# Full Articles

## Ionization potentials of halides. Substituent effects in Cl-, Br-, and I-centered radical cations

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The first vertical ionization potentials ($I$) of halides HalX (Hal = Cl, Br, I; X is an inorganic or organic substituent) are linearly related to the inductive ($\sigma_I$), resonance ($\sigma_R^+$), and polarizability ($\sigma_\alpha$) constants of the substituents X ($I = a + b\sigma_I + c\sigma_R^+ + d\sigma_\alpha$). As the atomic number of the Hal element in the Hal$^{\bullet+}$X radical cations increases, the inductive interaction is strengthened while the polarizability interaction is weakened. Conjugation remains virtually independent of the Hal atom. The resonance $\sigma_R^+$-constants of the MX$_3$ (M = Si, Ge, Sn, Pb) substituents bound to the Hal$^{\bullet+}$ radical cation centers were first calculated.

**Key words:** halides, ionization potential, radical cation, inductive effect, conjugation, polarizability effect.

Basic to the determination of the ionization potentials of molecules by photoelectron spectroscopy[1,2] is the gas-phase photoionization reaction

$$\mathrm{DX} \xrightarrow{h\nu} \mathrm{D}^{\bullet+}\mathrm{X} + \mathrm{e}, \qquad (1)$$

where DX is the neutral molecule, D$^{\bullet+}$X is the radical cation, X is the substituent, and e is an electron.

Let us impose two limitations on the reaction (1). First, we will consider only such processes in which an electron is detached from the highest occupied molecular orbitals (HOMOs) of the DX molecules. In this case, by definition,[2] one gets

$$\Delta_r H^\circ(T) = I, \qquad (2)$$

where $\Delta_r H^\circ(T)$ is the standard enthalpy of the reaction (1) at temperature $T$ and $I$ is the first vertical ionization potential of the DX molecules. Second, we will study only those DX molecules for which the HOMOs are mainly localized on the reaction center D rather than substituent X. This means that reaction (1) results in D-centered radical cations D$^{\bullet+}$X while no photoionization of the

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orbitals of the substituents X occurs. By studying the interaction between the substituent X and the reaction center D$^{\bullet+}$ one can obtain information on the structure of the D$^{\bullet+}$X radical cations.[2–7] Among Hal-centered radical cations, only the I$^{\bullet+}$X systems have been studied so far.[5]

The aim of this work was to perform a comparative analysis of the ionization potentials for three series of HalX molecules (Hal = Cl, Br, I), to study the effects of inorganic and organic substituents X in the Hal-centered radical cations Hal$^{\bullet+}$X, and to calculate the resonance $\sigma_R^+$-constants for a number of organometallic substituents containing Si, Ge, Sn, and Pb atoms.

## Calculation Procedure

The method employed in this work is based on the fact that any reaction of the type (1) obeys the linear free energy relationship (LFER) if two above-mentioned limitations are allowed for. There are three important aspects of the LFER.

1. Taking into account relationship (2), the Gibbs—Helmholtz equation for the reaction (1),

$$\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T\Delta_r S^\circ(T), \quad (3)$$

has the form

$$\Delta_r G^\circ(T) = I - T\Delta_r S^\circ(T), \quad (4)$$

where $\Delta_r G^\circ(T)$ is the standard Gibbs free energy and $\Delta_r S^\circ(T)$ is the standard entropy of the reaction (1) at temperature $T$.

Earlier,[2] we have shown that in this case the entropy contribution, $T\Delta_r S^\circ(T)$, to $\Delta_r G^\circ(T)$ is at most 5% in the temperature range from 0 to 500 K. Therefore, to a good approximation relationship (4) can be rewritten as follows

$$\Delta_r G^\circ(T) = I. \quad (5)$$

From relationship (5) it follows that the change in the Gibbs free energy of reaction (1) due to substituents X is linearly related to the change in the ionization potentials of the DX molecules due to these substituents.

2. When using the LFER in practice, it is of great importance that the contributions of the inductive, resonance, and other possible effects (they depend on specific features of the system under study) to the change in the free energy are independent and additive. According to this well substantiated postulate (see, *e.g.*, Refs. 8 and 9), the following relationship holds for the process (1):

$$\Delta G = \Delta G_{\text{Ind}} + \Delta G_{\text{Res}} + \Delta G_{\text{Pol}}, \quad (6)$$

where $\Delta G$ is the abbreviation of $\Delta_r G^\circ(T)$ and $\Delta G_{\text{Ind}}$, $\Delta G_{\text{Res}}$, and $\Delta G_{\text{Pol}}$ are respectively the contributions of the inductive, resonance, and polarizability effects to the total change in $\Delta G$. The polarizability effect is a feature of the gas-phase process (1) which involves the formation of radical cations D$^{\bullet+}$X bearing a large positive charge $q$ on the reaction center. The charge $q$ polarizes the substituent X, thus inducing a dipole in the X. In the classical electrostatics (for details, see Ref. 10) the energy of the cation—dipole interaction is expressed as follows

$$E_{\text{es}} = -q^2\alpha/(2\varepsilon r^4), \quad (7)$$

where $\alpha$ is the polarizability of the substituent X, $\varepsilon$ is the dielectric constant, and $r$ is the distance between the charge and the induced dipole. The energy of the cation—dipole interaction varies in proportion to $r^{-4}$, thus being strongly dependent on the distance $r$. Therefore, the polarizability effect seems not to occur in the $Alk_2C^+C_6H_4X$-*p* systems that are traditionally used in studies of conjugation between substituents X and the positively charged reaction center[8] because of the long distances $r$. However, this effect is expected to be marked in the Hal$^{\bullet+}$X radical cations characterized by short distances $r$. Taking into account relationship (5), Eq. (6) can be written as follows

$$I = I_{\text{Ind}} + I_{\text{Res}} + I_{\text{Pol}}, \quad (8)$$

where $I_{\text{Ind}}$, $I_{\text{Res}}$, and $I_{\text{Pol}}$ are respectively the contributions of the inductive, resonance, and polarizability effects of the substituent X to the total change in the ionization potentials of the DX molecules.

3. The LFER is separately applied to each (out of three) contributions given in Eqs. (6) and (8) rather than the overall values $\Delta G$ and $I$. In the system of the Hammett—Taft correlation equations these contributions are characterized by corresponding $\sigma$-constants of substituents X.[8,9]

The inductive effect can be characterized by universal $\sigma_I$ constants. According to the classical concepts,[8,11] the value of the $\sigma_I$ constant of the substituent X is independent of the nature of the reaction center.

Conjugation depends on the charge on the reaction center (see, *e.g.*, Refs. 8, 9, 11). Therefore, quantitative estimation of conjugation can be done using several types of constants (*e.g.*, $\sigma_R^0$, $\sigma_R$, $\sigma_R^+$, and $\sigma_R^-$ parameters). In this work, conjugation in the D$^{\bullet+}$X radical cations was characterized using the $\sigma_R^+$-constants of substituents X. By definition,[8] the $\sigma_R^+$-parameters are employed if the reaction center (in our case, the D$^{\bullet+}$ center) bears a large positive charge.

Universal $\sigma_\alpha$-constants of substituents X serve as a measure of the polarizability effect.[8] It is more convenient to use the $\sigma_\alpha$-constants (they are normalized to other $\sigma$-constants and tabulated for most of substituents[8]) rather than carry out labor-consuming calculations using formula (7) when performing a correlation analysis procedure.

Thus, generally one can expect that the ionization potential, $I$, of the DX molecules, as well as the standard Gibbs free energy of the reaction (1), $\Delta G$, are single-valued linear functions of three arguments

$$I(\Delta G) = f(\sigma_I, \sigma_R^+, \sigma_\alpha), \quad (9)$$

where $\sigma_I$, $\sigma_R^+$ and $\sigma_\alpha$ are respectively the inductive, resonance and polarizability constants of the substituent X involved in the chemical bonding with the radical cation center D$^{\bullet+}$.

Particular forms of the correlation equations (9) are strongly dependent on the nature of the reaction center D$^{\bullet+}$. This is typical of both the C-centered radical cations $R_\pi{}^{\bullet+}X$ ($R_\pi$ is an aromatic or heteroaromatic ring, a double or a triple bond[3]) and the $E^{\bullet+}X_3$ (E = N,[2] P, As[6]) and $E^{\bullet+}X_2$ (E = S, Se)[7] systems with the radical cation center on the heteroatom E. General

**Table 1.** First vertical ionization potentials ($I(n_{Hal})$/eV) of HalX molecules (Hal = Cl, Br, I) and σ-constants[a] of substituents X

| Compound | X | $I(n_{Cl})^b$ | $I^1(n_{Br})^c$ | $I^2(n_{Br})^c$ | $I(n_{Br})^c$ | $I(n_I)^d$ | $\sigma_I$ | $\sigma_R^+$ | $\sigma_\alpha$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | H | 12.79 | 11.64 | 11.98 | 11.81 | 10.72 | 0 | 0 | 0 |
| **2** | Me | 11.30 | 10.53 | 10.85 | 10.69 | 9.86 | −0.05 | −0.26 | −0.35 |
| **3** | Et | 11.06 | 10.30 | 10.61 | 10.46 | 9.64 | −0.05 | −0.25 | −0.49 |
| **4** | Pr | 10.88 | 10.18 | 10.49 | 10.34 | 9.54 | −0.05 | −0.25 | −0.54 |
| **5** | $Pr^i$ | 10.78 | 10.12 | 10.41 | 10.27 | 9.44 | −0.03 | −0.25 | −0.62 |
| **6** | Bu | 10.84 | 10.13 | 10.44 | 10.29 | 9.52 | −0.05 | −0.25 | −0.57 |
| **7** | $Bu^i$ | 10.66 | 10.10 | 10.41 | 10.26 | 9.46 | −0.03 | −0.25 | −0.61 |
| **8** | $Bu^t$ | 10.61 | 9.95 | 10.24 | 10.10 | 9.27 | −0.07 | −0.19 | −0.75 |
| **9** | CN | 12.35 | 11.88 | 12.07 | 11.98 | 11.18 | 0.51 | 0.15 | −0.46 |
| **10** | $CF_3$ | 13.08 | 11.93 | 12.23 | 12.08 | 11.09 | 0.38 | 0.23 | −0.25 |
| **11** | $CH_2Cl$ | 11.40 | 10.77 | 11.06 | 10.92 | 10.06 | 0.13 | −0.14 | −0.54 |
| **12** | F | 12.81 | 11.86 | 12.19 | 12.03 | 10.97 | 0.45 | −0.52 | 0.13 |
| **13** | $Bu^s$ | 10.65 | — | — | — | — | −0.03 | −0.25 | −0.68 |
| **14** | $C_5H_{11}$ | — | 10.09 | 10.40 | 10.25 | 9.45 | −0.05 | −0.25 | −0.58 |
| **15** | $Me_3CCH_2$ | — | 10.04 | 10.34 | 10.19 | — | −0.03 | −0.25 | −0.67 |
| **16** | *cyclo*-$C_6H_{11}$ | — | 9.87 | 10.16 | 10.02 | 9.18 | −0.03 | −0.26 | −0.76 |
| **17** | $C_8H_{17}$ | — | 10.06 | 10.37 | 10.22 | — | −0.05 | −0.25 | −0.59 |
| **18** | $C_9H_{19}$ | — | 10.07 | 10.37 | 10.22 | — | −0.05 | −0.25 | −0.59 |
| **19** | $CH_2Br$ | — | 10.73 | 11.03 | 10.88 | — | 0.14 | −0.12 | −0.61 |
| **20** | OH | 11.22 | — | — | — | — | 0.33 | −1.25 | −0.03 |
| **21** | Cl | — | 11.01 | 11.27 | 11.14 | 10.40 | 0.42 | −0.31 | −0.43 |

[a] Standard sets of the $\sigma_I$-, $\sigma_R^+$-, and $\sigma_\alpha$-constants are the same as those used previously.[2—7]

[b] The $I(n_{Cl})$ values for molecules **1**, **2**, **9**, **11**, **12**, and **20** were taken from Ref. 1; those for molecules **3** and **10** were taken from Ref. 12. The $I(n_{Cl})$ values for molecules **4** and **6** were taken from Ref. 13; those for molecules **5**, **7**, **8**, and **13** were taken from Ref. 14.

[c] The $I(n_{Br})$ values for molecules **1**, **9—12**, **19**, and **21** were taken from Ref. 1; those for molecules **2—6**, **8**, and **14** were taken from Ref. 15. The $I(n_{Br})$ values for molecules **7**, **15**, and **16** were taken from Ref. 16; those for molecules **17** and **18** were taken from Ref. 17.

[d] The $I(n_I)$ values were taken from Ref. 5.

patterns of the substituent effects in radical cations (ratio between the inductive, resonance, and polarizability contributions, interrelation between the resonance and polarizability effects as well as conjugation involving organometallic substituents and its dependence on the nature of the radical cation center, *etc.*) are still poorly studied.

Table 1 lists the first vertical ionization potentials of the ClX ($I(n_{Cl})$), BrX ($I^1(n_{Br})$ and $I^2(n_{Br})$) and the average values, $I(n_{Br})$), and IX molecules (average values $I(n_I)$), determined by photoelectron spectroscopy with an accuracy of 0.01 eV. Joint analysis of the results of photoelectron spectroscopy measurements and quantum-chemical calculations showed[5,12—17] that for all HalX molecules studied in this work (see Table 1) the HOMOs are mainly localized on the 3p- (ClX), 4p- (BrX), and 5p-orbitals (IX molecules) of the lone electron pairs (LEPs) of the Hal atoms. Each Hal atom has three LEPs that form a σ-orbital and two degenerate π-orbitals, namely, $n(p_x)$ and $n(p_y)$. The first ionization potentials considered in this work correspond to detachment of an electron from the n-orbitals, which is emphasized by designation $I(n_{Hal})$ (Hal = Cl, Br, I).

In the general form the photoionization reaction (1) for the HalX molecules can be written as follows

$$\mathrm{HalX} \xrightarrow{h\nu} \mathrm{Hal}^{\bullet+}\mathrm{X} + e, \qquad (10)$$

where Hal = Cl, Br, I.

The unpaired electron in the $Hal^{\bullet+}X$ radical cations has the spin magnetic moment, $S = \pm 1/2$, and the orbital magnetic moment, $L = 1$. Because of the spin-orbit interaction the total angular momentum, $L + S$, takes the values 3/2 and 1/2, which corresponds to an energy difference Δ, and the band (in the photoelectron spectrum) corresponding to detachment of an electron from the n-orbitals of the Hal atoms is split into a doublet (for details, see Refs. 5 and 15—17).

Let us consider the relationships characterizing the spin-orbit interaction taking the ionization potentials of the BrX molecules as examples

$$\Delta = I^1(n_{Br}) - I^2(n_{Br}), \qquad (11)$$

$$I(n_{Br}) = [I^1(n_{Br}) + I^2(n_{Br})]/2, \qquad (12)$$

where $I^1(n_{Br})$ and $I^2(n_{Br})$ are the components of the doublet, Δ is the difference between these components (spin-orbit splitting); and $I(n_{Br})$ is the average value of the ionization potentials $I^1(n_{Br})$ and $I^2(n_{Br})$. The ionization potentials of the ClX and IX molecules are designated analogously to expression (12). The $I^1(n_I)$ and $I^2(n_I)$ values for the IX molecules were reported in Ref. 5. The spin-orbit interaction is sharply strengthened as the atomic number of the Hal element increases.[15] For instance, the $HalCH_3$ molecules are characterized by Δ values of ~0.03,[12] 0.32, and 0.63 eV for Hal = Cl, Br, and I, respectively. Therefore, comparative study of chlorides, bromides, and iodides can be performed only with the average values $I(n_{Hal})$ listed in Table 1.

As mentioned above, the HOMOs of the HalX molecules presented in Table 1 are mainly localized on the n-orbitals of the

Hal atoms. Nevertheless, the orbitals of the substituents X also contribute to the HOMOs. That is why the effects of substituents X cause the ionization potentials to vary over a wide range. These effects were studied using correlation analysis.

Correlation equations were obtained using the "Statgraphics 3.0" program package on an AT 286 personal computer. The data were processed by the least squares method at a 95% confidence level.

## Results and Discussion

Let us assume that the ionization potentials, $I(n_{Hal})$, of the HalX molecules (three series; Hal = Cl, Br, I) depend only on the inductive and resonance effects of substituents X, *i.e.*, the influence of substituents on the $I(n_{Hal})$ values is described by two-parameter equations

$$I(n_{Cl}) = 11.38 + 3.09\sigma_I + 0.95\sigma_R^+, \quad (13)$$

$S_a = 0.20$, $S_b = 0.74$, $S_c = 0.46$, $S_Y = 0.58$, $r = 0.766$, $n = 14$;

$$I^1(n_{Br}) = 10.59 + 2.74\sigma_I + 1.10\sigma_R^+, \quad (14)$$

$S_a = 0.15$, $S_b = 0.45$, $S_c = 0.54$, $S_Y = 0.37$, $r = 0.862$, $n = 19$;

$$I^2(n_{Br}) = 10.88 + 2.68\sigma_I + 1.05\sigma_R^+, \quad (15)$$

$S_a = 0.16$, $S_b = 0.48$, $S_c = 0.57$, $S_Y = 0.39$, $r = 0.841$, $n = 19$;

$$I(n_{Br}) = 10.74 + 2.71\sigma_I + 1.07\sigma_R^+, \quad (16)$$

$S_a = 0.15$, $S_b = 0.46$, $S_c = 0.56$, $S_Y = 0.38$, $r = 0.852$, $n = 19$;

$$I(n_I) = 9.92 + 2.53\sigma_I + 0.99\sigma_R^+, \quad (17)$$

$S_a = 0.14$, $S_b = 0.42$, $S_c = 0.50$, $S_Y = 0.34$, $r = 0.879$, $n = 15$,

where $S_a$, $S_b$, $S_c$ are the standard deviations of the coefficients of the correlation equation; $S_Y$ is the standard error of approximation; $r$ is the correlation coefficient; and $n$ is the sample volume.

Low correlation coefficients $r$ and large errors $S_Y$ indicate that substituents X affect the ionization potentials not only by the inductive and conjugation mechanisms and that the commonly accepted Koopmans approximation is too rough to describe the $I(n_{Hal})$ values of the HalX molecules under study. In the Koopmans approximation (see, *e.g.*, Refs. 1, 12) one has

$$I = -E_{HOMO}, \quad (18)$$

where $I$ is the first ionization potential and $E_{HOMO}$ is the HOMO energy. Earlier,[18] quantum-chemical calculations of neutral $R_\pi X$ molecules (three series; $R_\pi$ = $C_6H_5$, $H_2C{=}CH$, $HC{\equiv}C$) revealed that the $E_{HOMO}$ energies depend only on the inductive and resonance effects of substituents X. The "frozen" orbital approximation (18) means that both neutral molecules and radical cations (*e.g.*, HalX and $Hal^{\bullet +}X$, respectively) can be characterized by the same wave functions.[1,13] This ignores at least two important aspects of the rearrangement of the electronic system of the HalX molecules in gas-phase processes (10). First, the resonance properties of substituents X in neutral molecules and in radical cations are quantitatively described using different parameters, namely, the $\sigma_R^0$-constants in the former and the $\sigma_R^+$-constants in the latter case.[8,11] Usually, the stronger the resonance electron-donor properties of a substituent, the larger the difference between its $\sigma_R^0$- and $\sigma_R^+$-constants. Second, the Koopmans approximation (18) ignores the polarizability effect, which indeed does not occur in neutral molecules but plays an important role in the $R_\pi^{\bullet +}X$, $E^{\bullet +}X_2$, and $E^{\bullet +}X_3$ radical cations.[2,3,6,7]

Thus, bad statistical characteristics of Eqs. (13)—(17) are due to ignoring the polarizability effect in gas-phase processes (10). On going from these equations to the corresponding three-parameter relationships

$$I(n_{Cl}) = 12.76 + 1.26\sigma_I + 1.54\sigma_R^+ + 2.53\sigma_\alpha, \quad (19)$$

$S_a = 0.08$, $S_b = 0.15$, $S_c = 0.08$, $S_d = 0.13$, $S_Y = 0.09$, $r = 0.994$, $n = 14$;

$$I^1(n_{Br}) = 11.57 + 1.64\sigma_I + 1.37\sigma_R^+ + 1.73\sigma_\alpha, \quad (20)$$

$S_a = 0.06$, $S_b = 0.11$, $S_c = 0.12$, $S_d = 0.09$, $S_Y = 0.08$, $r = 0.994$, $n = 19$;

$$I^2(n_{Br}) = 11.92 + 1.51\sigma_I + 1.33\sigma_R^+ + 1.83\sigma_\alpha, \quad (21)$$

$S_a = 0.06$, $S_b = 0.11$, $S_c = 0.11$, $S_d = 0.09$, $S_Y = 0.08$, $r = 0.994$, $n = 19$;

$$I(n_{Br}) = 11.75 + 1.57\sigma_I + 1.34\sigma_R^+ + 1.77\sigma_\alpha, \quad (22)$$

$S_a = 0.06$, $S_b = 0.11$, $S_c = 0.11$, $S_d = 0.09$, $S_Y = 0.08$, $r = 0.994$, $n = 19$;

$$I(n_I) = 10.69 + 1.66\sigma_I + 1.19\sigma_R^+ + 1.41\sigma_\alpha, \quad (23)$$

$S_a = 0.06$, $S_b = 0.11$, $S_c = 0.11$, $S_d = 0.09$, $S_Y = 0.07$, $r = 0.995$, $n = 15$,

where $\sigma_\alpha$ is the polarizability constant of substituent X, the correlation coefficients $r$ sharply increase and the standard deviations of the coefficients ($S_a$, $S_b$, $S_c$) and the error of approximation ($S_Y$) substantially decrease.

In contrast to relationships (13)—(17) the absolute terms of Eqs. (19)—(23) virtually coincide with the corresponding ionization potentials, $I(n_{Hal})$, of the HalH molecules, since the $\sigma_I$, $\sigma_R^+$, and $\sigma_\alpha$-constants for X = H

**Table 2.** Contributions Ind, Res, and Pol (%) to the overall change in the ionization potentials $I(n_{Hal})$ of HalX molecules due to the influence of substituents X

| Ionization potential $I(n_{Hal})$ | Equation | Sample volume $n$ | Ind | Res | Pol |
|---|---|---|---|---|---|
| | | | | % | |
| $I(n_{Cl})$ | (19) | 14 | 14±2 | 44±2 | 42±2 |
| $I^1(n_{Br})$ | (20) | 19 | 27±2 | 29±3 | 44±2 |
| $I^2(n_{Br})$ | (21) | 19 | 25±2 | 29±3 | 46±2 |
| $I(n_{Br})$ | (22) | 19 | 26±2 | 29±2 | 45±2 |
| $I(n_I)$ | (23) | 15 | 31±2 | 29±3 | 40±3 |
| $I(n_{Cl})$ | (25) | 12 | 16±2 | 30±3 | 54±3 |
| $I(n_{Br})$ | (26) | 12 | 27±2 | 27±3 | 46±3 |
| $I(n_I)$ | (27) | 12 | 32±3 | 28±3 | 40±3 |

equal zero (see Table 1). Correlation equations (19)—(23) can be written in the general form

$$I(n_{Hal}) = I_H + b\sigma_I + c\sigma_R^+ + d\sigma_\alpha, \quad (24)$$

where $b\sigma_I$ = Ind, $c\sigma_R^+$ = Res, and $d\sigma_\alpha$ = Pol are respectively the contributions of the inductive, resonance, and polarizability effects to the total change in the ionization potentials of unsubstituted HalH molecules due to the influence of substituents X on going from HalH to HalX (Table 2).

Analysis of the data listed in Table 2 shows that the Pol contribution is superior to the Ind and Res contributions, being comparable with the Res value only for the ClX molecules. Therefore, the influence of substituents on the ionization potentials cannot be even rough estimated ignoring the polarizability effect.

By and large, the ratio of the three contributions under consideration is a function of the sample size, $n$. As $n$ varies, the range of changes in the $\sigma_I$, $\sigma_R^+$ and $\sigma_\alpha$ values and, hence, the ratio of the Ind, Res, and Pol contributions also changes. For instance, the series of the ClX molecules ($n$ = 14) described by Eq. (19) is characterized by variation of the $\sigma_R^+$ values from −1.25 (X = OH) to 0.23 (X = $CF_3$) and by the Res contribution of 44% (see Table 2). The BrX molecules are described by Eq. (22). Here we deal with the largest sample volume ($n$ = 19); however, the $\sigma_R^+$ values vary in much narrower range from −0.52 (X = F) to 0.23 (X = $CF_3$), which causes a decrease in the Res contribution down to 29% (see Table 2). For this reason, we chose the same sample volume ($n$ = 12) for three series of the HalX molecules (Hal = Cl, Br, I) with the same substituents X (compounds **1—12**, see Table 1) and then calculated the correlation equations (25)—(27).

$$I(n_{Cl}) = 12.79 + 1.18\sigma_I + 1.70\sigma_R^+ + 2.56\sigma_\alpha, \quad (25)$$

$S_a = 0.08$, $S_b = 0.17$, $S_c = 0.16$, $S_d = 0.13$, $S_Y = 0.10$, $r = 0.995$, $n = 12$;

$$I(n_{Br}) = 11.74 + 1.60\sigma_I + 1.26\sigma_R^+ + 1.77\sigma_\alpha, \quad (26)$$

$S_a = 0.06$, $S_b = 0.12$, $S_c = 0.12$, $S_d = 0.10$, $S_Y = 0.07$, $r = 0.996$, $n = 12$;

$$I(n_I) = 10.67 + 1.68\sigma_I + 1.16\sigma_R^+ + 1.37\sigma_\alpha, \quad (27)$$

$S_a = 0.07$, $S_b = 0.14$, $S_c = 0.13$, $S_d = 0.11$, $S_Y = 0.08$, $r = 0.994$, $n = 12$.

Using Eqs. (25)—(27), we calculated the Ind, Res, and Pol contributions (see Table 2) and their ratios (Table 3). These data allowed a pioneering comparative study of the effects of substituents X in the $Hal^{\cdot+}X$ radical cations. On going successively from Hal = Cl to Br and I the ratios of the contributions vary as follows.

1. The Ind/Res and Ind/Pol ratios increase. Because of this, both the Ind/(Res + Pol) ratio (see Table 3) and the Ind contribution = Ind/(Ind + Res + Pol) (see Table 2) also increase. Thus, the "sensitivity" of the reaction center, $Hal^{\cdot+}$, to the inductive effect of substituents X in the $Hal^{\cdot+}X$ radical cations increases in the order Cl < Br < I as the Hal atom changes.

2. The Res/Ind ratio decreases while the Res/Pol ratio increases. In this case the Res/(Ind + Pol) ratio (see Table 3) and the Res contribution (see Table 2) are virtually independent on the nature of the Hal atom (Cl, Br, I). Therefore, variation of the reaction center, $Hal^{\cdot+}$, in the $Hal^{\cdot+}X$ (Hal = Cl, Br, I) radical cations has little effect on conjugation between $Hal^{\cdot+}$ and substituents X. The reaction center $Hal^{\cdot+}$ is a resonance acceptor (donor) toward the substituent X exhibiting the properties of a resonance donor (acceptor). In this connection mention may be made of nearly identical (from the standpoint of the $\sigma_R$, $\sigma_R^+$, and $\sigma_R^-$ constants)[8] electron-donor properties of neutral substituents Cl, Br, and I toward various reaction centers that are either electrically neutral or bear a partial positive (negative) charge.

3. The Pol/Ind, Pol/Res, and Pol/(Ind + Res) ratios, as well as the Pol contribution decrease (see Tables 2

**Table 3.** Ratios of the Ind, Res, and Pol contributions for HalX (Hal = Cl, Br, I) molecules

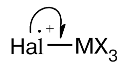
| Ratio | ClX (Eq. (25)) | BrX (Eq. (26)) | IX (Eq. (27)) |
|---|---|---|---|
| Ind/Res | 0.5 | 1.0 | 1.1 |
| Ind/Pol | 0.3 | 0.6 | 0.8 |
| Ind/(Res + Pol) | 0.2 | 0.4 | 0.5 |
| Res/Ind | 1.9 | 1.0 | 0.9 |
| Res/Pol | 0.6 | 0.6 | 0.7 |
| Res/(Ind + Pol) | 0.4 | 0.4 | 0.4 |
| Pol/Ind | 3.3 | 1.7 | 1.2 |
| Pol/Res | 1.8 | 1.7 | 1.4 |
| Pol/(Ind + Res) | 1.2 | 0.8 | 0.7 |

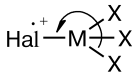
and 3). This means that the polarizability effect in the Hal$^{\bullet+}$X radical cations strongly depends on the type of the reaction center Hal$^{\bullet+}$ and decreases in the order Cl > Br > I. This can be rationalized by analyzing Eq. (7), according to which the energy of the interaction between the cation and induced dipole (and, hence, the Pol contribution) in the Hal$^{\bullet+}$X systems sharply decreases as the distance $r$ between the radical cation center Hal$^{\bullet+}$ and the dipole induced in the substituent X increases. To a first approximation, $r$ can be set equal to the Hal—X bond lengths in neutral HalX molecules.[10] The Hal—X bond is appreciably lengthened as the atomic number of the Hal atom increases. For instance, the Hal—C bond lengths in the HalCH$_3$ molecules are 1.778, 1.933, and 2.133 Å for Hal = Cl, Br, and I, respectively.[19] Thus, the first factor affecting a decrease in the Pol contribution upon going from one Hal atom to another is an increase in the $r$ distance in the order Cl < Br < I. The second factor, which affects the Pol contribution according to formula (7), is the magnitude of the positive charge $q$ on the radical cation center Hal$^{\bullet+}$. The charge $q$ cannot be considered completely localized on the reaction center Hal$^{\bullet+}$ of the Hal$^{\bullet+}$X radical cations. Delocalization of the unpaired electron (and, hence, the positive charge $q$) is due to conjugation in the Hal$^{\bullet+}$—X fragments and to the inductive effect of substituents X. As shown above, conjugation in the Hal$^{\bullet+}$—X fragments (*i.e.*, the Res contribution, see Table 2) is virtually independent of the Hal atom (Cl, Br, I). Therefore, conjugation in the three series of Hal$^{\bullet+}$X systems under study affects the charge $q$ in a nearly identical manner (see Eqs. (25)—(27)), whereas the main reason for variation of the charge $q$ is the inductive effect of substituents X. Indeed, the Ind contribution increases on going from Cl to Br and then to I (see Table 2); hence, the inductive effect responsible for delocalization of the unpaired electron and the positive charge $q$ increases in importance, while the charge $q$ and the Pol contribution decrease.

Thus, from Eqs. (25)—(27) it follows that isostructural radical cations Cl$^{\bullet+}$X, Br$^{\bullet+}$X, and I$^{\bullet+}$X are characterized by virtually the same Res contribution, an increase in the Ind contribution, and a decrease in the Pol contribution on going from Cl to Br and then to I. Nearly constant values of the Res contributions give an indication of interrelation between the Ind and Pol contributions. As shown above, with the same X the distance between the radical cation center Hal$^{\bullet+}$ and the dipole induced in the substituent X increases in order Cl$^{\bullet+}$X—Br$^{\bullet+}$X—I$^{\bullet+}$X (an increase in the distance $r$ in formula (7)). Let us assume, to a rough approximation, that the positive charge $q$ on the radical cation center Hal$^{\bullet+}$ is independent on the nature of Hal$^{\bullet+}$ and that it is an increase in $r$ that is responsible for the decrease in the Pol contribution in the above-mentioned isostructural radical cations. Then, taking into account that the Res contribution is independent on the nature of the Hal$^{\bullet+}$ center, an increase in the Ind contribution (see Table 2) in this series of radical cations is a natural consequence of the decrease in the Pol contribution. In this connection it should be emphasized that the assumption made needs further substantiation.

Let us consider now the ionization potentials, $I(\mathrm{n_{Hal}})$, of fourtheen organometallic compounds HalMH$_3$ (Hal = Cl, Br, I; M = Si, Ge) and HalMMe$_3$ (Hal = Cl, Br; M = Si, Ge, Sn, Pb) listed in Table 4. Only for the ClMMe$_3$ (M = Si, Ge, Sn, Pb) molecules the interpretation of the photoelectron spectra seems to be contradictory.[11,20,21,23] The $I(\mathrm{n_{Cl}})$ potentials taken from Ref. 21 (see Table 4) seem to be more substantiated. Based on the $I(\mathrm{n_{Hal}})$ values[1,20—22] and the $\sigma_I$ and $\sigma_\alpha$ constants,[2,3,5,7] we calculated the resonance $\sigma_R^+$-constants of the substituents SiH$_3$, GeH$_3$, and MMe$_3$ (M = Si, Ge, Sn, Pb) using Eqs. (19)—(23) and (25)—(27). They are listed in Table 4. Analysis of the $\sigma_R^+$ values allows a number of general conclusions.

1. The signs of the $\sigma_R^+$-constants alternate. In the Hal$^{\bullet+}$MX$_3$ (X = H, Me) radical cations, similarly to related neutral molecules[11], the MX$_3$ substituents exhibit dual resonance properties (both acceptor and donor properties simultaneously) toward the reaction center Hal$^{\bullet+}$. The resonance acceptor effect of substituents MX$_3$ (M = Si, Ge, Sn, Pb) toward Hal$^{\bullet+}$ (d,n-conjugation) is the interaction between the n-orbital of the unpaired electron of the Hal atom and the nd-orbital of the M atom and the σ*-orbitals of the M—X bonds. When d,n-conjugation dominates over the oppositely directed resonance donor effect, the $\sigma_R^+$-constants of substituents MX$_3$ are positive. The resonance donor effect of substituents MX$_3$ toward Hal$^{\bullet+}$ (σ,n-conjugation) is the interaction between the σ-orbitals of the M—X bonds and the n-orbital of the unpaired electron of the Hal atom. When σ,n-conjugation dominates over d,n-conjugation, the $\sigma_R^+$-constants of substituents MX$_3$ are negative.





2. The effect of d,n-conjugation weakens, first, as the atomic number of the element M increases. This follows from a decrease in the positive values of the $\sigma_R^+$-constants of substituents MH$_3$ in the Hal$^{\bullet+}$MH$_3$ radical cations on going from M = Si to M = Ge (see Table 4). Second, d,n-conjugation weakens on going from the Hal$^{\bullet+}$SiH$_3$ radical cations (Hal = Cl, Br) to the corresponding Hal$^{\bullet+}$SiMe$_3$ radical cations.

3. A feature of the Cl$^{\bullet+}$MMe$_3$ and Br$^{\bullet+}$MMe$_3$ radical cations is noticeable "competition" between the two resonance effects of the MMe$_3$ substituents. d,n-Conjugation dominates for M = Si, while σ,n-conjugation is predominant for M = Ge, Sn, and Pb. The resonance donor effect σ,n-conjugation is strengthened as the atomic number of the element M increases. This follows from an increase in the negative values of the $\sigma_R^+$-constants of the MMe$_3$

**Table 4.** $\sigma_R^+$-Constants[a] of organometallic substituents containing Si, Ge, Sn, and Pb atoms calculated using Eqs. (19)—(23) and Eqs. (25)—(27) based on the $I(n_{Hal})$ values

| Compound | $I(n_{Hal})$/eV | Substituent | $\sigma_R^+$ | | | | | | | | | Average $\sigma_R^+$ value |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | (19) | (20) | (21) | (22) | (23) | (25) | (26) | (27) | [b] | |
| $ClSiH_3$ | 11.65[c] | $SiH_3$ | 0.28 | — | — | — | — | 0.25 | — | — | — | 0.26±0.02 |
| $BrSiH_3$ | 10.96,[c,d] 11.10,[c] 11.03[c] | $SiH_3$ | — | 0.35 | 0.24 | 0.28 | — | — | 0.31 | — | — | 0.30±0.06 |
| $ISiH_3$ | 10.06[c] | $SiH_3$ | — | — | — | — | 0.23 | — | — | 0.23 | 0.13 | 0.20±0.07 |
| $ClGeH_3$ | 11.30[c] | $GeH_3$ | 0.07 | — | — | — | — | 0.06 | — | — | — | 0.06±0.01 |
| $BrGeH_3$ | 10.61,[c,d] 10.83,[c] 10.72[c] | $GeH_3$ | — | 0.11 | 0.05 | 0.07 | — | — | 0.08 | — | — | 0.08±0.03 |
| $IGeH_3$ | 9.86[c] | $GeH_3$ | — | — | — | — | 0.08 | — | — | 0.07 | 0.01 | 0.05±0.04 |
| $ClSiMe_3$ | 10.84[e] | $SiMe_3$ | 0.06 | — | — | — | — | 0.04 | — | — | — | 0.05±0.01 |
| $BrSiMe_3$ | 10.23,[d,f] 10.43,[f] 10.33[f] | $SiMe_3$ | — | 0.12 | 0.05 | 0.07 | — | — | 0.08 | — | — | 0.08±0.04 |
| $ClGeMe_3$ | 10.35[f] | $GeMe_3$ | −0.49 | — | — | — | — | −0.45 | — | — | — | −0.47±0.02 |
| $BrGeMe_3$ | 9.78,[d,f,g] 10.05,[g] 9.92[g] | $GeMe_3$ | — | −0.42 | −0.44 | −0.45 | — | — | −0.46 | — | — | −0.44±0.02 |
| $ClSnMe_3$ | 10.16[f] | $SnMe_3$ | −0.60 | — | — | — | — | −0.55 | — | — | — | −0.58±0.03 |
| $BrSnMe_3$ | 9.60,[d,f] 9.85,[f] 9.72[f] | $SnMe_3$ | — | −0.53 | −0.56 | −0.58 | — | — | −0.60 | — | — | −0.57±0.04 |
| $ClPbMe_3$ | 9.70[f] | $PbMe_3$ | −0.90 | — | — | — | — | −0.83 | — | — | — | −0.86±0.04 |
| $BrPbMe_3$ | 9.30,[d,f] 9.55,[f] 9.42[f] | $PbMe_3$ | — | −0.75 | −0.80 | −0.81 | — | — | −0.85 | — | — | −0.80±0.05 |

[a] The $\sigma_R^+$-constants were calculated using a standard set of the $\sigma_I$ and $\sigma_\alpha$ constants of the $MH_3$ and $MMe_3$ substituents; see Refs. 2, 3, 5, and 7.

[b] The $\sigma_R^+$ values were taken from Ref. 5.

[c] The $I(n_{Hal})$ values of $HalMH_3$ molecules were taken from Ref. 1.

[d] Three $I(n_{Hal})$ values given for each bromo derivative $BrMH_3$ and $BrMMe_3$ are $I^1(n_{Br})$, $I^2(n_{Br})$, and the average value, $I(n_{Br})$.

[e] The $I(n_{Cl})$ values were taken from Ref. 20.

[f] The $I(n_{Hal})$ values were taken from Ref. 21.

[g] The values were taken from Ref. 22.

substituents with variation of the M atom in the series Ge—Sn—Pb. Analysis of the $\sigma_R^+$ values suggests that the $MMe_3$ (M = Ge, Sn, Pb) substituents belong to typical resonance electron donors. For instance, the donor properties of the $PbMe_3$ group are intermediate between those of the F and OH substituents (see Tables 1 and 4).

4. Noteworthy is that the resonance properties of the $SiH_3$, $GeH_3$, $SiMe_3$, $GeMe_3$, $SnMe_3$, and $PbMe_3$ substituents are virtually independent of the reaction center ($Cl^{\bullet+}$, $Br^{\bullet+}$, $I^{\bullet+}$). This is indicated by close values of the $\sigma_R^+$-constants of the $SiH_3$ ($GeH_3$) substituent in the $Hal^{\bullet+}SiH_3$ ($Hal^{\bullet+}GeH_3$) radical cations with different Hal atoms (see Table 4). For more detailed consideration, let us denote the parameters characterizing the resonance interaction in organometallic chlorides and bromides as $\sigma_R^+(Cl)$ and $\sigma_R^+(Br)$, respectively (see Table 5). Conjugation between organometallic substituents and the radical cation center $S^{\bullet+}$ or the benzene ring, which can either bear an excess positive charge or be a radical cation center, is characterized by the $\sigma_R^+(S)$ and $\sigma_R^+(B)$ constants, respectively.**24** They are also listed in Table 5.

**Table 5.** $\sigma_R^+$-Parameters of $MX_3$ substituents bound to different radical cation centers

| Substituent | $\sigma_R^+(Cl)$ | $\sigma_R^+(Br)$ | $\sigma_R^+(S)$[a] | $\sigma_R^+(B)$[b] |
|---|---|---|---|---|
| $SiH_3$ | 0.26 | 0.30 | 0.24 | 0.03 |
| $SiMe_3$ | 0.05 | 0.08 | 0.15 | 0.02 |
| $GeH_3$ | 0.06 | 0.08 | 0.16[b] | −0.03 |
| $GeMe_3$ | −0.47 | −0.44 | −0.10 | −0.11 |
| $SnMe_3$ | −0.58 | −0.57 | −0.15 | −0.21 |
| $PbMe_3$ | −0.86 | −0.80 | −0.31 | −0.26 |

[a] Data taken from Ref. 24.

[b] Data taken from Refs. 7 and 24.

There is a linear correlation between the $\sigma_R^+(Cl)$ and $\sigma_R^+(Br)$ parameters

$$\sigma_R^+(Cl) = -0.03 + 1.01\sigma_R^+(Br), \tag{28}$$

$$S_a = 0.01,\ S_b = 0.02,\ S_Y = 0.02\ r = 0.999,\ n = 6.$$

Here, the absolute term virtually equals zero while the slope is almost unity. This is yet another argument in favor of the assumption that resonance interactions in the $Hal^{\bullet+}MX_3$ systems are independent of the type of the radical cation center ($Cl^{\bullet+}$, $Br^{\bullet+}$). An analogous conclusion was also drawn for the $Hal^{\bullet+}X$ (Hal = Cl, Br, I) radical cations containing inorganic and organic substituents X (see above).

Correlation equations

$$\sigma_R^+(Cl) = -0.25 + 2.04\sigma_R^+(S), \tag{29}$$

$$S_a = 0.01,\ S_b = 0.05,\ S_Y = 0.02,\ r = 0.999,\ n = 6$$

and

$$\sigma_R{}^+(\mathrm{Br}) = -0.22 + 2.02\sigma_R{}^+(\mathrm{S}), \quad (30)$$

$$S_a = 0.02,\ S_b = 0.08,\ S_Y = 0.04,\ r = 0.997,\ n = 6,$$

have good statistical characteristics, which indicates similarity between conjugation in the Cl-, Br-, and S-centered radical cations containing the organometallic substituents $MX_3$ (M = Si, Ge, Sn, Pb; X = H, Me).

However, statistical characteristics of the correlation equations

$$\sigma_R{}^+(\mathrm{Cl}) = 0.07 + 3.53\sigma_R{}^+(\mathrm{B}), \quad (31)$$

$$S_a = 0.06,\ S_b = 0.44,\ S_Y = 0.12,\ r = 0.971,\ n = 6$$

and

$$\sigma_R{}^+(\mathrm{Br}) = 0.10 + 3.50\sigma_R{}^+(\mathrm{B}), \quad (32)$$

$$S_a = 0.06,\ S_b = 0.42,\ S_Y = 0.12,\ r = 0.972,\ n = 6$$

are somewhat poorer compared to those of relationships (29) and (30). This can be due to more efficient delocalization of the unpaired electron and positive charge in the $C_6H_5{}^{\bullet+}MX_3$ systems compared to the Cl-, Br-, and S-centered radical cations.

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