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Substituent Effects in I-Centered Radical Cations

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Abstract—The inductive, resonance, and polarization effects of substituents on the ionization potential of iodine *n* orbitals in IX, $ISnR_3$, and IC≡CX molecules, and also on the energy of the charge-transfer band in the UV spectra of the complexes of IX and $ISnR_3$ with tetracyanoethylene and iodine were studied. The radical cations generated by photoionization of individual molecules in the gas phase and occurring as components of contact radical ion pairs (excited state of charge-transfer complexes) in solution have similar electronic structure. The resonance parameters σ_R^+ of organosilicon, organogermanium, and organotin substituents bound to the radical cation centers $I^{+\cdot}$ and $I^{+\cdot}C{\equiv}C$ were calculated for the first time.

The positive charge and unpaired electron in radical cations $R_\pi^{+\cdot}X$ and $Z^{+\cdot}X_nY_m$ [R_π is an aromatic or heteroaromatic ring, and Z is an atom with lone electron pairs (N, P, S, Se)] determine the character of intramolecular interaction of the reaction centers $R_\pi^{+\cdot}$ and $Z^{+\cdot}$ with inorganic and/or organic substituents X and Y [1–6]. The resonance effect of substituents X and Y can be quantitatively described by the parameters σ_R^+ not only in the systems $R_\pi^{+\cdot}X$, but also in $Z^{+\cdot}X_nY_m$. In the radical cations $R_\pi^{+\cdot}X$ and $Z^{+\cdot}X_nY_m$ occurring in the gas phase or as components of radical ion pairs [$A^{-\cdot}$, $R_\pi^{+\cdot}X$] and [$A^{-\cdot}$, $Z^{+\cdot}X_nY_m$] in solution (such radical ion pairs are excited states of charge-transfer complexes with acceptors A, e.g., iodine or tetracyanoethylene), the substituent effects are not limited to the inductive and resonance effects. A comparable, and sometimes even prevailing contribution is made by the polarization effect associated with the polarizability of substituents X and Y under the influence of the positive charge on the reaction centers $R_\pi^{+\cdot}$ and $Z^{+\cdot}$ [3, 6]. Therefore, within the framework of the Hammett–Taft correlation equations, the total effect of substituents in the radical cations is described not only by the inductive (σ_I) and resonance (σ_R^+) parameters, but also by the polarization σ_α parameter of substituents X and Y [1–6].

Using our approach, it is possible to illustrate the substituent effects on the ionization potentials by applying the Hammett–Taft equation to the published large sets of ionization potentials. It also allows quantitative evaluation of the resonance parameters σ_R^+ of organosilicon, organogermanium, and organotin substituents bound to the radical cation centers. Such estimation is very urgent, because the parameters σ_R^+ of organometallic substituents are not universal (they depend on particular reaction center), as follows from the modern concept of conjugation of silicon group elements [7].

The considered method for evaluating the substituent effects was developed previously for the systems $R_\pi^{+\cdot}X$ [1–3] and also for N-, P-, S-, and Se-centered [4–6] radical cations.

Proceeding with these studies, we studied the substituent effects in I-centered radical cations generated by photoionization of neutral molecules and formed upon electronic excitation of charge-transfer complexes of these molecules with tetracyanoethylene or iodine; also we calculated the parameters of organosilicon, organogermanium, and organotin substituents.

The first vertical ionization potentials (*IP*) of I–X (series A) and I–C≡C–X (series B) molecules, determined by photoelectron spectroscopy with an accuracy of several hundredth of electron-volt, are listed in Tables 1 and 2. In Table 3, the *IP* values for some I–X molecules (series C) are compared with the electronic transition energies $h\nu_{CT}$ in the spectra of their charge-transfer complexes with tetracyanoethylene. The corresponding data for $ISnR_3$ molecules (series D) and their charge-transfer complexes with iodine are listed in Table 4.

The ionization potential of IH corresponds to electron removal from the highest occupied molecular orbital (HOMO) localized on the 5*p* orbitals of the iodine lone electron pairs [8]. Three lone electron pairs of iodine form two degenerate π orbitals, $n(p_x)$ and $n(p_y)$, and a σ orbital. In going from IH to IX (Table 1), I–C≡C–X (Table 2), and $ISnR_3$ (Table 4), the HOMO

Table 1. Ionization potentials (eV) of iodine *n* orbitals $IP(A_1)$ and $IP(A_2)$, differences $\Delta(A) = IP(A_2) - IP(A_1)$, parameters $IP(A) = [IP(A_1) + IP(A_2)]/2$, and σ parameters of substituents X in organyl iodides IX (series A)[a]

Comp. no.	X	$IP(A_1)$	$IP(A_2)$	$\Delta(A)$	$IP(A)$	σ_I[b]	σ_R^+	σ_P^+	σ_α
1	H	10.39	11.05	0.66	10.72	0	0	0	0
2	Me	9.54	10.17	0.63	9.86	–0.05	–0.26	–0.31	–0.35
3	Et	9.35	9.93	0.58	9.64	–0.05	–0.25	–0.30	–0.49
4	Pr	9.26	9.83	0.57	9.54	–0.05	–0.25	–0.30	–0.54
5	*i*-Pr	9.18	9.74	0.56	9.46	–0.03	–0.25	–0.28	–0.62
6	Bu	9.23	9.79	0.56	9.51	–0.05	–0.25	–0.30	–0.57
7	*i*-Bu	9.20	9.76	0.56	9.48	–0.03	–0.25	–0.28	–0.61
8	*t*-Bu	9.04	9.59	0.55	9.32	–0.07	–0.19	–0.26	–0.75
9	C_5H_{11}	9.18	9.72	0.54	9.45	–0.05	–0.25	–0.30	–0.58
10	*i*-C_5H_{11}	9.17	9.72	0.55	9.44	–0.03	–0.25	–0.28	–0.61
11	CMe_2Et	8.93	9.50	0.57	9.22	–0.07	–0.19	–0.26	–0.82
12	C_6H_{13}	9.17	9.73	0.56	9.45	–0.05	–0.25	–0.30	–0.59
13	*cyclo*-C_6H_{11}	8.91	9.45	0.54	9.18	–0.03	–0.26	–0.29	–0.76
14	$CH{=}CH_2$	9.35	10.08	0.73	9.72	0.13	–0.29	–0.16	–0.50
15	CN	10.91	11.45	0.54	11.18	0.51	0.15	0.66	–0.46
16	CH_2Cl	9.76	10.35	0.59	10.06	0.13	–0.14	–0.01	–0.54
17	F	10.62	11.32	0.70	10.97	0.45	–0.52	–0.07	0.13
18	Cl	10.08	10.72	0.64	10.40	0.42	–0.31	0.11	–0.43
19	Br	9.83	10.42	0.59	10.12	0.45	–0.30	0.15	–0.59
20	$H_2C{=}CHCH_2$	9.32	10.26 9.72	0.94 0.40	9.79 9.52	–0.06	–0.16	–0.22	–0.57
21	CF_3	10.81	11.37	0.56	11.09	0.38	0.23	0.61	–0.25
22	SiH_3	9.78	10.33	0.55	10.06	–0.04	0.13 0.13 0.13 (0.13)	0.09 0.09 0.09 (0.09)	–0.59
23	GeH_3	9.59	10.14	0.55	9.86	–0.04	0.01 0.01 0.01 (0.01)	–0.03 –0.03 –0.03 (–0.03)	–0.60
24	$SnMe_3$	8.95	9.34	0.39	9.14	–0.13	–0.30 –0.44 –0.37 (–0.37)	–0.43 –0.57 –0.50 (–0.50)	–0.60

[a] The $IP(A_1)$ and $IP(A_2)$ values for compounds **1, 2, 15, 17–19, 22**, and **23** are taken from [8]; those for compounds **3–8, 14**, and **16**, from [9]; those for compounds **9–11**, from [10]; those for compounds **12, 13, 20**, and **21**, from [11]; and those for compound **24**, from [12]. [b] The standard set of constants σ_I, σ_R^+, $\sigma_P^+ = \sigma_I + \sigma_R^+$, and σ_α was used by us previously [1–6].

energy (if characterized by *IP*) changes. However, despite a contribution from the orbitals of substituents X. C≡C–X, and SnR_3, the HOMO, according to [8–15], remains mainly localized on the iodine *n* orbitals (a particular case of compound **20** in Table 1 is considered below).

A characteristic feature of the photoelectron spectra of the iodine derivatives is pronounced spin–orbital coupling.

Photoionization of neutral IX (or IC≡CX, $ISnR_3$) molecules yields radical cations $I^{+\cdot}X$:

$$IX + h\nu \longrightarrow I^{+\cdot}X + \bar{e}. \qquad (1)$$

The unpaired electron in $I^{+\cdot}X$ can be characterized by the orbital magnetic momentum $L = 1$ and spin magnetic momentum $S = \pm 1/2$. With spin–orbital coupling, the total angular momentum $J = L + S$ takes two values (3/2 and 1/2) corresponding to different energies. Therefore, the first band in the photoelectron spectrum, originating from ionization (1) and corre-

Table 2. Ionization potentials (eV) of iodine *n* orbitals $IP(B_1)$ and $IP(B_2)$, differences $\Delta(B) = IP(B_1) - IP(B_2)$, values of $IP(B) = [IP(B_1) + IP(B_2)]/2$, and σ parameters of substituents X in iodoacetylene derivatives I–C≡C–X (series B)[a]

Comp. no.	X	$IP(B_1)$	$IP(B_2)$	$\Delta(B)$	$IP(B)$	σ_I	σ_R^+	σ_P^+	σ_α
1	H	9.71	10.11	0.40	9.91	0	0	0	0
2	Me	9.18	9.54	0.36	9.36	–0.05	–0.26	–0.31	–0.35
3	*t*-Bu	9.00	9.24	0.24	9.12	–0.07	–0.19	–0.26	–0.75
4	CF_3	10.17	10.58	0.41	10.38	0.38	0.23	0.61	–0.25
5	Cl	9.44	9.75	0.31	9.60	0.42	–0.31	0.11	–0.43
6	Br	9.34	9.68	0.34	9.51	0.45	–0.30	0.15	–0.59
7	$SiMe_3$	9.21	9.50	0.29	9.36	–0.15	0.02	–0.13	–0.72
							0.03	–0.12	
							0.03	–0.12	
							(0.03)	(–0.12)	
		9.25	9.54	0.29	9.4	–0.15	0.05	–0.10	–0.72
							0.06	–0.09	
							0.06	–0.09	
							(0.06)	(–0.09)	
8	$GeMe_3$	9.09	9.35	0.26	9.22	–0.11	–0.16	–0.27	–0.60
							–0.19	–0.30	
							–0.17	–0.28	
							(–0.17)	(–0.28)	

[a] The $IP(B_1)$ and $IP(B_2)$ values for compounds **1, 2, 4**, and **5** are taken from [9]; those for compounds **3, 7**, and **8**, from [13, 14]; and those for compound **6**, from [10]. For the standard set of σ parameters, see Table 1.

Table 3. Electronic transitions energies (eV) $h\nu_{CT}(C_1)$ and $h\nu_{CT}(C_2)$, differences $\Delta(C) = h\nu_{CT}(C_2) - h\nu_{CT}(C_1)$, and values of $h\nu_{CT}(C) = [h\nu_{CT}(C_1) + h\nu_{CT}(C_2)]/2$ in the spectra of charge-transfer complexes with tetracyanoethylene; ionization potentials (eV) of iodine *n* orbitals $IP(C_1)$, $IP(C_2)$, differences $\Delta(C) = IP(C_2) - IP(C_1)$, and values of $IP(C) = [IP(C_1) + IP(C_2)]/2$ for alkyl iodides IX (series C)[a]

Comp. no.	X	$h\nu_{CT}(C_1)$	$h\nu_{CT}(C_2)$	$\Delta(C)$	$h\nu_{CT}(C)$	$IP(C_1)$	$IP(C_2)$	$IP(C)$
1	Me	3.26	3.76	0.50	3.51	9.54	10.17	9.86
2	Et	3.18	3.59	0.41	3.38	9.35	9.93	9.64
3	*i*-Pr	3.14	3.49	0.35	3.32	9.18	9.74	9.46
4	Bu	3.15	3.53	0.38	3.34	9.23	9.79	9.51
5	*t*-Bu	3.06	3.44	0.38	3.25	9.04	9.59	9.32

[a] The $h\nu_{CT}(C_1)$ and $h\nu_{CT}(C_2)$ values were taken from [15]. For the *IP* values, see Table 1.

sponding to electron removal from iodine *n* orbitals, is a doublet. The components of the doublet are denoted in series A as $IP(A_1)$ and $IP(A_2)$; in series B, as $IP(B_1)$ and $IP(B_2)$; etc. In Tables 1–4, we also give the spin–orbital splittings Δ and mean ionization potentials, which are denoted consistently for all the series, e.g., Δ(A) and $IP(A) = [IP(A_1) + IP(A_2)]/2$ for series A.

According to the general theory (see, e.g., [16]), the spin–orbital coupling in hydrogen-like atoms increases in proportion to the fourth power of the nucleus charge. Therefore, the spin–orbital splitting Δ of the first bands corresponding to electron removal from the halogen *n* orbitals dramatically decreases in the series IH–BrH–ClH–FH: 0.66, 0.34, 0.08, and ~0.04 eV, respectively [8].

The spin–orbital coupling is also manifested in the UV spectra of the charge-transfer complexes of IX molecules (series C) with tetracyanoethylene (Table 3). Therefore, two electronic transitions are observed with the energies $h\nu_{CT}(C_1)$ and $h\nu_{CT}(C_2)$ depending on substituent X.

It is convenient to consider the substituent effects in I-centered radical cations on the basis of the linear free energy relationship; its applicability to ionization potentials was proved in [5], and to charge-transfer complexes, e.g., in [17]. This relationship, in combination with the postulate that the substituent effects are independent and additive, allows the Hammett–Taft equation for reaction series (1) to be written as follows:

$$IP = IP_{\mathrm{H}} + a\sigma_I + b\sigma_R^+ + c\sigma_\alpha. \qquad (2)$$

Here, IP_{H} is the ionization potential in the absence of substituents (X = H); σ_I, σ_R^+, and σ_α are, respectively, the inductive, resonance, and polarization parameters of substituents X.

Neutral donor molecules IX form in solutions charge-transfer complexes with acceptors A (tetracyanoethylene, iodine):

$$\mathrm{A + IX} \rightleftarrows [\mathrm{A, IX}] \overset{h\nu_{\mathrm{CT}}}{\rightleftarrows} [\mathrm{A}^{-\cdot}, \mathrm{I}^{+\cdot}\mathrm{X}]. \qquad (3)$$

In the ground state of a charge-transfer complex [A, IX], the A and IX molecules are bonded weakly. The excited state of a charge-transfer complex, $[\mathrm{A}^{-\cdot}, \mathrm{I}^{+\cdot}\mathrm{X}]$, formed from the ground state under the action of a quantum $h\nu_{\mathrm{CT}}$, is a radical ion species. In this structure, an electron is transferred from the HOMO of the donor IX (localized mainly on the iodine *n* orbitals [8–15]) to the lower unoccupied molecular orbital of acceptor A. Thus, both types of radical cations $\mathrm{I}^{+\cdot}\mathrm{X}$, those formed as components of radical ion pairs $[\mathrm{A}^{-\cdot}, \mathrm{I}^{+\cdot}\mathrm{X}]$ and in process (1), are I-centered.

Similarly to relationship (2), the Hammett–Taft equation for excitation of a charge-transfer complex can be written as

$$h\nu_{\mathrm{CT}} = h\nu_{\mathrm{CT(H)}} + a\sigma_I + b\sigma_R^+ + c\sigma_\alpha. \qquad (4)$$

Here, $h\nu_{\mathrm{CT}}$ is the energy of the charge-transfer band in the UV absorption spectrum of the charge-transfer complex; $h\nu_{\mathrm{CT(H)}}$ is $h\nu_{\mathrm{CT}}$ at X = H [3].

Let us briefly consider the validity of the chosen parameters of Eqs. (2) and (4).

The inductive effect of substituents on *IP* and $h\nu_{\mathrm{CT}}$ is characterized by the universal constant σ_I.

The resonance effect of inorganic and organic substituents on *IP* and $h\nu_{\mathrm{CT}}$ was estimated using the σ_R^+ parameters. The reaction center in the $\mathrm{I}^{+\cdot}\mathrm{X}$ radical cations ($\mathrm{I}^{+\cdot}\text{–C≡CX}$, $\mathrm{I}^{+\cdot}\mathrm{SnR_3}$) has a large positive charge. Extensive studies of heterolytic and homolytic processes [18], ionization potentials [1–6], and charge-transfer complexes [3, 6, 17] showed that conjugation of substituents with electron-deficient reaction centers is described by the electrophilic parameters σ_R^+.

Table 4. Electronic transtion energies (eV) $h\nu_{\mathrm{CT}}$(D) in the spectra of charge-transfer complexes with iodine, ionization potentials (eV) of iodine *n* orbitals $IP(\mathrm{D_1})$ and $IP(\mathrm{D_2})$, differences $\Delta(\mathrm{D}) = IP(\mathrm{D_2}) - IP(\mathrm{D_1})$, and the values of $IP(\mathrm{D}) = [IP(\mathrm{D_1}) + IP(\mathrm{D_2})]/2$ for trialkyliodostannanes $\mathrm{ISnR_3}$ (series D)[a]

R	$h\nu_{\mathrm{CT}}$(D)	$IP(\mathrm{D_1})$	$IP(\mathrm{D_2})$	Δ(D)	*IP*(D)
Me	4.17	8.95	9.34	0.39	9.14
Et	4.10	8.64	8.98	0.34	8.81
Pr	4.08	8.61	8.94	0.33	8.78
i-Pr	4.06	8.48	8.72	0.24	8.60
Bu	4.08	8.54	8.82	0.28	8.68
i-Bu	4.06	8.51	8.80	0.29	8.66
s-Bu	4.02	8.39	8.58	0.19	8.48

[a] The values of $h\nu_{\mathrm{CT}}$(D), $IP(\mathrm{D_1})$, and $IP(\mathrm{D_2})$ are taken from [12].

In contrast to σ_I and σ_R^+, inclusion into Eqs. (2) and (4) of the polarization parameters σ_α is not, at first glance, so obvious. As follows from detailed studies [1–6, 19], ionic gas-phase processes, e.g., reaction (1), are characterized by one more mechanism of interaction of a substituent with a positively charged reaction center, along with the inductive and resonance mechanisms, namely, by electrostatic attraction between the charge *q* of radical cations $\mathrm{R}_\pi^{+\cdot}\mathrm{X}$ or $\mathrm{Z}^{+\cdot}\mathrm{X}_n\mathrm{Y}_m$ and the dipole moment induced by this charge in substituents X and Y.

Equation (5) of classical electrostatics allows only rough estimation of the energy of electrostatic stabilization of charge *q* in radical cation (for more details, see, e.g., [20]):

$$E_{ST} = -q^2\alpha/2\varepsilon r^4. \qquad (5)$$

Here, α is the polarizability of substituent X; ε, dielectric constant; and *r*, distance from the charge *q* to the induced dipole.

The stabilization of charge *q* can be taken into account rigorously by *ab initio* calculation of constants σ_α of substituents X and Y [1–6, 19]. By definition, the ionization potential is equal to the difference between the total energies of the radical cation and neutral molecule [8]:

$$IP = E_{\mathrm{tot}}^{+\cdot} - E_{\mathrm{tot}}. \qquad (6)$$

As the negative value of σ_α grows (Tables 1–3), the electrostatic stabilization of the charge q increases, which results in decreased total energy of the radical cation $E_{\mathrm{tot}}^{+\cdot}$ and in decreased IP. This also directly follows from Eq. (2).

By analogy with radical cations $R_\pi^{+\cdot}X$ [3] and $Z^{+\cdot}XY$ [6] (Z = S, Se) as donor components of the charge-transfer complexes in the excited state [$A^{-\cdot}$, $R_\pi^{+\cdot}X$] and [$A^{-\cdot}$, $Z^{+\cdot}XY$], we believe that the electrostatic stabilization of the charge of radical cations $I^{+\cdot}X$ formed by scheme (3) can also be characterized by the σ_α constants of substituents X [third parameter in Eq. (4)].

The correlation equations were calculated using standard programs of the Statgraphics 3.0 package. The least-squares treatment was performed on the 95% confidence level.

Let us consider the effect of substituents on the ionization potential of compounds **1**–**19** of series A (Table 1). Attempts to characterize IP by two parameters (σ_I and σ_R^+) or their sum (σ_P^+) do not lead to even approximate correlations for $IP(A_1)$, $IP(A_2)$, and $IP(A)$: The correlation coefficients r are as low as 0.80 – 0.84.

Introduction of the third parameter, σ_α, leads to correlations (7)–(12).

$$IP(A_1) = 10.47 + 1.60\sigma_I + 1.55\sigma_R^+ + 1.40\sigma_\alpha; \quad (7)$$

S_a 0.05, S_b 0.08, S_c 0.11, S_d 0.07, S_Y 0.06, r 0.994, n 19.

$$IP(A_1) = 10.48 + 1.58\sigma_P^+ + 1.41\sigma_\alpha; \quad (8)$$

S_a 0.03, S_b 0.06, S_c 0.06, S_d 0.06, r 0.995, n 19.

$$IP(A_2) = 11.11 + 1.63\sigma_I + 1.43\sigma_R^+ + 1.55\sigma_\alpha; \quad (9)$$

S_a 0.04, S_b 0.06, S_c 0.08, S_d 0.05, S_Y 0.05, r 0.997, n 19.

$$IP(A_2) = 11.16 + 1.56\sigma_P^+ + 1.58\sigma_\alpha; \quad (10)$$

S_a 0.03, S_b 0.05, S_c 0.05, S_Y 0.05, r 0.997, n 19.

$$IP(A) = 10.79 + 1.61\sigma_I + 1.49\sigma_R^+ + 1.48\sigma_\alpha; \quad (11)$$

S_a 0.04, S_b 0.06, S_c 0.09, S_d 0.06, S_Y 0.05, r 0.996, n 19.

$$IP(A) = 10.82 + 1.57\sigma_P^+ + 1.50\sigma_\alpha; \quad (12)$$

S_a 0.03, S_b 0.05, S_c 0.06, S_Y 0.05, r 0.996, n 19.

Relationships (7), (9), and (11) can be written in the general form as follows:

$$IP = IP_{\mathrm{H}} + Ind + Res + Pol. \quad (13)$$

Then, we can calculate the inductive ($Ind = a\sigma_I$), resonance ($Res = b\sigma_R^+$), and polarization ($Pol = c\sigma_\alpha$) contributions to the total change in the ionization potential of compounds **1**–**19** of series A under the influence of substituents (Table 5).

Table 5 shows that the *Pol* contribution is prevailing. The *Ind* and *Res* contributions to the total change in the ionization potential are approximately equal. Therefore, in going to three-parameter equations (7), (9), and (11) to the corresponding two-parameter equations (8), (10), and (12), the statistical characteristics of the correlations (coefficient r, standard deviations of coefficients S, and standard approximation error S_Y), at least, do not get worse.

Thus, the σ_R^+ constant is a quantitative measure of the resonance interaction of substituents X with the reaction center in radical cations $I^{+\cdot}X$ of series A (Table 1, compounds **1**–**19**). This result is consistent with the data obtained previously for radical cations of type $R_\pi^{+\cdot}X$ (R_π is an aromatic, heteroaromatic, or α,β-unsaturated group) [1–3] and $Z^{+\cdot}X_nY_m$ (Z = N, P, S, Se) [4 – 6, 21]. Hence, the σ_R^+ constants, initially introduced for quantitative characterization of the conjugation of substituents X with the positively charged reaction center in classical aromatic systems of type 4-$XC_6H_4\overset{+}{C}H_2$ (see, e.g., [18, 19]), have wider applications [4 – 6, 21, 22].

Let us consider relationships (7)–(13) in connection with the widely used Koopmans approximation [8] according to which, in particular, the first ionization potential of the molecule is equal to the energy of its HOMO with opposite sign:

$$IP_1^0 = -E_{\mathrm{HOMO}}. \quad (14)$$

The modern quantum chemistry does not allow calculation of the ionization potential of a complex molecule with the same accuracy as that of its experimental determination. For example, in calculation of the total energy of the radical cation [$E_{\mathrm{tot}}^{+\cdot}$ in Eq. (6)], problems arise with taking into account changes in the wave functions of the neutral molecule due to the relaxation (R) and correlation (C) energies [8]. The Koopmans approximation neglects the R and C terms in the rigorous expression for the ionization potential:

$$IP_1 = IP_1^0 - R + C. \quad (15)$$

As a result, the *Pol* contribution [Eq. (13)], reaching, e.g., 40% for compounds **1**–**19** of series A (Table 5), is ignored.

There is one more argument against the applicability of the Koopmans approximation. The resonance properties of substituents are characterized by the σ_R^0 parameters in neutral molecules (see, e.g., quantum-chemical calculation [23]) and by the α_R^+ parameters

Table 5. Contributions *Ind, Res*, and *Pol* (%) to the total change in the ionization potentials *IP* and in $h\nu_{CT}$ under the influence of substituents X

Series	$IP(h\nu_{CT})$	Equation	Sample size n	*Ind*	*Res*	*Pol*
A	$IP(A_1)$	(7)	19	28±1	32±2	40±2
	$IP(A_2)$	(9)	19	28±1	28±2	44±2
	$IP(A)$	(11)	19	28±1	30±2	42±2
	$IP(A_1)$	(18)	21	28±2	31±3	41±2
	$IP(A_2)$	(19)	21	29±2	28±3	43±3
	$IP(A)$	(20)	21	29±2	29±2	42±2
	$IP(A_1)$	(24)	6	31±2	24±2	45±2
	$IP(A_2)$	(25)	6	30±2	19±3	51±3
	$IP(A)$	(26)	6	30±2	22±3	48±3
B	$IP(B_1)$	(21)	6	27±2	44±2	29±3
	$IP(B_2)$	(22)	6	26±2	40±4	34±4
	$IP(B)$	(23)	6	26±2	42±3	32±3
C	$IP(C_1)$	(27)	5	13±4[a]		87±5
	$IP(C_2)$	(28)	5	18±6[a]		82±6
	$IP(C)$	(29)	5	17±6[a]		83±6
	$h\nu_{CT}(C_1)$	(30)	5	5±19[a]		95±21
	$h\nu_{CT}(C_2)$	(31)	5	24±17[a]		76±18
	$h\nu_{CT}(C)$	(32)	5	19±14[a]		81±14

[a] Sum of *Ind* and *Res* contributions.

in radical cations [Eqs. (7)–(12)]. It is known [18] that the σ_R^0 and σ_R^+ parameters are essentially different, especially for electron-donor substituents. Therefore, the approximation under consideration is too rough, and, generally, the experimental values of the first ionization potentials cannot be used as measures of the HOMO energies of neutral molecules.

Relationships (9) and (11) allow correct assignment of the $IP(A_2)$ bands in the photoelectron spectrum of allyl iodide [and, hence, correct calculation of $IP(A)$; Table 1, compound **20**]. According to [11], $IP(A_2)$ 10.26 eV, and our calculations give $IP(A)$ 9.79 eV. With these values, the correlation coefficients r of Eqs. (9) and (11) decrease to 0.986 and 0.993, respectively, and the standard approximation error S_Y increases to 0.10 and 0.07. Quite probably, the value of 10.26 eV for $IP(A_2)$ of allyl iodide [11] is erroneous. With the correct values, $IP(A_2)$ 9.72 and $IP(A)$ 9.52 eV, correlations (16) and (17) are obtained:

$$IP(A_2) = 11.09 + 1.66\sigma_I + 1.40\sigma_R^+ + 1.55\sigma_\alpha; \quad (16)$$

S_a 0.05, S_b 0.08, S_c 0.11, S_d 0.07, S_Y 0.06, r 0.995, n 20.

$$IP(A) = 10.78 + 1.62\sigma_I + 1.47\sigma_R^+ + 1.48\sigma_\alpha; \quad (17)$$

S_a 0.04, S_b 0.07, S_c 0.10, S_d 0.06, S_Y 0.06, r 0.995, n 20.

Their statistical characteristics only slightly differ from r and S_Y in Eqs. (9) and (11).

In the photoelectron spectra of compounds **1**–**19**, the components of the doublet arising from the spin–orbital coupling, corresponding to the ionization potentials $IP(A_1)$ and $IP(A_2)$, are narrow bands. High accuracy of measuring $IP(A_1)$ and $IP(A_2)$ results in excellent correlations (7)–(12). In the spectra of compounds **20** and **21** (Table 1), these bands are broadened [11]. Therefore, in the correlation equations for the whole set of compounds **1**–**21** of series A (Table 1), the r values are slightly lower, and S_Y, slightly higher than in relationships (7), (9), and (11).

$$IP(A_1) = 10.40 + 1.56\sigma_I + 1.33\sigma_R^+ + 1.37\sigma_\alpha; \quad (18)$$

S_a 0.05, S_b 0.09, S_c 0.11, S_d 0.08, S_Y 0.08, r 0.993, n 21.

$$IP(A_2) = 11.01 + 1.62\sigma_I + 1.18\sigma_R^+ + 1.51\sigma_\alpha; \quad (19)$$

S_a 0.06, S_b 0.10, S_c 0.11, S_d 0.09, S_Y 0.08, r 0.993, n 21.

$$IP(A) = 10.71 + 1.58\sigma_I + 1.25\sigma_R^+ + 1.44\sigma_\alpha; \quad (20)$$

S_a 0.05, S_b 0.09, S_c 0.10, S_d 0.08, S_Y 0.07, r 0.993, n 21.

This slightly decreases the accuracy of determining the *Ind*, *Res*, and *Pol* contributions (Table 5), but the ratio of these contributions to the total change in the ionization potentials following from Eqs. (18)–(20) remains the same as in using Eqs. (7), (9), and (11).

The resonance parameters σ_R^+ of organosilicon, organogermanium, and organotin substituents are not universal. Their values vary depending on the type of the reaction center [7]. From the ionization potentials of compounds **22**–**24** and the values of σ_I and σ_α (Table 1), we calculated the σ_R^+ parameters for substituents SiH_3, GeH_3, and $SnMe_3$ bound to the reaction center $I^{+\cdot}$. The first, second, and third values of σ_R^+ for each substituent were calculated by Eqs. (7), (9), and (11), respectively; the mean values are given in parentheses.

It is known [7] that the total resonance effect of substituents MX_3 (M = Se, Ge, Sn) toward the reaction (indicator) *n*-type center Z in R_mZMX_3 molecules (R = Alk) includes the acceptor (*d,n* conjugation) and donor (σ,*n* conjugation) components. The *d,n* conjugation effect [interaction of vacant *nd* orbitals of M atom and antibonding σ*(M–X) orbitals with the lone electron pairs of Z atom (O, N, etc.)] weakens with increasing atomic number M, whereas σ,*n* conjugation of the M–X σ orbitals with *n* orbitals of the Z atom is enhanced.

A similar trend is observed in $I^{+\cdot}MX_3$ radical cations (Table 1). In this case, the positive value of σ_R^+ of the substituent SiH_3 indicates that the *d,n* conjugation prevails over σ,*n* conjugation. In the $I^{+\cdot}GeH_3$ radical cation, these effects are comparable in value, as indicated by nearly zero value of σ_R^+ of the GeH_3 group. The negative value of σ_R^+ of $SnMe_3$ indicates that the σ,*n* conjugation in the $I^{+\cdot}SnMe_3$ radical cation prevails over *d,n* conjugation.

Let us then consider the effects of substituents X in radical cations $I^{+\cdot}$–C≡C–X (series B, Table 2). As in series A, the ionization potentials of compounds **1**–**6** of series B depend not only on the inductive and resonance effects of the substituents. This follows from the low correlation coefficients of the relationships of the type $IP = f(\sigma_I, \sigma_R^+)$ (*r* 0.90–0.92) and $IP = f(\sigma_P^+)$ (*r* 0.82–0.85).

Three-parameter correlations (21)–(23) are excellent:

$$IP(B_1) = 9.73 + 0.78\sigma_I + 1.23\sigma_R^+ + 0.58\sigma_\alpha; \quad (21)$$

S_a 0.02, S_b 0.05, S_c 0.07, S_d 0.06, S_Y 0.03, *r* 0.998, *n* 6.

$$IP(B_2) = 10.14 + 0.84\sigma_I + 1.28\sigma_R^+ + 0.77\sigma_\alpha; \quad (22)$$

S_a 0.04, S_b 0.08, S_c 0.11, S_d 0.09, S_Y 0.04, *r* 0.996, *n* 6.

$$IP(B) = 9.93 + 0.82\sigma_I + 1.26\sigma_R^+ + 0.68\sigma_\alpha; \quad (23)$$

S_a 0.03, S_b 0.06, S_c 0.08, S_d 0.07, S_Y 0.03, *r* 0.997, *n* 6.

From Eqs. (21)–(23) and (13), we calculated the *Ind*, *Res*, and *Pol* contributions to $IP(B_1)$, $IP(B_2)$, and *IP*(B) for compounds **1**–**6** of series B (Table 5).

Let us compare the *Ind*, *Res*, and *Pol* contributions to *IP* of compounds of series A and B. The ratio of these contributions within the series can depend on the sample size; therefore, in series A we chose six compounds (nos. **1, 2, 8, 18, 19**, and **21** in Table 1) containing the same substituents X as compounds **1**–**6** in series B. For these six compounds of series A, the following correlations are valid:

$$IP(A_1) = 10.39 + 1.40\sigma_I + 1.05\sigma_R^+ + 1.42\sigma_\alpha; \quad (24)$$

S_a 0.03, S_b 0.07, S_c 0.10, S_d 0.08, S_Y 0.04, *r* 0.998, *n* 6.

$$IP(A_2) = 11.05 + 1.39\sigma_I + 0.86\sigma_R^+ + 1.62\sigma_\alpha; \quad (25)$$

S_a 0.04, S_b 0.09, S_c 0.12, S_d 0.10, S_Y 0.05, *r* 0.997, *n* 6.

$$IP(A) = 10.72 + 1.38\sigma_I + 0.96\sigma_R^+ + 1.52\sigma_\alpha; \quad (26)$$

S_a 0.04, S_b 0.08, S_c 0.12, S_d 0.10, S_Y 0.05, *r* 0.997, *n* 6.

The *Ind*, *Res*, and *Pol* contributions (Table 5) were calculated from Eqs. (24)–(26). Let us compare these contributions in series A and B at the same sample size (*n* = 6).

Table 5 shows that the *Ind* contributions in series A and B are close, whereas the ratios of the *Res* and *Pol* contributions are opposite. The distance *r* [Eq. (5)] from the charge *q* of the photoionization center $I^{+\cdot}$ to the dipole induced by this charge in substituent X is much longer in radical cations $I^{+\cdot}$–C≡C–X (series B) than in $I^{+\cdot}X$ (series A). It could be expected that, in going from series A to B, the *Pol* contribution would drastically decrease. However, this is not the case (Table 5). In the $I^{+\cdot}$–C≡C–X radical cations, the unpaired electron and the positive charge *q* are partially delocalized over the π system. The system behaves as if substituent X were closer to charge *q*, i.e., the parameter *r* in Eq. (5) decreases, increasing the *Pol* contribution in series B.

The calculated σ_R^+ coefficients of the substituents $SiMe_3$ and $GeMe_3$ are listed in Table 2. The first, second, and third values of σ_R^+ for each substituent were calculated by Eqs. (21)–(23), respectively; the mean values are given in parentheses. The ionization potentials of $IC{\equiv}CSiMe_3$ reported in [13] [$IP(B_1)$ 9.21, $IP(B_2)$ 9.50, *IP*(B) 9.36 eV] and [14] {only *IP*(B) 9.4 eV is reported; the values of $IP(B_1)$ 9.25 and $IP(B_2)$ 9.54 eV were estimated by us using Δ(B) 0.29 eV from [13]} somewhat differ, which results in two mean values of σ_R^+ for $SiMe_3$ groups: 0.03 and 0.06. The first value seems to be more accurate.

In contrast to *d,n* and σ,*n* conjugation effects in series A ($I^{+\cdot}MX_3$), the resonance interaction of substituents MMe_3 (M = Si, Ge) with the remaining part of radical cations of series B ($I^{+\cdot}$–C≡C–MMe_3), apparently, has a combined mechanism. It includes conjugation of MMe_3 not only with the photoionization center $I^{+\cdot}$, but also with the triple bond. With respect to the total resonance effect, $SiMe_3$ behaves as a weak acceptor (small positive σ_R^+), and $GeMe_3$, as a moderate donor (negative σ_R^+, Table 2).

The values of *IP* and $h\nu_{CT}$ in series C (Table 3), despite small sample size ($n = 5$), allow comparison of the effects of substituents X in radical cations $I^{+\cdot}X$ of two types.

The radical cations of the first type are formed by photoionization of individual IX molecules in the gas phase [scheme (1)], and the following correlations are valid for them:

$$IP(C_1) = 10.64 + 1.86\sigma_P^+ + 1.49\sigma_\alpha; \qquad (27)$$

S_a 0.22, S_b 0.63, S_c 0.08, S_Y 0.01, r 0.999, n 5.

$$IP(C_2) = 11.85 + 3.34\sigma_P^+ + 1.88\sigma_\alpha; \qquad (28)$$

S_a 0.39, S_b 1.07, S_c 0.14, S_Y 0.02, r 0.997, n 5.

$$IP(C) = 11.35 + 2.87\sigma_P^+ + 1.72\sigma_\alpha; \qquad (29)$$

S_a 0.36, S_b 1.00, S_c 0.13, S_Y 0.01, r 0.997, n 5.

From Eqs. (27)–(29), we calculated the total *Ind* + *Res* contribution and the *Pol* contribution to the ionization potential in series C (Table 5).

Radical cations $I^{+\cdot}X$ of the second type (series C, Table 3) occur in CH_2Cl_2 solution as components of radical ion pairs [$TCE^{-\cdot}$, $I^{+\cdot}X$] (TCE denotes tetracyanoethylene). They are formed by scheme (3) upon electronic excitation of the charge-transfer complex of tetracyanoethylene with an IX molecule. The energy of the charge-transfer bands $h\nu_{CT}$ in the UV absorption spectra of the charge-transfer complexes correlates with the effects of substituents X as follows:

$$h\nu_{CT}(C_1) = 3.51 + 0.22\sigma_P^+ + 0.51\sigma_\alpha; \qquad (30)$$

S_a 0.29, S_b 0.81, S_c 0.11, S_Y 0.01, r 0.986, n 5.

$$h\nu_{CT}(C_2) = 5.08 + 2.97\sigma_P^+ + 1.18\sigma_\alpha; \qquad (31)$$

S_a 0.75, S_b 2.07, S_c 0.28, S_Y 0.03, r 0.970, n 5.

$$h\nu_{CT}(C) = 4.32 + 1.69\sigma_P^+ + 0.85\sigma_\alpha; \qquad (32)$$

S_a 0.41, S_b 1.14, S_c 0.15, S_Y 0.02, r 0.985, n 5.

From Eqs. (30)–(32), we calculated the total *Ind* + *Res* contribution and the *Pol* contribution to $h\nu_{CT}$ in series C (Table 5).

Table 5 shows that, in series C, the *Ind* + *Res* and *Pol* contributions to $h\nu_{CT}$ involve a considerably larger error than the contributions to *IP*. This is due to several factors: (1) lower accuracy of determining $h\nu_{CT}$, compared to *IP*; (2) errors that arise when resolving a complex band in the UV spectrum of a charge-transfer complex into the components $h\nu_{CT}(C_1)$ and $h\nu_{CT}(C_2)$ [15]; and (3) small sample size in series C consisting of alkyl iodides only. Taking into account poor accuracy of determining the *Ind* + *Res* and *Pol* contributions to $h\nu_{CT}$, we can consider them, to a first approximation, about the same as the corresponding contributions to *IP* (Table 5). The best agreement is observed for the mean values of *IP*(C) and $h\nu_{CT}$(C).

This is fully consistent with the fact that the *Ind*, *Res*, and *Pol* contributions to $h\nu_{CT}$ and *IP* of DX donor molecules (π-electron systems [3], sulfides, selenides [6]) and their charge-transfer complexes with various acceptors A (tetracyanoethylene, hexacyanobenzene, trinitrobenzene, iodine) are approximately equal. The invariant effect of substituents X (similar *Ind*, *Res*, and *Pol* contributions to the ionization potentials and $h\nu_{CT}$) is due to specific features of the transition state of the charge-transfer complex formed in the equilibrium processes [3, 6]

$$A + IX \rightleftarrows [A,\ IX] \overset{h\nu_{CT}}{\rightleftarrows} [A^{-\cdot},\ I^{+\cdot}X]. \qquad (33)$$

Pulse laser spectroscopic studies of process (33) [24, 25] showed that the charge-transfer complex passes from the ground state [A, DX] to the excited state [$A^{-\cdot}$, $D^{+\cdot}X$] within approximately 1 ps under the action of a laser pulse of the energy $h\nu_{CT}$. The reverse transition is also very fast; it is described by a first-order kinetic equation with the rate constant of 10^8–10^{11} s^{-1} depending on particular A and DX. Solvent molecules are not inserted between the components $A^{-\cdot}$ and $D^{+\cdot}X$ of the contact radical ion pair. Therefore, the donor component $D^{+\cdot}X$ of the contact radical ion pair [$A^{-\cdot}$, $D^{+\cdot}X$] in the solution and the radical cation generated by photoionization of a DX molecule in the gas phase are similar in the electronic state, and the *Ind*, *Res*, and *Pol* contributions to $h\nu_{CT}$ are essentially similar to the corresponding contributions to the ionization potential [3, 6].

Table 5 shows that the polarization factor exerts a predominant effect on *IP* and $h\nu_{CT}$ in series C. Let us then consider the effects of alkyl substituents R in radical cations $I^{+\cdot}SnR_3$ of series D (Table 4).

In the photoelectron spectra of trialkyliodostannanes (series D), the first band is a doublet, which is due to spin–orbital coupling [12] [see $IP(D_1)$ and $IP(D_2)$ in Table 4]. On the contrary, no splitting of the charge-transfer band due to spin–orbital coupling was observed in the UV spectra of charge-transfer complexes of $ISnR_3$ with iodine (in CCl_4) [12]. At the same time, such a splitting is detected in the spectra of charge-transfer complexes of series C compounds with tetracyanoethylene (Table 3). Therefore, the $h\nu_{CT}$(D) values [12] should be, apparently, considered as mean values, similar to $h\nu_{CT}$(C) in Table 3.

The $h\nu_{CT}$(D) values correlate with the mean *IP*(D) values as follows:

$$h\nu_{CT}(D) = 0.218IP(D) + 2.18; \quad (34)$$

$$S_a\ 0.017,\ S_b\ 0.15,\ S_Y\ 0.01,\ r\ 0.983,\ n\ 7.$$

A characteristic feature of $h\nu_{CT}$(D) and *IP*(D) is their dependence on the polarization parameter σ_α of alkyl groups R in $ISnR_3$ as a single parameter:

$$h\nu_{CT}(D) = 4.32 + 0.14\sigma_\alpha; \quad (35)$$

$$S_a\ 0.02,\ S_b\ 0.01,\ S_Y\ 0.01,\ r\ 0.988,\ n\ 7.$$

$$IP(D) = 9.80 + 0.64\sigma_\alpha; \quad (36)$$

$$S_a\ 0.06,\ S_b\ 0.04,\ S_Y\ 0.03,\ r\ 0.990,\ n\ 7.$$

Introduction of additional parameters (σ_I, σ_R^+, σ_P^+, or Taft inductive parameter σ^* [19]) makes correlations (35) and (36) worse.

Apparently, deeper insight into intramolecular interactions in series D can be gained using the σ_I, σ_R^+, and σ_P^+ parameters of substituents SnR_3. However, such data are as yet lacking.

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