Substituent Effects at Elements Other than Carbon. II. Ionization Potentials

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Ionization potentials of XF, XCl, XBr, XI, X_2O, XOMe, XSH, XSMe, XSEt, X_3N, and X_3P were correlated with the extended Hammett equation $Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h$ with generally good results. For X_nY, $\alpha_Y = m\chi_Y + c$. For XY, $\alpha_Y = m\sigma_{I,Y} + c$; $\beta_Y = m'\sigma_{R,Y} + c'$. It is concluded that substituent effects on ionization potentials in compounds substituted at halogen, oxygen, sulfur, nitrogen, or phosphorus may be represented by substituent constants derived from compounds substituted at carbon.

In the first paper of this series[1] we have shown that rate and equilibrium data for P-substituted phosphorus oxy acids are correlated by the Hammett equation[2] in the extended form (eq 1). We consider in this paper

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \tag{1}$$

the application of eq 1 to sets of ionization potentials for compounds of the type X_nY where Y is an element whose Pauling electronegativity is greater than 2.0 and where $n \leqq 3$. Successful correlation with eq 1 would permit us to determine the magnitude and composition of electrical substituent effects as a function of Y, and to compare the electrical substituent effect upon the ionization of *n* electrons with that observed for the ionization of π electrons in substituted benzenes and ethylenes.

A number of previous studies on the correlation of ionization potentials of substituted benzenes[3-6] and substituted pyridines[7] with the simple Hammett equation (2) have been reported. Correlations of ionization

$$Q_X = \rho\sigma_X + h \tag{2}$$

potentials of substituted benzyl radicals,[8] substituted phenoxy radicals,[9] and substituted alkyl radicals[10] with eq 2 have appeared. Ionization potentials of substituted ethylenes and substituted carbonyl derivatives have been correlated with eq 1.[11]

Many molecules possess two or more nonequivalent orbitals from which electrons are likely to be lost. In order for correlation with eq 1 to be meaningful, all of the members of the set must lose an electron from the same type of orbital on the same group. Specifically, in the sets studied here, all of the members of the set must lose an electron from a nonbonding orbital on the Y atom. In determining the orbital from which electron loss has occurred, we have assumed that electrons are lost most readily from π orbitals of benzene and ethylene, next from nonbonding orbitals, and least readily from σ orbitals. Thus, consider, for example, the series of compounds (ionization potentials are given in parentheses) PhF (9.20), C_2H_3 (10.37), MeF (12.80), and MeH (12.98). On the basis of this assumption we may now proceed to examine some of the sets studied. In set 1 all of the compounds have available only σ orbitals or nonbonding orbitals on F, and therefore the latter must suffer the loss of the electron. In set 2 all of those compounds which have available only σ orbitals or nonbonding Cl orbitals must lose the electron from the latter. A comparison of the ionization potentials of CF_3Cl and $C_3F_7CH_2Cl$ with that of CF_4 suggests that the electron in the former compounds is lost from a Cl *n* orbital. We have shown that, that for sets of XY where X is held constant and Y, an atom or group of atoms from which electron loss occurs, is varied[12]

$$I_{X,Y} = mI_{Me,Y} + c \tag{3}$$

where $I_{X,Y}$ is the ionization potential of XY and $I_{Me,Y}$ is the ionization potential of MeY. As I_{CNCl} and I_{ClCH_2CN} lie on the line for I_{CNY}, we conclude that electron loss must be from the *n* orbital on chlorine in these compounds. By means of arguments analogous to those used above, we may show that in the remaining sets electron loss does in fact occur from the same type of orbital on the same group.

The sets studied have been correlated with eq 1 by multiple linear regression analysis. The data used are reported in Table I. The substituent constants used are generally from the first paper in this series or from sources reported therein. Substituent constants from other sources are given in Table II.

In the correlation of sets of X_nY where $n > 1$ we have assumed that interaction terms may be neglected and therefore

$$Q_X = \sigma\epsilon\alpha_{I,X} + \beta\epsilon\sigma_{R,X} + h \tag{4}$$

Then

$$Q_X = \alpha n\sigma_{I,X} + \beta n\sigma_{R,X} + h \tag{5}$$

$$Q_X = \alpha'_{I,X} + \beta'_{R,X} + h \tag{6}$$

Correlations have been made with eq 6.

Results

Results of correlations with eq 1 are reported in Table III.

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[9] J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *ibid.*, **84**, 4 (1962).

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[11] M. Charton, Abstracts, 2nd Mid-Atlantic Regional Meeting of the American Chemical Society, 1967, p 88.

[12] M. Charton, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968, p S112.

TABLE I

IONIZATION POTENTIALS USED IN CORRELATIONS[a]

1. XF									
X	H	F	SF_5	Me	Et	CH_2F	CF_3	CHF_2	
IP	15.77^b	15.7^b	19.3^c	12.80^d	12.00^c	12.55^d	14.9^e	13.84^d	
2. XCl									
X	H	Cl	Me	Et	Pr	*i*-Pr	Bu	*s*-Bu	*i*-Bu
IP	12.74^b	11.48^b	11.28^b	10.97^b	10.82^b	10.78^b	10.67^b	10.65^b	10.66^b
X-Bu	*t*-Bu	CF_3	$ClCH_2$	Cl_2CH	Cl_3C	CN	$ClCH_2CH_2$	CH_2CN	$CF_3CF_2CF_2CH_2$
IP	10.2^d	12.8^b	11.35^b	11.42^b	11.47^b	12.49^c	11.12^b	12.2^b	11.84^b
3. XBr									
X	H	Br	Cl	Me	Et	Pr	*i*-Pr	Bu	*s*-Bu
IP	11.62^b	10.55^b	11.1^c	10.53^b	10.24^b	10.18^b	10.08^b	10.13^b	9.98^b
X	CN	CF_3	$ClCH_2$	$BrCH_2$	$BrCH_2CH_2$	$ClCH_2CH_2$			
IP	11.95^c	11.78^b	10.77^b	10.49^b	10.30^c	10.63^b			
4. XI									
X	I	Cl^-	Br	H	Me	Et	Pr	*i*-Pr	Bu
IP	9.28^b	10.31^c	9.98^c	10.38^b	9.54^b	9.33^b	9.26^b	9.17^b	9.21^b
X	*s*-Bu	*i*-Bu	*t*-Bu	CF_3CH_2	CF_3	CN	CF_3CF_2	ICH_2	$CF_3CF_2CF_2CH_2$
IP	9.09^b	9.18^b	9.02^b	10.00^b	10.40^b	10.98^c	10.36^b	9.34^b	9.96^b
5. X_2O									
X	F	H	Me	Et	Pr	*i*-Pr	Bu	$ClCH_2CH_2$	
IP	13.7^c	12.59^b	10.00^b	9.53^b	9.27^b	9.20^b	9.18^b	9.85^b	
6. XOMe									
X	Me	CH_2OMe	Et	CH_2Cl	Cl_2CH	H			
IP	10.00^b	10.00^b	9.81^c	10.25^b	10.25^b	10.85^b			
7. XSH									
X	SH	H	Me	Et	Pr	Bu	*t*-Bu	MeS	EtS
IP	10.2^c	10.46^b	9.44^b	9.29^b	9.20^b	9.14^b	8.79^b	8.8^c	9.4^c
8. XSMe									
X	H	Me	Et	Pr	*i*-Pr	MeS	CN		
IP	9.44^b	8.69^b	8.55^b	8.80^c	8.7^c	8.46^b	10.065^b		
9. XSEt									
X	H	Me	Et	EtS	CN				
IP	9.29^b	8.55^b	8.43^b	8.27^b	9.89^b				
10. X_3N									
X	H	Me	Et	Pr	CF_3CF_2	F			
IP	10.154^b	7.92^b	7.50^b	7.23^b	11.7^b	12.9^d			
11. X_3P									
X	H	CF_3	Cl	Me	Et				
IP	10.11^c	11.31^c	10.75^c	8.60^c	8.27^c				

[a] R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, N. J. 1965, p 301. Ionization potentials are reported in electron volts. [b] Photoionization method. [c] Electron impact method. [d] Vacuum ultraviolet spectroscopy method. [e] R. W. Kiser and D. L. Hobrook, *J. Amer. Chem. Soc.*, **87**, 922 (1965).

TABLE II

SUBSTITUENT CONSTANTS[a,b]

X	σ_I	Ref	σ_R	Ref	X	σ_I	Ref	σ_R	Ref
C_3F_7	0.39	*c*	0.17	*c, d*	CH_2F	0.18	*e*	−0.04	*f*
$C_3F_7CH_2$			−0.05	*f*	CHF_2			0.03	*g*
CH_2CH_2Cl	0.05	*h*	−0.10	*f*	CH_2CN			−0.01	*i*
CH_2CH_2Br	0.05	*h*	−0.10	*f*	CH_2OMe			−0.03	*f*
CF_3CF_2	0.41	*c*	0.17	*c, d*	CHO	0.36	*j*	0.07	*k*
SF_5	0.55	*l*	0.11	*l*					

[a] From sources other than ref 1 or references cited therein. [b] σ_R values calculated from $\sigma_R = \sigma_p - \sigma_I$. References to source of σ_p. [c] W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965). [d] Calculated from $\sigma_R^0 = a\sigma_R + b$. [e] Calculated from $\sigma_{I,XCH_2} = a''\sigma_{I,X} + b''$. [f] Calculated from $\sigma_{p,XCH} = a'\sigma_{I,X_2} + b'$. [g] R. Pollet, R. van Poucke, and A. de Cat, *Bull. Soc. Chim. Belges*, **75**, 40 (1966). [h] Calculated from the pK_a of the corresponding substituted acetic acid. [i] O. Exner and J. Jonas, *Coll. Czech. Chem. Commun.*, **27**, 2296 (1962). [j] Calculated from $\sigma_I = (3\sigma_m - \sigma_p)/2$. [k] A. A. Humffray, J. J. Ryan, J. P. Warren, and Y. H. Yung, *Chem. Commun.*, 610 (1965). [l] W. A. Sheppard, *J. Amer. Chem. Soc.*, **84**, 3072 (1962).

Halogen Derivatives.—The correlations obtained for the fluorine compounds (set 1) are very poor. Exclusion of the point for X = H (set 1A) gave an improved correlation which remains very poor. Further exclusion of the point for X = F (set 1B) resulted in decreased correlation. By contrast, the correlations obtained for the chloro, bromo, and iodo compounds (sets 2, 3, and 4) are excellent. Exclusion of the value for X = H from these sets gave a very much improved correlation in all three cases (sets 2A, 3A, and 4A). Further exclusion of the value for X = Cl from the chloro compounds gave slightly improved results (set 2B). Further exclusion of the point for X = Br from the bromo compounds gave improved results (set 3B), whereas the exclusion of the point for X = I from the iodo compounds gave a very much improved

TABLE III

RESULTS OF CORRELATIONS

Set	α	β	h	R[a]	F[b]	r[c]	s_{estd}[d]	s_α[d]	s_β[d]
1	6.54	2.63	12.21	0.717	2.649	0.019	1.96	2.95	4.01
1A	8.38	1.84	12.30	0.853	5.356	09031	1.61	2.61	3.32
2	1.39	5.21	11.56	0.809	14.27	0.400	0.476	0.586	1.51
2A	1.82	3.94	11.34	0.883	24.83	0.447	0.353	0.450	1.18
2B	1.02	6.26	11.56	0.898	27.11	0.816	0.343	0.734	2.06
3	1.68	3.51	10.73	0.860	17.03	0.182	0.425	0.425	1.00
3A	1.96	2.72	10.56	0.941	42.74	0.232	0.222	0.276	0.660
3B	2.26	1.97	10.49	0.958	55.91	0.451	0.198	0.289	0.699
4	1.66	2.02	9.59	0.818	15.18	0.271	0.361	0.400	0.859
4A	1.88	1.57	9.47	0.879	23.73	0.307	0.298	0.338	0.726
4B	2.17	1.15	9.44	0.942	51.30	0.349	0.214	0.255	0.533
5	17.2	15.7	11.82	0.917	13.27	0.924	0.818	4.17	6.00
5A	4.08	−5.60	8.99	0.981	52.26	0.978	0.380	3.57	5.61
6	0.624	4.77	10.47	0.692	1.377	0.114	0.339	1.09	2.95
6A	1.06	0.659	10.03	0.872	3.177	0.0664	0.130	0.432	1.49
7	3.22	9.06	10.37	0.953	29.87	0.579	1.99	0.585	1.19
7A	3.07	8.29	10.26	0.916	13.08	0.645	0.211	0.667	1.78
8	0.892	4.33	9.25	0.977	41.83	0.403	0.152	0.285	0.656
8A	1.08	3.75	9.14	0.990	73.45	0.513	0.108	0.220	0.536
9	0.651	4.99	9.15	0.984	19.94	0.437	0.174	0.354	0.837
9A	0.906	4.35	9.01	0.994	38.13	0.605	0.147	0.355	0.853
10	8.65	0.520	8.45	0.925	8.909	0.277	0.188	2.11	2.65
10A	9.36	−0.311	7.90	0.995	93.13	0.230	0.388	0.709	0.891
11	4.33	3.28	9.34	0.929	6.312	0.0163	0.693	1.32	2.56
11A	5.01	2.17	8.92	0.995	48.95	0.122	0.264	0.537	1.03

Set	s_h[d]	n[e]	C.L.[f]	Set	s_h[d]	n[e]	C.L.[f]
1	1.01	8	<90.0	6	0.250	6	<90.0
1A	0.961	7	90.0	6A	0.143	5	<90.0
2	0.190	18	99.9	7	0.150	9	99.9
2A	0.153	17	99.9	7A	0.239	8	97.5
2B	0.224	16	99.9	8	0.0926	7	99.5
3	0.142	15	99.9	8A	0.0831	6	99.5
3A	0.0978	14	99.9	9	0.123	5	95.0
3B	0.0944	13	99.9	9A	0.147	4	<90.0
4	0.129	18	99.9	10	0.583	6	90.0
4A	0.114	17	99.9	10A	0.222	5	97.5
4B	0.0818	16	99.9	11	0.413	5	<90.0
5	0.725	8	99.0	11A	0.196	4	<90.0
5A	0.729	7	99.5				

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient for correlation of σ_I with σ_R. [d] Standard deviations of the estimate, α, β, and h. [e] Number of points in the set. [f] Confidence level of regression.

correlation. We believe that the poor results obtained for the fluoro compounds are due largely to the small size of the set, and to a lack of variation in substituent type. The difficulty encountered in this set is that most of the functional groups which may be bonded to fluorine have n or π electrons which are more readily lost than are the n electrons on the fluorine atom.

Oxygen and Sulfur Derivatives.—Very good results were obtained for the X_2O (set 5). Exclusion of the value for X = H gave excellent results (set 5A). The high value of r indicates little separation into localized and delocalized effects. The correlation obtained for the XOMe is very poor (set 6). Although the results are improved by the exclusion of the point for X = H, they remain poor (set 6A). This is probably due to the small size of the set and to the low degree of variability in the substituent effects of the set members.

The correlation obtained for the substitued thiols (set 7) is excellent. It is of interest to note that exclusion of the point for X = H leads to poorer correlation (set 7A). The MeSX gave excellent results (set 8) which are improved by the exclusion of the unsubstituted compound (set 8A). Fair results were obtained for the EtSX (set 9). Elimination of the value for the unsubstituted compound may result in improvement (set 9A). Unfortunately, the set is too small to permit a definite conclusion.

Nitrogen and Phosphorus Derivatives.—A poor correlation was obtained for the X_3N (set 10). Exclusion of the value for X = H gave good results (set 10A). The X_3P gave a poor correlation (set 11), again, however, the results were improved by exclusion of the unstubstituted compound from the set, a good correlation being obtained (set 11A).

Discussion

Magnitude of the Electrical Effect.—In Table IV we have collected values of α, β, h, $\sigma_{I,Y}$, $\sigma_{R,Y}$, χ_Y, and I_{MeY}. Values obtained in previous work on the ionization potentials of substituted ethylenes and carbonyl derivatives[11] have been included for purposes of comparison.

Inspection of the values in Table IV suggests a linear

TABLE IV

VALUES OF α, β, h, $\sigma_{I,Y}$, $\sigma_{R,Y}$, χ_Y, AND I_{MeY}

Y	Set	α	β	h	$\sigma_{I,Y}$	$\sigma_{R,Y}$	χ_Y[a]	I_{MeY}
F	1A	8.38	[b]	12.30	0.52	−0.46	4.0	12.80
Cl	2A	1.82	3.74	11.34	0.47	−0.24	3.0	11.28
Br	3A	1.96	2.72	10.56	0.45	−0.22	2.8	10.53
I	4A	1.88	1.57	9.47	0.39	−0.12	2.5	9.54
OMe	6A	1.06	[b]	10.47	0.25	−0.52		10.00
SH	7A	3.07	8.29	10.26	0.25	−0.15		9.44
SMe	8A	1.08	3.75	9.14	0.25	−0.25		9.69
SEt	9A	0.906	4.35	9.01	0.25	−0.22		8.55
N	10A	3.12[c]	[b]				3.0	
P	11A	1.67[c]	0.723				2.1	
C_2H_3	[d]	1.32	2.51	9.85	0.09	−0.11		9.73
Ph	[d]	0.916	1.39	9.46	0.10	−0.11		8.82
HCO	[d]	3.87	1.34	10.31	0.36	0.07		10.21
Ac	[d]	3.01	0.589	9.60	0.29	0.21		9.69
Bz	[d]	2.42	[b]	9.29	0.29	0.17		9.27

[a] Pauling electronegativity. [b] β For this set is not significant. [c] Calculated from α' by dividing by n. [d] From ref 11.

TABLE V

RESULTS OF CORRELATIONS WITH EQ 7, 8, 9, AND 12

Set	m[a]	c[b]	r[c]	t[d]	s_{estd}[e]	s_m[f]	n[g]	C.L.[h]
A1	3.64	−7.42	0.887	3.851	1.35	0.945	6	98.0
A2	9.16	−0.351	0.595	2.455	1.69	3.73	13	95.0
A2A	9.49	−0.548	0.614	2.462	1.73	3.85	12	95.0
B1	−8.05	2.11	0.536	1.795	1.99	4.48	10	80.0
B1A	−7.03	1.67	0.842	4.129	0.753	1.70	9	99.0
H1	0.799	2.12	0.935	8.734	0.350	0.0915	13	99.9
H1A	0.823	1.83	0.954	10.10	0.308	0.0815	12	99.9

[a] Slope. [b] Intercept. [c] Correlation coefficient. [d] Student "t" test. [e] Standard error of the estimate. [f] Standard error of the slope. [g] Number of points in the set. [h] Confidence level.

relationship between α and χ_Y in X_nY (eq 7). Correlation of α with χ gives good results (set A1, Table V).

$$\alpha_Y = m\chi_Y + c \tag{7}$$

Where Y is a group as in XY, the eq 8 is roughly obeyed.

$$\alpha_Y = m\sigma_{I,Y} + c \tag{8}$$

Fair results are obtained for this correlation (set A2). Exclusion of the value for Y = SH gives only slight improvement (set A2A).

The values of β seem to follow eq 9. The correlation

$$\beta_Y = m'\sigma_{R,Y} + c' \tag{9}$$

obtained is not significant (set B1). Exclusion of the value for Y = SH gives very good results, however (set B1A).

Composition of the Electrical Effect.—We characterize the composition of the electric effect by eq 10. From

$$\epsilon = \beta/\alpha \tag{10}$$

eq 8 and 9, we obtain eq 11.

$$\epsilon = (m'\sigma_{R,Y} + c')/(m\sigma_{I,Y} + c) \tag{11}$$

The Intercept h as a Function of Eq. 3.—Equation 3 relates $I_{X,Y}$ to I_{MeY}. The intercept h obtained in correlation with eq 1 is equivalent to the ionization potential of reference substituent X°. Then h should be correlated by eq 12. This relationship is in fact

$$h = mI_{Me,Y} + c \tag{12}$$

observed (set H1, Table V). The correlation is excellent. The results are improved by the exclusion of the value for Y = SH.

Applicability of Eq 1.—Of the eleven sets studied we have obtained excellent results in five (set 2A, 3A, 4A, 5A, and 8A), very good results in two (sets 7A and 10A), and poor but significant results in one (set 1A). Although very poor correlation (with regard to the confidence level) was obtained for the other three sets, in two there were only four members in the set (sets 9A and 11A) and in the third only five. We believe that better results would have been obtained had more data been available. We conclude, therefore, that substituent effects on ionization potentials in compounds bearing the substituent on halogen, oxygen, sulfur, nitrogen, and phosphorus may be represented by substituent constants derived from compounds bearing the substituent on carbon.

It should be noted that, in general, the value for X = H deviates significantly from the set. This phenomenon has also been observed for many correlations of substituted carbon compounds.