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INDUCTIVE EFFECTS ON MOLECULAR IONIZATION POTENTIALS—X

ALKYL AND HYDROGEN HALIDES

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Abstract—The ionization potentials of alkyl and hydrogen halides are found to be excellent linear fractions of the polar and inductive substituent constants, indicating that the effect of alkyl substituents on the electron density of the halogen atoms is inductive. The slopes of the four regression lines vary widely in the order RF > RCl > RBr > RI, which shows that the susceptibility of the halogen atoms to inductive effects varies in the same order. Values of σ_I and σ^* for alkyl groups not previously available are estimated.

Recently we have shown that the ionization energies of the alcohols,[1] ethers,[2] amines,[3] thiols,[4] thioethers,[5] disulfides,[6] alkenes,[7] alkynes,[8] ketones,[9] and carboxylic acids[10] are linear functions of the inductive substituent constants, σ_I, and the polar substituent constants, σ^*. This allows one to calculate by means of a simple single-parameter equation, to a good approximation, values of the ionization potentials of compounds which yield a low abundance of the primary radical cation, or are difficult to obtain in a purified state.

We now demonstrate that the ionization energies of alkyl halides, RX, (where R = alkyl or H) are likewise a linear function of σ_I and σ^*. The first ionization energy of the alkyl halides corresponds to the removal of an electron from the highest occupied MO,[11-13] a non-bonding lone pair *p*-electron[14] from the halogen atom. The gas-phase expulsion of an electron from the halogen lone pair is in accord with the following equation:

$$R{-}X \xrightarrow{E_I} e + R{-}X^{+}$$

It is quite obvious that electron releasing alkyl groups should increase the electron density at the halogen atom and thereby facilitate electron removal, whereas electron-withdrawing groups should increase the requisite ionization energy.* It is interesting that we are able to include the hydrogen halides as the simplest "alkyl halides" in the series presented.

Table 1 presents the σ_I[16] and σ^*[17] values together with new σ values calculated here, when no previous estimate was available. The experimentally observed adiabatic photoionization (PI)[14] E_I values for the hydrogen halides and various alkyl fluorides, chlorides, bromides, and iodides are given in Table 2. Data[18-20] has just become available through the technique of photoelectron spectroscopy (PES)[21] for several halides whose E_I's had not previously been obtained,† and these adiabatic values are also given in Table 2.

Good correlations are shown in Fig 1 where the E_I values are plotted *vs* σ_I. The equation for the regression lines is given by the following:

$$E_{RX} = E_{HX} + a_I\sigma_I$$

The slopes, a_I, are found from a least squares fit to be 66·9, 31·8, 24·0 and 18·6, respectively, for the fluorides, chlorides, bromides, and iodides,

Table 1. Taft aliphatic substituent constants used in the correlations

Substituent	σ_I[a]	σ^*[b]
H	0	+0·49
Me	0·046	0
Et	0·055	0·10
n-Pr	0·058	0·12
i-Pr	0·064	−0·19
n-Bu	0·060[c]	0·13
i-Bu	0·064[d]	0·13
s-Bu	0·068[d]	0·21
t-Bu	−0·074	0·30
n-Am	−0·064[d]	0·16[c]
neo-Pt	−0·065[d]	−0·16
t-Am	0·078[d]	0·33[d]
cy-Hx	0·067[d]	0·15 (−0·20)[e]

[a] From Ref. 16
[b] From Ref. 17.
[c] From Ref. 1.
[d] Values calculated in the present paper.
[e] From Ref. 22

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* The same effect should manifest itself in a greater basicity, the greater the electron density at the halogen atom, similar to that demonstrated for alcohols.[15]

† Where the PI values of Ref. 14 were repeated by PES on the same compounds, agreement within 0·02 eV was nearly always observed.

Table 2. Experimental and calculated ionization potentials of various alkyl and hydrogen halides

Compound	E_i[a] (Exptl.)	E_i (Calc., Eq. 2)	Compound	E_i[a] (Exptl.)	E_i (Calc., Eq. 2)
HF	15.77[b]	15.77	n-BuBr	10.13	10.12
MeF	12.80	12.70	s-BuBr	9.98	9.98
EtF	12.00	12.08	i-BuBr	10.09	10.08
i-PrF	[c]	11.49	t-BuBr	9.89	9.84
t-BuF	[c]	10.82	n-AmBr	10.10	10.08
HCl	12.74	12.74	neo-PtBr	10.03[d]	10.06
MeCl	11.28	11.28	cyc-HxBr	10.02[d]	10.01
EtCl	10.98	10.99	HI	10.38	10.38
n-PrCl	10.82	10.89	MeI	9.54	9.53
i-PrCl	10.78	10.70	EtI	9.37[e]	9.36
n-BuCl	10.67	10.83	n-PrI	9.26	9.30
s-BuCl	10.65	10.58	i-PrI	9.17	9.19
i-BuCl	10.66	10.70	n-BuI	9.21	9.26
t-BuCl	10.61	10.38	s-BuI	9.09	9.11
HBr	11.62	11.62	i-BuI	9.18	9.19
MeBr	10.53	10.52	t-BuI	9.02	9.00
EtBr	10.29	10.30	n-AmI	9.19	9.19
n-PrBr	10.18	10.23	neo-PtI	9.21[e]	9.17
i-PrBr	10.07	10.08	t-AmI	8.93[f]	8.93

[a] From Ref. 14

[b] Ref. 18 gives this E_i as 16.05 eV

[c] Experimental value not available

[d] From Ref. 19

[e] From Ref. 18

[f] From Ref. 20

and therefore we have:

$$E_{RF} = E_{HF} + a_I\sigma_I = 15.77 + 66.8\,\sigma_I \qquad (2a)^*$$

$$E_{RCl} = E_{HCl} + a_I\sigma_I = 12.74 + 31.8\,\sigma_I \qquad (2b)$$

$$E_{RBr} = E_{HBr} + a_I\sigma_I = 11.62 + 24.0\,\sigma_I \qquad (2c)$$

$$E_{RI} = E_{HI} + a_I\sigma_I = 10.38 + 18.6\,\sigma_I \qquad (2d)$$

In terms of the polar substituent constants, σ^*, the correlation equations are:

$$E_{RF} = E_{MeF} + a^*\sigma^* = 12.80 + 6.29\,\sigma^* \qquad (3a)$$

$$E_{RCl} = E_{MeCl} + a^*\sigma^* = 11.28 + 2.99\,\sigma^* \qquad (3b)$$

$$E_{RBr} = E_{MeBr} + a^*\sigma^* = 10.53 + 2.25\,\sigma^* \qquad (3c)$$

$$E_{RI} = E_{MeI} + a^*\sigma^* = 9.54 + 1.75\,\sigma^* \qquad (3d)$$

These correlations† indicate that the effect of alkyl substituents on the electron density at the halogen atoms is primarily an inductive one.

In the last column of Table 2 we show a comparison between the experimentally obtained ionization energies and those values of E_i calculated using Eqs. (2). The agreement is seen to be excellent. A calculated value is also given for Me_2CHF and Me_3CF for which PI or PES values have not yet been obtained.

E_i data are also available for other organic halides such as ϕX and ϕCH_2X, but these have not been included in the present study, because the electron loss occurs from the π-system in these compounds, and not from the halogen lone pair.

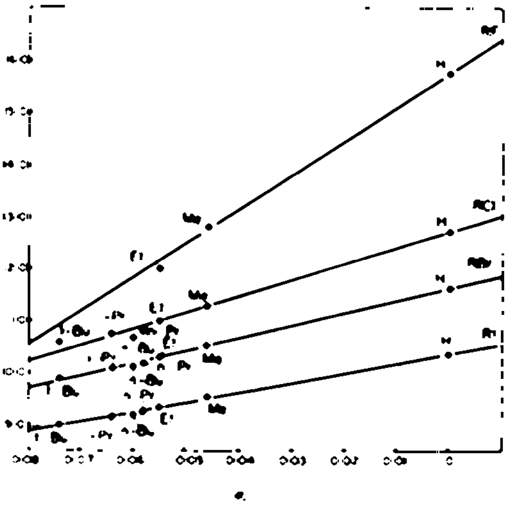

Fig. 1. Plots of the experimental ionization energies, E_i, of various alkyl and hydrogen halides vs the corresponding inductive substituent constants, σ_I, for the alkyl groups.

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* The corresponding correlation coefficients for Eqs. 2 are, respectively, 0.999, 0.988, 0.998 and 0.998.

† A recent correlation, for RI only, was reported as $E_i = 9.79 + 1.81\,\sigma^*$ (Ref. 18).

Although the a_I constant has units of energy (eV), it is analogous to the reaction constant, ρ_I, and constitutes a measure of the susceptibility of the reaction site, the halogen atom, to substituent effects. The a_I values obtained here (Eqs. 2) may be compared to those observed in the correlation of E_I's of alcohols[1] (37·5), ethers[2] (28·0), amines[3] (13·8), thiols[4] (22·2), thioethers[5] (18·8), and disulfides[6] (13·6).

It is seen that the a_I values for the alkyl halides vary widely with the halogen atom: $a_{I(F)} \gg a_{I(Cl)} > a_{I(Br)} > a_{I(I)}$. This effect is also observed with the alcohols and thiols, and with the ethers and thioethers, where in both cases $a_{I(O)} \gg a_{I(S)}$. The explanation for this probably lies in the magnitude of the electronegativity and atomic radius of the atom in question.

Reliable values for the inductive substituent constants for i-Bu, s-Bu, n-Am, neo-Pt, t-Am and cyc-Hx do not appear to be available. Good and consistant estimates for these can, however, be readily made directly from the plots in Fig 1, from which we find the following best values for the groups in question (Table 1): i-Bu = −0·064, s-Bu = −0·068, n-Am = −0·064, neo-Pt = −0·065; t-Am = −0·078; and cyc-Hx = −0·067. We also recommend the following values for polar constants not previously available (Table 1): t-Am = −0·33, and cyc-Hx = −0·20, (replacing the value −0·15 which is obviously in error).

REFERENCES

[1] L. S. Levitt and B. W. Levitt, *Chem. & Ind.* 990 (1970)

[2] B. W. Levitt and L. S. Levitt, *Experientia* 26, 1183 (1970)

[3] B. W. Levitt and L. S. Levitt, *Israel J. Chem.* 9, 71 (1971)

[4] L. S. Levitt and B. W. Levitt, *J. Org. Chem.* 37, 332 (1972)

[5] B. W. Levitt and L. S. Levitt, *Isr. J. Chem.* 9, 711 (1971).

[6] L. S. Levitt and B. W. Levitt, *Chem. & Ind.* (in press)

[7] L. S. Levitt, B. W. Levitt and C. Párkányi, *Tetrahedron* 28, 3369 (1972)

[8] L. S. Levitt, *Israel J. Chem.* (submitted for publication)

[9] B. W. Levitt and L. S. Levitt, *Chem. & Ind.* 724 (1972)

[10] B. W. Levitt and L. S. Levitt, *Ibid.* (in press)

[11] R. S. Mulliken, *J. Chem. Phys.* 3, 564 (1935), *Phys. Rev.* 74, 736 (1948)

[12] T. Koopmans, *Physica* 1, 104 (1933)

[13] J. C. Lorquet, *Rev. Mod. Phys.* 32, 312 (1960)

[14] K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spectros. Radiat. Transfer* 2, 369 (1962)

[15] L. S. Levitt and B. W. Levitt, *J. Phys. Chem.* 74, 1812 (1970), *Tetrahedron* 27, 3777 (1971)

[16] R. W. Taft, Jr. and I. C. Lewis, *Tetrahedron* 5, 210 (1959)

[17] R. W. Taft, Jr. in M. S. Newman (Ed.) *Steric Effects in Organic Chemistry*, p. 619. J. Wiley, New York (1956)

[18] A. D. Baker, D. Betteridge, N. R. Kemp and R. E. Kirby, *Anal. Chem.* 43, 375 (1971)

[19] J. A. Hashmall and E. Heilbronner, *Angew. Chem. Int. Edit.* 9, 305 (1970)

[20] B. J. Cocksey, J. H. D. Eland and C. J. Danby, *J. Chem. Soc.* (B), 790 (1971)

[21] S. D. Worley, *Chem. Rev.* 71, 295 (1971)

[22] A. B. Haefelmeyer and C. K. Hancock, *J. Am. Chem. Soc.* 77, 4746 (1955)