as attractive mnemonically.

(32) Linear Multiple Correlation by Least Squares, Version 2, by S. Unger and C. G. Swain, 12 pp, deposited as Document No. 9970 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $2.50 for photoprints, or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table III. Correlations *vs.* σ_m and σ_p

No.	Reaction series[a]	n	a	b	i	E_Z	C
1	δ_m	42	1.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00	1.000
2	σ_p	42	0.00 ± 0.00	1.00 ± 0.00	0.00 ± 0.00	0.00	1.000
3	$\sigma_p{}^-$	18	−0.24 ± 0.38	1.59 ± 0.34	0.09 ± 0.06	0.18	0.970
4	$\sigma_p{}^+$	23	−0.84 ± 0.28	1.81 ± 0.20	−0.07 ± 0.06	0.18	0.939
5	σ'	14	2.26 ± 0.14	−0.62 ± 0.11	−0.01 ± 0.03	0.07	0.990
6	σ'	5	1.42 ± 0.19	−0.35 ± 0.11	−0.02 ± 0.04	0.05	0.978
7	σ''	5	1.11 ± 0.15	−0.30 ± 0.08	0.01 ± 0.04	0.04	0.974
8	$\sigma_m{}^+$	20	0.53 ± 0.20	0.20 ± 0.15	0.06 ± 0.04	0.10	0.906
9	σ_3	5	0.74 ± 0.22	0.14 ± 0.14	0.02 ± 0.05	0.06	0.981
10	σ_4	9	−0.26 ± 0.14	1.31 ± 0.09	0.05 ± 0.03	0.05	0.997
11	σ_5	9	0.38 ± 0.15	0.28 ± 0.09	0.06 ± 0.03	0.05	0.981
12	σ_6	8	0.23 ± 0.03	0.31 ± 0.02	0.01 ± 0.01	0.01	0.999
13	σ_7	7	0.11 ± 0.10	0.35 ± 0.06	0.00 ± 0.02	0.03	0.988
14	σ^0	13	0.64 ± 0.07	0.43 ± 0.05	−0.01 ± 0.02	0.03	0.992
15	$\sigma_m{}^{\mathrm{I}}$	5	1.13 ± 0.47	0.11 ± 0.37	7.77 ± 0.08	0.10	0.971
16	$\sigma_p{}^{\mathrm{I}}$	6	−0.86 ± 0.84	1.96 ± 0.62	7.71 ± 0.17	0.24	0.888
17	$\sigma_m{}^{\mathrm{Q}}$	8	0.99 ± 0.41	0.12 ± 0.23	34.64 ± 0.09	0.11	0.943
18	$\sigma_m{}^{\mathrm{F}}$	15	−8.52 ± 1.06	2.36 ± 0.61	0.56 ± 0.26	0.44	0.942
19	$\sigma_p{}^{\mathrm{F}}$	15	9.84 ± 4.74	−22.1 ± 2.8	1.90 ± 1.14	2.10	9.959
20	$\sigma_p{}^{\mathrm{C}}$	14	7.62 ± 4.27	−14.6 ± 2.6	1.40 ± 1.07	1.76	0.917
21	σ^{R}	14	−1.46 ± 29	151.0 ± 19.0	−0.55 ± 6.26	11.8	0.926
22	I	11	20.0 ± 1.9	−4.49 ± 1.64	0.56 ± 0.52	1.08	0.982
23	$\sigma_p{}^{\mathrm{n}}$	16	0.22 ± 0.15	0.69 ± 0.09	0.04 ± 0.03	0.06	0.985
24	$\sigma_m{}^0$	13	0.96 ± 0.09	0.03 ± 0.06	0.00 ± 0.02	0.03	0.991
25	$\sigma_p{}^0$	13	0.47 ± 0.11	0.57 ± 0.07	0.01 ± 0.03	0.04	0.993
26	σ^*	21	2.87 ± 0.20	−0.63 ± 0.14	0.00 ± 0.04	0.12	0.980
27	σ^*	7	2.05 ± 2.31	1.26 ± 1.64	0.33 ± 0.09	0.16	0.974
28	σ^*	6	6.39 ± 0.17	−1.73 ± 0.24	−0.02 ± 0.02	0.03	0.999
29	σ^*	7	1.54 ± 0.36	−0.59 ± 0.30	−0.08 ± 0.03	0.06	0.977
30	σ^*	4	1.71 ± 1.05	−0.88 ± 0.76	−0.13 ± 0.05	0.05	0.896
31	σ^*	9	−0.03 ± 0.31	1.12 ± 0.23	−0.01 ± 0.07	0.09	0.967
32	σ_{I}	25	1.39 ± 0.08	−0.38 ± 0.05	−0.01 ± 0.02	0.06	0.977
33	$\sigma_{\mathrm{R}}{}^m$	13	−0.49 ± 0.09	0.50 ± 0.06	0.00 ± 0.02	0.03	0.940
34	$\sigma_{\mathrm{R}}{}^0$	12	−0.95 ± 0.14	0.88 ± 0.10	−0.03 ± 0.03	0.05	0.939
35	σ^0	11	0.45 ± 0.08	0.49 ± 0.05	−0.02 ± 0.02	0.03	0.992
36	F_{Dewar}	41	1.73 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00	1.000
37	M	41	−5.99 ± 0.84	6.87 ± 0.58	−0.13 ± 0.19	0.71	0.905
38	F'	41	1.57 ± 0.13	0.21 ± 0.09	−0.02 ± 0.03	0.11	0.977
39	M'	41	−7.81 ± 1.09	8.96 ± 0.76	−0.17 ± 0.24	0.92	0.905
40	$\sigma_{\mathrm{p}}{}^+$	42	−0.84 ± 0.14	1.81 ± 0.11	−0.07 ± 0.03	0.00	1.000
41	$\mathcal{F}$	42	2.18 ± 0.03	−0.58 ± 0.02	−0.01 ± 0.01	0.00	1.000
42	$\mathcal{R}$	42	−1.46 ± 0.14	1.98 ± 0.11	−0.07 ± 0.03	0.00	1.000
43	$\sigma_p - \sigma_m$	42	1.00 ± 0.00	−1.00 ± 0.00	0.00 ± 0.00	0.00	1.000

[a] More complete descriptions and references given in Table II.

natural series seem preferable, because in the synthetic series experimental errors are often magnified by random or arbitrary introduction of secondary standards or by small differences between two reaction series. The σ values recorded are mostly $(1/\rho)$ log (k/k^{H}) values at 25°, but some are log (k/k^{H}) or $P - P^{\mathrm{H}}$ or simply P values (where that is what the author tabulated), where k is a rate or equilibrium constant or P is an energy difference from spectral data or any property linearly related to such an energy difference, and superscript H refers to the unsubstituted compound. The value for H (substituent *19*) is 0.00 except for reaction series **15–17**, **27**, **29**, and **30**. Subtraction of the P or log k for H, or division by ρ, does not change the ratio of a to b values, nor any of the correlation coefficients or $\%\ \mathcal{R}$ values which follow. Therefore, we have used numbers tabulated by the authors in the literature without converting them to strictly comparable energy quantities. However, since division by ρ does change (proportionately) the absolute magnitudes of a, b, i, and all of the standard deviations, we do give ρ for the natural series in the footnotes to Table II wherever a different value than unity was used for a multiplier $(1/\rho)$ of a log (K/K^{H}) or log (k/k^{H}). Only reaction series with four or more substituents (counting H as one substituent) are included.

Correlation *vs.* σ_m and σ_p. Table III shows the result of using σ_m and σ_p as the independent sets (X and Y). It is reasonable to begin with these as the independent variables in the first multiple correlation because they are the most venerable of the substituent constants and still experimentally the two most complete and accurate sets of data available. Of the 19 other natural sets listed, all but two have correlation coefficients (C) of 0.900 or greater, and the average correlation coefficients is 0.963. The average correlation for all 43 sets is 0.967. The square of the correlation coefficient is the "coefficient of determination" and represents the fraction of the experimental variation of the dependent set (Z) which is explained by the variations of the independent sets (X and Y). Thus, on the average, 93% of the variation is explained or predictable from eq 3, leaving only 7% attributable to experimental errors and failures of the theory. Thus, this correlation is surprisingly satisfactory. (See also section below on superfluity of three independent variables.)

The working definition used to calculate the coefficient of determination (C^2) is $1 - (w/v)$, where w is $\Sigma(\sigma - \sigma_{\text{calcd}})^2/(n - 3)$ and v is $\Sigma(\sigma - \bar{\sigma})^2/(n - 1)$, *i.e.*, w and v are population-corrected squares of standard deviations of observed values (Z) from calculated values ($aX + bY + i$) and from the mean experimental value ($\bar{Z}$), respectively, and n is the number of substituents (including H) on which correlation is based. The ± values reported in Table III are standard deviations, also properly calculated for the correct number of degrees of freedom

$$a = \begin{vmatrix} \sum XZ & \sum XY & \sum X \\ \sum YZ & \sum Y^2 & \sum Y \\ \sum Z & \sum Y & n \end{vmatrix} \Big/ D \pm (w(n\sum Y^2 - (\sum Y)^2)/D)^{1/2}$$

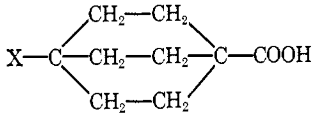
$$b = \begin{vmatrix} \sum X^2 & \sum XZ & \sum X \\ \sum XY & \sum YZ & \sum Y \\ \sum X & \sum Z & n \end{vmatrix} \Big/ D \pm (w(n\sum X^2 - (\sum X)^2)/D)^{1/2}$$

$$i = \begin{vmatrix} \sum X^2 & \sum XY & \sum XZ \\ \sum XY & \sum Y^2 & \sum YZ \\ \sum X & \sum Y & \sum Z \end{vmatrix} \Big/ D \pm (w(\sum X^2\sum Y^2 - (\sum XY)^2)/D)^{1/2}$$

$$D = \begin{vmatrix} \sum X^2 & \sum XY & \sum X \\ \sum XY & \sum Y^2 & \sum Y \\ \sum X & \sum Y & n \end{vmatrix}$$

where the bars denote the indicated determinants. E_Z is the error in Z, *i.e.*, the standard deviation between calculated and observed values of the dependent variable, $E_Z = \sqrt{w}$. Values of σ and C generally were rounded to three figures, and other values to two, in the final preparation of the tables in this paper, to permit presentation in a reasonable space.

The correlation coefficient is extraordinarily high (0.990) for σ' (series **5**[17]), based on the effect of 4-substituents (X) on the dissociation of bicyclo[2.2.2]octane-1-carboxylic acids.



Among the natural series, it is also high for alkaline hydrolysis of ethyl arylacetates (0.992) and for the σ_p^- series based on ionization of phenols (0.970). It is much lower for σ_p^+ (0.939) and for most of the resonance measures that have been proposed (0.940 – 0.905 for σ_R, σ_R^m, σ_R^0, M, and M'). Similarly, correlations with one of these resonance measures as one of the independent variables give poorer results. For example, correlations *vs.* σ_I and σ_R^0 (instead of *vs.* σ_m and σ_p) give relatively low correlation coefficients (average of 0.910 for the natural sets or 0.927 for all sets).

Calculation of $\mathcal{F}$ and $\mathcal{R}$. The principal deficiency of correlations *vs.* σ_m and σ_p (Table III) arises from the hybrid natures of σ_m and σ_p. Resonance still contributes to some extent to σ_m; likewise, field factors cannot be ignored in σ_p. To sort out these hybrid constants into pure field and resonance components, two more assumptions must be made about the quantitative importance of field (or resonance) effects for particular reaction series or substituents. One often made assumption is that any given substituent exerts the same field effect in the *meta* position as in the *para* position. We are not willing to adopt this assumption because the field effect could well be greater from a *meta* position (because it is closer) and, in fact, K_A is significantly larger for benzoic acids with a *m*-trimethylammonium or -dimethylsulfonium substituent than with the same group *para* (*cf.* σ_m and σ_p in Table I). Instead, we have adopted the assumption that the effect of 4-substituents on the dissociation constants of bicyclo[2.2.2]octane-1-carboxylic acids is entirely a field effect, *i.e.*, in this particular reaction series there is no resonance interaction at all (because there is no intervening conjugation or unsaturation). Our only other assumption (to be discussed further below) is that the trimethylammonium substituent has no resonance effect even in the σ_p series.

For pure and quite satisfactory field constants, we can use σ', based on 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids in this way. Unfortunately, the most extensive σ' series measured under accurately comparable conditions (series **5** of Table II, for 50% ethanol–50% water by weight) includes only 14 of the 42 substituents. However, this series has a very high correlation coefficient (0.990) when expressed in terms of σ_m and σ_p (Table III). Therefore, we can evaluate a and b in $\sigma' = a\sigma_m + b\sigma_p$ by least squares using these 14 experimental values, then calculate $\mathcal{F}$ values (calculated σ' values, series **41**) for all 42 substituents with confidence from $\mathcal{F} = a\sigma_m + b\sigma_p$. The two-parameter equation (2) is used rather than the three-parameter equation (3) at this point to force $\mathcal{F}$ for H to be exactly zero, to agree with the usual convention for substituent constants. The average deviation between calculated values ($\mathcal{F}$) and observed values (σ'), for the 14 where both exist, is less than 0.04.

This $\mathcal{F}$ set ($\mathcal{F}$ of Table I and series **41** of Table II) based on effect of 4-substituents on bicyclo[2.2.2]octane-1-carboxylic acid ionization appears to be a reasonable measure of the field potential or capability of substituents. The order of decreasing electron supply or increasing electron withdrawal by this measure is carboxylate anion (−0.22), *t*-butyl (−0.10), ethyl (−0.07), methyl (−0.05), amino (+0.04), phenyl (+0.14), methoxy (+0.41), acetylamino (+0.47), carboxy (+0.55), acetoxy (+0.68), chloro (+0.69), fluoro (+0.71), nitro (+1.11), and trimethylammonium cation (+1.46).

To obtain $\mathcal{R}$ values that are satisfactory measures of the resonance potential of substituents, field contributions may be removed from the σ_p set. The σ_p set (Table I and series **2** of Table II) includes significant field terms ($f\mathcal{F}$) mixed in with its not always dominant resonance terms ($r\mathcal{R}$). To remove these field terms, we make the final assumption that the resonance potential of the trimethylammonium ion substituent ($(CH_3)_3N^+$) is negligible ($\mathcal{R} = 0.0$) in the σ_p series. On the other hand, it does exert an extremely strong field ($\mathcal{F} = +1.46$).

The assumption that resonance is negligible for the trimethylammonium substituent in the σ_p series is reasonable theoretically because its nitrogen has no unshared electron pair to donate and, being a first-row element, also cannot expand its valence shell to accomodate more than eight electrons. The assumption is supported experimentally by the fact that ultraviolet spectra, which are strongly influenced by resonance in the excited singlet state and quite different for benzene and nitrobenzene derivatives, are practically identical for benzene and trimethylanilinium ion derivatives,[33] and by the fact that σ_p (+0.82) is less than σ_m (+0.88) by about the amount expected for the greater distance if resonance is negligible.[6,34] Thus, the trimethylammonium ion substituent appears to be incapable of either donating or accepting electrons by resonance. We are aware of discussions attributing large and variable entropy (electrostriction) effects to this substituent,[35] but are convinced that the Hammett equation and other *free*-energy correlations work in spite of entropy variations, that entropy effects of a similar kind and magnitude operate with CO_2^- and other charged substituents with which we must deal anyway, and that such effects can be considered as subcomponents of the field effect.

Using eq 4 α was calculated to be 0.56 by setting $\mathcal{R}$

$$\sigma_p = \alpha\mathcal{F} + \mathcal{R} \tag{4}$$

equal to zero for $(CH_3)_3N^+$. $\mathcal{R}$ values (set **42**) for all other substituents were calculated from eq 4 using this α, which is the weighting factor (regression coefficient) for the field constant ($\mathcal{F}$) in the σ_p set.

The resulting $\mathcal{R}$ set (Table I) is qualitatively reasonable as a measure of the resonance potential or capability of substituents. Amino, hydroxy, methoxy, acetylamino, methyl, and *t*-butyl are resonance electron donors of decreasing strength ($\mathcal{R}$ values of −0.68, −0.64, −0.50, −0.27, −0.14, and −0.14). Fluorine is about twice as strong a resonance donor as chlorine, bromine, or iodine (−0.34, −0.16, −0.18, −0.20). The best electron acceptor by resonance is the diazonium cation group (+0.36), but methylsulfonyl, acetyl, trifluoromethyl, cyano, nitro, carboxy, and carboxylate anion are also high (+0.22, +0.20, +0.19, +0.18, +0.16, +0.14, +0.12). However, these acceptors all have much larger positive field effects than resonance effects. Resonance effects are smaller for phenyl (−0.09 *vs.* +0.14 for its field effect), close to zero for dimethylsulfonium cation, methylsulfinyl, and sulfonate anion (−0.04, +0.01, +0.06), and zero by our basic assumption for trimethylammonium.

Only alkyl or substituted alkyl or silyl substituents among these 42 are electron donors by both $\mathcal{F}$ and $\mathcal{R}$ mechanisms. Far stronger electron donors are amino, hydroxy, and substituted amino and hydroxy substituents, which donate entirely through $\mathcal{R}$. Still better donors should be O^-, S^-, and NH^-, but there are not yet sufficient quantitative data on these substituents to permit their inclusion in this analysis. Other $\mathcal{F}$ acceptor but $\mathcal{R}$ donor substituents are mercapto (SH), methylthio (SCH_3), phenyl, and the halogens. Since $\mathcal{F}$ is larger than $\mathcal{R}$ but opposite in sign for the halogens, their field effect will usually be dominant except in reactions particularly sensitive to resonance (such as orientation in aromatic substitution). Presumably nitroso (NO) should also be in this group, but again not sufficient data are available. The only substituent out of the 42 which is an $\mathcal{F}$ *donor*, but $\mathcal{R}$ *acceptor*, is carboxylate anion.

Very strong electron acceptors by both $\mathcal{F}$ and $\mathcal{R}$ mechanisms are diazonium (N_2^+), nitro (NO_2), iodoxy (IO_2), methylsulfonyl (SO_2CH_3), cyano (CN), sulfamoyl (SO_2NH_2), trifluoromethyl (CF_3), acetyl ($COCH_3$), and carboxy (COOH). For these substituents, the *relative* importance of resonance ($\mathcal{R}/\mathcal{F}$) decreases in the order acetyl (0.38), trifluoromethyl (0.29), sulfamoyl (0.28), carboxy (0.25), methylsulfonyl (0.24), cyano (0.22), nitro (0.14), iodoxy and diazonium ion (0.13). This relatively high ratio for trifluoromethyl is in accord with expectation from the three equivalent $=CF_2F^-$ resonance structures that have been considered.[36]

Correlation *vs.* $\mathcal{F}$ and $\mathcal{R}$. The $\mathcal{F}$ and $\mathcal{R}$ sets (sets **41** and **42**) were used as new independent variables in a second multiple correlation ($f = a$, $r = b$), yielding Table IV. The correlation coefficient C ranges from 0.888 to 1.000, with a mean of 0.963 for the natural sets and 0.967 for all 43 sets.

The sensitivity to field effects (f) may be greater with *meta* substituents than with *para* (as for σ_m *vs.* σ_p or σ_m^{I} *vs.* σ_p^{I}) or may be greater with *para* substituents than with *meta* (as for σ_m^+ *vs.* σ_p^+ or σ_m^{F} *vs.* σ_p^{F}). Deviations from equality of f values for *meta* and *para* substituents do exceed 50%. It is therefore not a good approximation to assume that field effects are equal for *meta* and *para* substituents. The sensitivity to resonance effects (r) is much larger with *para* substituents than with *meta* (factor of 3.7 for σ_p *vs.* σ_m, or 4.6 for σ_p^+ *vs.* σ_m^+), but in general r is not close enough to zero to be negligible even in *meta*-substituted aromatic systems.

To assess the relative importance of field *vs.* resonance effects in different reaction series, one could compare the simple correlation coefficient in $\sigma = c\mathcal{F} + d$ with that in $\sigma = g\mathcal{R} + h$, or either the partial or the part correlation coefficient for $\mathcal{F}$ in $\sigma = f\mathcal{F} + r\mathcal{R} + i$ with the corresponding one for $\mathcal{R}$ in the same equation. Our program[32] calculates simple and partial correlation coefficients, but in Table IV we have listed instead "per cent characters," which also are calculated by the program.

These per cent characters afford the simplest meaningful way to assess the relative importance of $\mathcal{F}$ and $\mathcal{R}$ in different reaction series as contributing causes of the effects measured. Their principal advantage over simple or partial correlation coefficients is that they never add to more than 100%, whereas pairs of simple or partial correlation coefficients usually add to much more than 1.0 (typically 1.3 or more).

The "per cent resonance" (sensitivity to resonance effects) of any reaction series is defined in the simplest meaningful way, as

$$\%\mathcal{R} = \frac{100\psi|r|}{\phi|f| + \psi|r|}$$

where the bars denote absolute magnitudes and ϕ and ψ are merely scale factors with ϕ larger than ψ to correct for the fact that f values on the average will be smaller than r values because the average variation of $\mathcal{F}$ values from their mean ($\bar{\mathcal{F}}$) of 0.54 (for all 42 substituents) is slightly greater than the average variation of $\mathcal{R}$ values

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[35] Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4976 (1958).

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Table IV. Correlation *vs.* $\mathcal{F}$ and $\mathcal{R}$

No.	Reaction series[a]	n	f	r	i	E_z	C	% $\mathcal{R}$
1	σ_m	42	0.60 ± 0.00	0.27 ± 0.00	0.00 ± 0.00	0.00	1.000	22 ± 0
2	σ_p	42	0.56 ± 0.00	1.00 ± 0.00	0.00 ± 0.00	0.00	1.000	53 ± 0
3	σ_p^-	18	0.75 ± 0.06	1.52 ± 0.24	0.09 ± 0.06	0.18	0.970	56 ± 4
4	σ_p^+	23	0.51 ± 0.09	1.58 ± 0.14	−0.07 ± 0.06	0.18	0.939	66 ± 5
5	σ'	14	1.02 ± 0.04	−0.01 ± 0.08	−0.01 ± 0.03	0.07	0.990	1 ± 5
6	σ'	5	0.66 ± 0.07	0.03 ± 0.07	−0.02 ± 0.04	0.05	0.978	3 ± 6
7	σ''	5	0.50 ± 0.06	0.00 ± 0.05	0.01 ± 0.04	0.04	0.974	0 ± 7
8	σ_m^+	20	0.43 ± 0.05	0.34 ± 0.11	0.06 ± 0.04	0.10	0.906	33 ± 8
9	σ_3	5	0.53 ± 0.07	0.34 ± 0.09	0.02 ± 0.05	0.06	0.981	29 ± 6
10	σ_4	9	0.58 ± 0.04	1.24 ± 0.06	0.05 ± 0.03	0.05	0.997	57 ± 2
11	σ_5	9	0.39 ± 0.05	0.38 ± 0.06	0.06 ± 0.03	0.05	0.981	38 ± 5
12	σ_6	8	0.31 ± 0.01	0.38 ± 0.01	0.01 ± 0.01	0.01	0.999	43 ± 1
13	σ_7	7	0.26 ± 0.03	0.38 ± 0.04	0.00 ± 0.02	0.03	0.988	48 ± 4
14	σ^0	13	0.63 ± 0.03	0.61 ± 0.04	−0.01 ± 0.02	0.03	0.992	37 ± 2
15	σ_m^{I}	5	0.74 ± 0.11	0.41 ± 0.26	7.77 ± 0.08	0.10	0.971	26 ± 12
16	σ_p^{I}	6	0.58 ± 0.28	1.73 ± 0.44	7.71 ± 0.17	0.24	0.888	65 ± 12
17	σ_m^{Q}	8	0.66 ± 0.13	0.38 ± 0.14	34.64 ± 0.09	0.11	0.943	26 ± 8
18	σ_m^{F}	15	−3.81 ± 0.37	0.08 ± 0.38	0.56 ± 0.26	0.44	0.942	1 ± 6
19	σ_p^{F}	15	−6.46 ± 1.69	−19.4 ± 1.78	1.90 ± 1.14	2.10	0.959	65 ± 6
20	σ_p^{C}	14	−3.59 ± 1.52	−12.5 ± 1.68	1.40 ± 1.07	1.76	0.917	68 ± 10
21	σ^{R}	14	−3.12 ± 9.71	112.0 ± 12.7	−0.55 ± 6.26	1.18	0.926	96 ± 13
22	I	11	9.56 ± 0.59	0.88 ± 1.22	0.56 ± 0.52	1.08	0.982	5 ± 7
23	σ_p^{n}	16	0.52 ± 0.05	0.75 ± 0.06	0.04 ± 0.03	0.06	0.985	47 ± 3
24	σ_m^0	13	0.60 ± 0.03	0.29 ± 0.04	0.00 ± 0.02	0.03	0.991	23 ± 2
25	σ_p^0	13	0.60 ± 0.04	0.70 ± 0.04	0.01 ± 0.03	0.04	0.993	42 ± 2
26	σ^*	21	1.38 ± 0.06	0.14 ± 0.10	0.00 ± 0.04	0.12	0.980	6 ± 4
27	σ^*	7	1.94 ± 0.51	1.81 ± 1.03	0.33 ± 0.09	0.16	0.974	37 ± 15
28	σ^*	6	2.88 ± 0.06	−0.01 ± 0.20	−0.02 ± 0.02	0.03	0.999	0 ± 4
29	σ^*	7	0.60 ± 0.06	−0.17 ± 0.20	−0.08 ± 0.03	0.06	0.977	15 ± 15
30	σ^*	4	0.53 ± 0.22	−0.43 ± 0.48	−0.13 ± 0.05	0.05	0.896	33 ± 27
31	σ^*	9	0.61 ± 0.09	1.11 ± 0.16	−0.01 ± 0.07	0.09	0.967	53 ± 5
32	σ_{I}	25	0.60 ± 0.04	0.00 ± 0.05	−0.01 ± 0.02	0.06	0.956	0 ± 5
33	σ_{R}^m	13	−0.02 ± 0.03	0.36 ± 0.04	0.00 ± 0.02	0.03	0.940	92 ± 10
34	σ_{R}^0	12	−0.07 ± 0.05	0.63 ± 0.07	−0.03 ± 0.03	0.05	0.939	84 ± 10
35	σ^0	11	0.54 ± 0.03	0.61 ± 0.04	−0.02 ± 0.02	0.03	0.992	41 ± 2
36	F_{Dewar}	41	1.04 ± 0.00	0.47 ± 0.00	0.00 ± 0.00	0.00	1.000	22 ± 0
37	M	41	0.25 ± 0.27	5.27 ± 0.40	−0.13 ± 0.19	0.71	0.905	93 ± 7
38	F'	41	1.06 ± 0.04	0.63 ± 0.06	−0.02 ± 0.03	0.11	0.977	27 ± 2
39	M'	41	0.32 ± 0.35	6.86 ± 0.52	−0.17 ± 0.24	0.92	0.905	93 ± 7
40	σ_p^+	42	0.44 ± 0.00	1.65 ± 0.00	0.00 ± 0.00	0.00	1.000	70 ± 0
41	$\mathcal{F}$	42	1.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00	1.000	0 ± 0
42	$\mathcal{R}$	42	0.00 ± 0.00	1.00 ± 0.00	0.00 ± 0.00	0.00	1.000	100 ± 0
43	$\sigma_p - \sigma_m$	42	−0.04 ± 0.00	0.73 ± 0.00	0.00 ± 0.00	0.00	1.000	92 ± 0

[a] More complete descriptions and references given in Table II.

from their mean ($\bar{\mathcal{R}}$) of −0.13. Average deviations

$$\phi = \frac{\sum|\mathcal{F} - \bar{\mathcal{F}}|}{42} = 0.365$$

$$\psi = \frac{\sum|\mathcal{R} - \bar{\mathcal{R}}|}{42} = 0.228$$

are used instead of standard deviations to minimize the effect of extreme substituents such as N_2^+. The "per cent field" (sensitivity to field effects) is % $\mathcal{F}$ = 100 − % $\mathcal{R}$.

The uncertainty (standard deviation or error, E) in each calculated % $\mathcal{R}$ value is accordingly

$$E_{\%\mathcal{R}} = [E_r^2(\partial\%\mathcal{R}/\partial r)^2 + E_f^2(\partial\%\mathcal{R}/\partial f)^2]^{1/2} = \frac{100\phi\psi[E_r^2|f|^2 + E_f^2|r|^2]^{1/2}}{(\phi|f| + \psi|r|)^2}$$

and these uncertainties are appended as ± values to each % $\mathcal{R}$ reported in Table IV.

Of the 43 series listed, 27 show a preponderance of field effects, while 16 are dominated by resonance effects. The purest field substituent constants previously used appear to be σ' and σ_{I} (both >96% $\mathcal{F}$, <4% $\mathcal{R}$). Acid ionization of unconjugated systems is chiefly determined by $\mathcal{F}$ (5% $\mathcal{R}$ for *I*, 22% $\mathcal{R}$ for σ_m), but alkaline hydrolysis of ethyl arylacetates is less so (37% $\mathcal{R}$). As a measure of $\mathcal{R}$, σ_p is better (53%). Although σ_p^+, σ_p^{F}, and σ_{R}^0 are still better (65–84%), they have lower correlation coefficients than σ_m, σ_p, σ_p^-, σ', or σ'' (which are all above 0.970). Resonance is less important in stabilizing phenoxide ions (σ_p^-, 56%) than in stabilizing transition states leading to cumyl cations (σ_p^+, 66%). The purest resonance substituent constant previously used[33] has an average dependence on $\mathcal{R}$ of 92 ± 0% ($\sigma_p - \sigma_m$).

For reactions of aliphatic esters, Taft's method[19] of correcting for steric effects seems to be effective because the correlation coefficient for 21 X-substituted acetate esters (XCH_2COOR) is high (0.980) and the field effect strongly dominant (6 ± 4% $\mathcal{R}$) for this series (set **26**). Here there is only one interposed atom between substituent and reacting center, but steric terms have been approximately eliminated by cancellation between base- and acid-catalyzed reactions. Taft's σ_{I} (set **32**) is the same set (except for a multiplier of 0.45, four more data, and roundoff errors), and its analysis is similar (correlation coefficient 0.956, 0 ± 5% $\mathcal{R}$).

Either $\mathcal{F}$ or σ_I is a good substituent constant for field effects. However, $\mathcal{F}$ has the advantage of being based on only very accurately measurable equilibrium (pK_A) data for *meta*- and *para*-substituted benzoic acids in water at 25° and 4′-substituted bicyclooctanecarboxylic acids in 50% ethanol by weight at 25°, rather than being based on a larger collection of less accurate kinetic data, representing a wide mixture of alkyl (R′) groups, solvents, and temperatures, assuming the same ρ (2.48) for all, regardless of solvent.

On the other hand, resonance constants that have been based on σ_I, σ_p, and σ_m are not satisfactory, because they were derived on the assumption that the field effect is equal for *meta* and *para* positions, which was shown to be incorrect for several series above. In accord with this, their correlation coefficients are lower (0.940, 92 ± 10% $\mathcal{R}$ for $\sigma_R{}^m$; 0.939, 84 ± 10% $\mathcal{R}$ for $\sigma_R{}^0$).

The *F* constants of Dewar and Grisdale[24] (set **36**) correlate very well with our $\mathcal{F}$ and $\mathcal{R}$ (correlation coefficient 1.000, 22 ± 0% $\mathcal{R}$), but their *M* (set **37**) is not as satisfactory (0.905, 93 ± 7% $\mathcal{R}$). Reactions of substituted naphthalenes and other aromatic systems are very well expressed in terms of our $\mathcal{F}$ and $\mathcal{R}$ (correlation coefficients 0.981 to 0.999 for sets **9–13**).

The σ^- set (**3**, based on acidity of phenols) has a lower % $\mathcal{R}$ (56 ± 4%) than $\sigma_p{}^+$ (66 ± 5%) and one not significantly different from σ_p (53 ± 0%). In spite of this, the correlation is satisfactory (C = 0.970, better than the average of 0.967) and the deviations of calculated from experimental $\sigma_p{}^-$ values for the critical *p*-nitro and *p*-cyano substituents are smaller than the average error for the 18 substituents (and the error is not even in the same direction for *p*-nitro as for *p*-cyano). Evidently, *p*-nitro and *p*-cyano are not exceptional, but more of the stabilization of phenoxide ion by these substituents is due to the field effect of the substituent than has been supposed. These substituents do have considerably higher $\mathcal{F}$ values (1.11 and 0.85) than $\mathcal{R}$ values (0.16 and 0.18).

Superfluity of Three Independent Variables. The preceding analysis shows that two independent variables are in many cases necessary and in all cases sufficient to explain the variations within the 43 reaction series considered. No steric terms are required because the substituent is far enough from the reaction center that steric factors are essentially constant.

Both $\sigma_p{}^-$ and $\sigma_p{}^+$ are among the sets with high correlation coefficients (0.970 and 0.939, respectively, in the first correlation *vs.* σ_m and σ_p). This is surprising and significant because it has been considered prior to this work that different, unrelated kinds of resonance are operative in $\sigma_p{}^-$ and $\sigma_p{}^+$. The literature $\sigma_p{}^-$ values differ greatly from σ_p only for substituents that can accept electrons by resonance (NO_2, CN) and not for donor substituents (NH_2, OCH_3); the converse is true for $\sigma_p{}^+$ values. Therefore, we had assumed initially that three independent variables would be required

$$\sigma = f\mathcal{F} + r_a\mathcal{R}_a + r_d\mathcal{R}_d \qquad (5)$$

with r_a large (resonance effect of acceptor substituents dominant) but r_d close to zero (resonance effect of donor substituents negligible) for $\sigma_p{}^-$, and the converse for $\sigma_p{}^+$. Our calculations based on eq 1 were intended originally as only preliminary tests before going on to three-variable correlations with

$$\sigma_{4S} = c_{41}\sigma_{1S} + c_{42}\sigma_{2S} + c_{43}\sigma_{3S} + c_{4123} \qquad (6)$$

Instead, the correlation with eq 1 or 3 is already so satisfactory that this sheds serious doubt on the need for assuming two kinds of resonance rather than just one average value. We persevered anyway in a test of eq 6 (see below), but the further improvement in correlation coefficients with eq 6 is so small that it seems not to justify the additional parameter.

This question of whether or not an extra variable is justified was answered statistically. A SHARE program (SHARE 1194–MPR3) is available which makes the necessary calculations. It was modified slightly to operate with the σ data. All reaction types were used in the three independent variable multiple correlation. As sets of independent variables, both **40**, **41**, and **3**, and also **40**, **41**, and **2** were tried. The program required at least six substituent groups from all four reaction types to complete the stepwise regression. Significance was taken to mean over 99% confidence that the variable in question adds to the regression, as measured by an F test. The results were as follows. The total number of dependent sets with sufficient data is 54. The number in which only one variable is significant is 24. The number in which two variables are significant is 29. The number in which three variables is significant is 1; only reaction **8** ($\sigma_m{}^+$) correlated *vs.* **40**, **41** and **2** only (18 data points, F level for inclusion of the first variable 58.6, for the second 3.56, for the third 18.5; over-all correlation coefficient 0.962). The improvement in this one case is not so marked as in our opinion to warrant the use of three independent variables.

Superfluity of Double-Precision Calculations. The calculations were done using IBM 7094 computers. Programs were written by the authors, and first checked by redoing some multiple correlations of economic data, hand calculated by others. Since all standard deviations and correlation coefficients are calculated for the correct number of degrees of freedom, the results are automatically correct for any number of points without the need for a population correction.[37] Single-precision arithmetic was used (8 significant figures), but test runs using double-precision arithmetic (16 signficant figures) showed no change in calculated results.

Alternative Analyses. Correlations with $\sigma_p{}^+$ have frequently given better results than correlations with σ_p, especially for carbonium and radical reactions where resonance is abnormally important. Therefore, we tried correlations *vs.* σ_m and $\sigma_p{}^+$ and *vs.* $\mathcal{F}$ and $\sigma_p{}^+$ immediately after those *vs.* σ_m and σ_p, and also developed an $\mathcal{R}$ scale based on experimental $\sigma_p{}^+$ values rather than on σ_p values. The results did not differ significantly from those presented in Tables I–IV except in the following respects. Since only 23 experimental $\sigma_p{}^+$ values are available, the other 19 had to be calculated by least-squares fitting of $\sigma_p{}^+ = a\sigma_m + b\sigma_p$. The experimental value of $\sigma_p{}^+$ for trimethylammonium is abnormally low (0.408, 0.23 less than cal-

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[37] F. A. Pearson and K. R. Bennett, "Statistical Methods Applied to Agricultural Economics," John Wiley and Sons, Inc., New York, N. Y., 1942, p 170.

culated), presumably because of extreme electrostatic disfavoring of the incipient cumyl cation resonance form that has its positive charge on the *para* carbon. Use of this extreme 0.408 value gave an $\mathcal{R}$ set differing from the one above by having the following order (including some inversions compared to Table I): $F << Cl < Br \sim I < H \sim COO^-$ (0.04) $< S(CH_3)_2^+$ (+0.21) $<$ COOH (+0.27) $<$ CN $<$ NO_2. Although the halogen, cyano, and nitro parts seemed possible, we rejected this because we considered it unreasonable for $S(CH_3)_2^+$ to have such a positive $\mathcal{R}$ value, or for COO^- to be so different in its resonance capability from COOH. Also this use of mixed data (experimental where it exists, calculated otherwise) for σ' and σ_p^+ seemed less defensible than use of calculated throughout, and with calculated throughout the results are equivalent to those above ignoring σ_p^+ completely. Finally, the greater abundance and accuracy of pK_A measurements than of kinetic σ_p^+ data make σ_m, σ_p, and σ' more attractive as basis sets.

The use of experimental σ_p^- values in this way that we initially used σ_p^+ values was not attempted, because only 18 experimental values are available, and they represent a wider range of investigators, reactions, and solvents.

Significance of the Results. The correlation coefficients for linear correlation of the 21 natural reaction series *vs.* the field substituent constant $\mathcal{F}$ and the resonance substituent constant $\mathcal{R}$ as independent variables are so high that it appears practicable to drop the use of about 20 other synthetic hybrid σ sets, which are less pure field or resonance measures.

Correlation is not significantly improved by including both σ_p^+ and σ_p^- (in addition to $\mathcal{F}$); therefore, the use of two numbers to characterize the resonance effect, one to represent electron-donating ability and the other to represent electron-attracting ability, is a dubious improvement over characterization of resonance capabilities by a single number ($\mathcal{R}$).

Accepting the assumptions made, one is led to conclude that the order of field constants ($\mathcal{F}$ values) for 13 typical substituents is $COO^- <$ *t*-Bu $<$ Me $<$ H $<$ $NH_2 < C_6H_5 < OCH_3 \sim$ NHAc $<$ COOH $<$ Cl $\sim$ F $<$ $NO_2 < N(CH_3)_3^+$ and that the order of resonance constants ($\mathcal{R}$ values) is $NH_2 < OCH_3 < F <$ NHAc $<$ $Cl < CH_3 <$ *t*-Bu $< C_6H_5 < H \sim N(CH_3)_3^+ < COO^- \sim$ COOH $\sim NO_2$. Field effects are not equal for *meta* and *para* locations of the same substituent. Resonance effects are significant with *meta* substituents. The average importance of resonance (±5%) is 0% in $\mathcal{F}$ or σ', 22% in σ_m, 53% in σ_p, 56% in σ_p^-, 66% in σ_p^+, 92% in $(\sigma_p - \sigma_m)$, and 100% in $\mathcal{R}$.

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The Influence of Tunneling on the Relation between Tritium and Deuterium Isotope Effects. The Exchange of 2-Nitropropane-2-*t*[1]

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Abstract: Tritium and deuterium isotope effects can be related by an equation derived by Swain and coworkers,[2] without consideration of tunneling. The influence of tunneling on this relationship is explored, with consideration of deviations predicted by some theoretical models. It is shown that conspicuous deviation will occur only under some rather restricted conditions, even when tunneling is quite extensive. Three examples in which tunneling has been believed to be important are subjected to this test. The oxidation of 1-phenyl-2,2,2-trifluoroethanol by alkaline permanganate gives a tritium isotope effect, $k_H/k_T = 57.1$, in close agreement with the value 55.5 calculated with the Swain equation from the previously measured deuterium isotope effect.[3] A very large isotope effect, $k_H/k_T = 82.9$, is calculated from the deuterium isotope effect for the proton transfer from 2-nitropropane to 2,4,6-trimethylpyridine,[4] and the experimental value, $k_H/k_T = 79.1$, is nearly as large. The oxidation of leuco crystal violet by chloranil[5] gives a calculated tritium isotope effect, $k_H/k_T = 27.3$, significantly greater than that found experimentally, $k_Hk_T = 20.3$, and the discrepancy is reasonably concordant with that expected from the strong temperature dependence of the deuterium isotope effect. The rate of ionization of 2-nitropropane-2-*t* by 2,4,6-trimethylpyridine measured by exchange is less than that measured by iodination, unless allowance is made for the significantly slow exchange of the pyridinium ion with the aqueous *t*-butyl alcohol solvent.

The problem of tunneling in chemical reactions, although extensively discussed, is generally believed to be significant only in reactions for which the barrier is a restriction on the motion of a hydrogen atom, but it is not generally conceded that tunneling is always

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[1] Taken in part from the Ph.D. Thesis of J. K. Robinson, Rice University, 1966.

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