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Substituent Effects in P- and As-centered Radical Cations

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Abstract—The first vertical ionization potentials of isostructural P(III) and As(III) compounds EX_3 (E = P, As) whose highest occupied molecular orbital is preferentially localized on the lone electron pairs of atom E depend on the inductive, resonance, and polarization effects of substituents X. Hyperconjugation in fragments like $As^{+\cdot}$–C–H is the only resonance effect in radical cations $As^{+\cdot}X_3$. The same effect in similar P-centered radical cations is weaker.

The ionization potentials of neutral molecules, specifically, first ionization potentials (I_1), corresponding to ejection of an electron from the highest occupied molecular orbital (HOMO) of a neutral molecule, provide important information on substituent effects in radical cations. We recently examined the I_1 values of neutral molecules like $R_\pi X$ and ZX_n possessing π-type (R_π = aryl, hetaryl, vinyl, ethynyl, etc.) [1, 2] or *n*-type (Z = N, P, S, Se, I) [3–7] reaction centers bearing inorganic, organic, and organometallic (Si-, Ge-, and Sn-containing) substituents X. The substituents were chosen so that HOMOs in all series of compounds were mostly localized on R_π or Z. Under this condition, the I_1 values are a quantitative measure of the inductive, resonance, and polarization effects of substituents X and Y in radical cations $R_\pi^{+\cdot}X$ and $Z^{+\cdot}X_n$. We found that the resonance effects of organometallic substituents, as well as hyperconjugation in the above radical cations are not universal in nature. As judged from the available evidence for organic [8–11] and organometallic [3, 4, 6, 11] systems, the latter effect is enhanced by the positive charge on the reaction center.

Quite an important information was also obtained on the relationship between conjugation in Z-centered radicals and the atomic number of element Z [3–7]. Thus, conjugation does not sharply attenuate with increasing atomic number, when Z is a Group 17 element, as evidenced by the revelation of appreciable resonance interactions even in radical cations $I^{+\cdot}X$ [7]. In radical cations containing a Group 16 element, conjugation only slightly varies in going from $S^{+\cdot}X_2$ to $Se^{+\cdot}X_2$ [3, 6].

Unlike radical cations of Period IV and V elements (Se and I), conjugation in radical cations containing a Period III element (Group 15), such as $P^{+\cdot}X_3$, is very weak [4]. To proceed with research into the relationship of resonance interactions in radical anions on the position of element Z in the Periodic Table, it would be desirable to dwell now on radical cations $As^{+\cdot}X_3$. As known, conjugation effects in neutral As(III) compounds are weak [12]. Resonance interactions in the corresponding radical cations are still unexplored.

We set ourselves the task to study substituent effects in P- and As-centered radical cations and to correlate the hyperconjugation effect in these radical cations with the nature of the reaction center.

We considered the effects of substituents on the first vertical ionization potentials of neutral molecules PX_3 and AsX_3, measured to an accuracy of 0.01 eV by photoelectron spectroscopy (Table 1). The symbols $I_1(n_P)$ and $I_1(n_{As})$ imply that here we only deal with such EX_3 molecules (E = P, As) whose HOMOs, as follows from published data [13–19], are preferentially localized on the lone electron pairs of P or As. Therefore, phosphorus and arsenic compounds (Table 1) form two reaction series with the same set of substituents. Each of them contains one invariable reaction center (P or As). Only these reaction centers (not substituents X) take part in the gas-phase reaction (1) of photoionization of neutral molecules M, involving electron ejection from HOMO and giving radical cations $M^{+\cdot}$.

$$M \xrightarrow{h\nu} M^{+\cdot} + \bar{e}. \qquad (1)$$

Here M is neutral molecule and $M^{+\cdot}$ is radical cation.

According to the definition in [13], ionization potential (for instance, I_1) is equal to difference (2).

Table 1. First vertical ionization potentials $I_1(n_P)$ and $I_1(n_{As})$ of molecules EX_3 (E = P, As) and sums of the σ constants of substituents X[a]

Comp. no.	X_3	E = P, $I_1(n_P)$, eV	E = As, $I_1(n_{As})$, eV	$\Sigma\sigma_I$	$\Sigma\sigma_R^+$	$\Sigma\sigma_\alpha$
I	H_3	10.60	10.50	0	0	0
II	$H_2(C{\equiv}CH)$	9.77	9.90	0.22	–0.04	–0.60
III	HPh_2	8.30	8.40	0.24	–0.60	–1.62
IV	Ph_3	7.92	8.00	0.36	–0.90	–2.43
V	$(CF_3)_3$	11.60	11.41	1.14	0.69	–0.75
VI	F_3	12.23	13.00	1.35	–1.56	0.39
VII	Cl_3	10.52	10.95	1.26	–0.93	–1.29
VIII	Br_3	9.96	10.21	1.35	–0.90	–1.77
IX	H_2Me	9.63	9.50	–0.05	–0.26	–0.35
X	$H_2(CH{=}CH_2)$	9.60	9.60	0.13	–0.29	–0.50
XI	$H_2(CH_2CH{=}CH_2)$	9.32	9.19	–0.06	–0.16	–0.57
XII	$Me(CF_3)_2$	10.80	10.70	0.71	0.20	–0.85
XIII	$MeCl_2$	9.86	10.02	0.79	–0.88	–1.21
XIV	$(CH_2CH{=}CH_2)Cl_2$	9.58	9.52	0.78	–0.78	–1.43
XV	$MeBr_2$	9.66	9.58	0.85	–0.86	–1.53
XVI	HMe_2	9.08	8.87	–0.10	–0.52	–0.70
XVII	Me_2Ph	8.32	8.67	0.02	–0.82	–1.51
XVIII	Me_2CN	9.80	9.82	0.41	–0.37	–1.16
XIX	$Me_2(CF_3)$	9.70	9.80	0.28	–0.29	–0.95
XX	Me_2Cl	9.15	9.45	0.32	–0.83	–1.13
XXI	Me_2Br	9.24	9.29	0.35	–0.82	–1.29
XXII	Me_3	8.62	8.65	–0.15	–0.78	–1.05

[a] The $I_1(n_P)$ and $I_1(n_{As})$ values for **I**, **III–IX**, **XII**, **XIII**, **XV–XVII**, and **XIX–XXII** are taken from [13, 14], for **II** and **X**, from [15–17], for **XI** and **XIV**, from [18], and for **XVIII**, from [19]. A standard set of σ_I, σ_R^+, σ_α for inorganic and organic substituents X was used [1–7].

$$I_1 = E_{tot}^{+\cdot} - E_{tot}. \qquad (2)$$

Here $E_{tot}^{+\cdot}$ is the total energy of radical cation $M^{+\cdot}$ formed by reaction (1) and E_{tot} is the total energy of neutral molecule M. The $E_{tot}^{+\cdot}$ and E_{tot} values obtained by quantum-chemical calculations rank much below experimental I_1 values in accuracy.

In particular, relaxation (*R*) and correlation (*C*) energies that measure changes in wave functions in going from neutral molecule M to radical cation $M^{+\cdot}$ are difficult to calculate [13]. Therefore, ionization potentials are most frequently estimated in terms of the Koopmans approximation (4) that neglects the *R* and *C* contributions into I_1 [13], rather than by the rigorous equation (3) that includes relation (4).

$$I_1 = I_1^0 - R + C, \qquad (3)$$

$$I_1^0 = -E_{HOMO}, \qquad (4)$$

$$I_1 = -E_{HOMO}. \qquad (5)$$

Here I_1^0 is the ionization potential uncorrected for *R* and *C* and E_{HOMO} is the HOMO energy.

As found earlier [1–7] and will be shown below, Eq. (5) does not hold for the ionization potentials considered in the present work. Consequently, I_1 cannot be used as a measure of the HOMO energies.

In terms of physical organic chemistry, very important in studying substituent effects is that the I_1 values fit the linear free energy principle [5].

Actually, along with Eq. (2), I_1 (more exactly, ionization energy) can be estimated by Eq. (6) as the standard enthalpy of reaction (1) at temperature *T*.

$$I_1 = \Delta_r H^0(T). \qquad (6)$$

Here $\Delta_r H(T)$ is the enthalpy of reaction (1) and $\Delta_r H^0(T)$ is the standard enthalpy of reaction (1).

With account for Eq. (6), the Gibbs–Helmholtz equation (7) for the standard free energy of reaction (1) takes form (8).

$$\Delta_r G^0(T) = \Delta_r H^0(T) - T\Delta_r S^0(T), \qquad (7)$$

$$\Delta_r G^0(T) = I_1 - T\Delta_r S^0(T). \qquad (8)$$

Here $\Delta_r G^0(T)$ is the standard free energy of reaction (1) and $\Delta_r S^0(T)$ is the standard entropy of reaction (1).

According to [5], the entropy contribution $T\Delta_r S^0(T)$ into the free energy of reactions like (1) at T 0–500 K is no higher than 5%. Therefore, Eq. (8) can be simplified to Eq. (9) without sacrifice for precision.

$$I_1 = \Delta_r G^0(T). \quad (9)$$

The latter equation is the most laconic formulation of the linear free energy principle as applied to I_1. This principle can also be applied to the form of Hammett–Taft equations, assuming additivity and independence of the contributions of different intermolecular interactions into the free energy (for details, see [5]). Then the I_1 values for the series neutral molecules $R_\pi X$ and ZX_n should fit Eq. (10).

$$I_1 = I_1^H + a\Sigma\sigma_I + b\Sigma\sigma_R^+ + c\Sigma\sigma_\alpha. \quad (10)$$

Here I_1^H is I_1 for X = H; σ_I, σ_R^+, and σ_α are the inductive, resonance, and polarization parameters of substituents X attached to the reaction center of radical cation $R_\pi^{+\cdot}$ (R_π is aryl, hetaryl, vinyl, ethynyl) [1, 2] or $Z^{+\cdot}$ (Z = N, P, S, Se, I) [3, 7].

Equation (10) can be rewritten in form (11).

$$I_1 = I_1^H + Ind + Res + Pol. \quad (11)$$

Here $Ind = a\Sigma\sigma_I$, $Res = b\Sigma\sigma_R^+$, and $Pol = c\Sigma\sigma_\alpha$ are the inductive, resonance, and polarization contributions into the total change of the ionization potentials of unsubstituted molecules $R_\pi H$ or ZH_n belonging to series $R_\pi X$ or ZX_n, produced by substituent X; and *a*, *b*, and *c* are coefficients.

Let us now explain why we dwelt on these three contributions into I_1 [and, consequently, into the standard free energy $\Delta_r G^0(T)$ of reaction (1)] and, following [1–7], take a quick look on their characteristics.

The inductive effect on I_1 of substituents X is measured by their universal σ_I constants.

Conjugation in neutral molecules and radical cations cannot be characterized by universal parameters of substituents X, invariant to the charge on the reaction center. The conjugation of X with R_π and Z in neutral molecules $R_\pi X$ or ZX_n is quantitatively described in terms of the resonance parameters σ_R^0. With $R_\pi = C_6H_5$, $CH{=}CH_2$, and $HC{\equiv}C$, the traditional notion of σ_R^0 as a measure of π-electron exchange between R_π and X is supported by modern quantum-chemical methods [20].

When a radical cation is formed by reaction (1) from a neutral molecule, a large positive charge develops on the reaction center. By definition (see, for example, [8]), the parameters σ_R^+ are a quantitative measure of the conjugation of substituents with any electron-deficient center in transition or final states. This substantiates the use of the resonance parameters σ_R^+ in equations like (10).

The σ_R^+ values are generally appreciably differ from σ_R^0. The $\sigma_R^+ - \sigma_R^0$ differences are the largest for substituents classed with typical resonance electron donors (NR_2, OR, etc.) [21]. Therefore, the effect of substituents on I_1 is impossible to describe by the σ_R^0 parameters which relate to conjugation in the ground state of neutral molecules. Consequently, the Koopmans approximation (5), leaving room for such a description, fails in this case.

The polarization effect of substituents X is quantitatively characterized by the universal constants σ_α [1–7] obtained by *ab initio* quantum-chemical calculations [21, 22]. First the σ_α constants were used to account for the *Pol* contribution into the standard free energies of gas-phase ionic reactions [22]. Reaction (1) is one the simplest processes of this kind. The positive charge *q* of radical cations $R_\pi^{+\cdot}X$ and $Z^{+\cdot}X_n$ polarizes substituents X, rendering them dipolar. The electrostatic attraction energy E_{es} between the charge and the induced dipole is given by Eq. (12).

$$E_{es} = -q^2\alpha/2\varepsilon r^4. \quad (12)$$

Here α is the polarizability of substituent X, ε is the dielectric constant, *r* is the distance from the charge to the polarizability center of substituent X.

In attempted calculations by formula (12) we faced principal difficulties. For instance, when the unpaired electron (and, consequently, *q*) in the radical cation is delocalized, *r* becomes uncertain.

These difficulties are eliminated, if one accounts for *Pol* by applying to I_1 the linear free energy principle in the form of Hammett–Taft equations like (10). Therewith, the inclusion of *Pol* consists of treatment of I_1 as a function of three (σ_I, σ_R^+, and σ_α) rather than two (σ_I and σ_R^+) arguments. Interrelation between I_1 and E_{es} and σ_α is obvious. As the negative values of both E_{es} and σ_α (as a measure of the polarizability of substituents X) increase, the *q* charge of the radical cation is increasingly stabilized. Therefore, the total energy $E_{tot}^{+\cdot}$ of the radical cation [Eq. (2)], as well as I_1 decrease.

The *Pol* contribution exists in radical cations and is lacking in neutral molecules. This is one more evidence against the Koopmans approximation (5) which allows cation radicals to be described via the wave functions of neutral molecules.

The correlation equations were calculated using Statgraphics 3.0 programs. The least-squares treatment was performed at a 95% confidence level.

Attempted characterization of the effect of substituents X on the ionization potentials $I_1(n_\mathrm{P})$ and $I_1(n_\mathrm{As})$ for two large series (n 22) PX_3 and AsX_3 (Table 1) by the inductive σ_I or resonance σ_R^+ parameters of X separately or in combination ($\sigma_P^+ = \sigma_I + \sigma_R^+$) did not result in even approximate correlations dependences (r 0.58–0.72).

Inclusion of the polarization parameter σ_α improves r considerably and reduces the standard approximation error S_Y [Eqs. (13) and (14)].

$$I_1(n_\mathrm{P}) = 10.31 + 1.63\Sigma\sigma_I + 0.46\Sigma\sigma_R^+ + 1.11\Sigma\sigma_\alpha; \quad (13)$$

S_a 0.08, S_b 0.08, S_c 0.08, S_d 0.06, S_Y 0.18, r 0.985, n 22.

$$I_1(n_\mathrm{As}) = 10.24 + 1.78\Sigma\sigma_I + 0.13\Sigma\sigma_R^+ + 1.20\Sigma\sigma_\alpha; \quad (14)$$

S_a 0.10, S_b 0.10, S_c 0.11, S_d 0.08, S_Y 0.22, r 0.980, n 22.

Let us now dwell on Eqs. (13) and (14). They both include three arguments: σ_I, σ_R^+, and σ_α. The resonance contribution $Res = 0.13\Sigma\sigma_R^+$ into $I_1(n_\mathrm{As})$ is not too large but significant, as judged from the fact that its exclusion deteriorates the r value of Eq. (14).

Table 2 lists the contributions $Ind = a\Sigma\sigma_I$, $Res = b\Sigma\sigma_R^+$, and $Pol = c\Sigma\sigma_\alpha$ into the total changes of the ionization potentials of PH_3 and AsH_3 under the effect of substituents X. For both the series, the *Pol* contribution prevails over *Ind* and *Res*. Therefore, not accounting for polarization effects one cannot even roughly assess the effect of substituents X on I_1 in the PX_3 and AsX_3 series.

The free terms of the two equations (10.31 and 10.24) markedly differ from the ionization potentials of PH_3 (10.60 eV) and AsH_3 (10.50 eV) (Table 1).

Despite equal data sets (n 22), Eq. (13) has slightly better statistical characteristics (higher r and lower S_Y and standard deviations S) than Eq. (14). The *Res* contributions in full (n 22) PX_3 and AsX_3 series are characteristically different (Table 2), being for phosphines (16 ± 3%) much higher than for arsines (5 ± 4%).

Let us now consider separately compounds **I**–**VIII** (Table 1) containing no E–C–H fragments (i.e. X = Me, $CH_2CH{=}CH_2$, $CH{=}CH_2$) and compounds **IX**–**XXII** containing these fragments.

Compounds **I**–**VIII** fit correlations (15) and (16).

Table 2. Inductive (*Ind*), resonance (*Res*), and polarization (*Pol*) contributions of substituents X (%) into the ionization potentials of EH_3 (E = P, As)

E	Eq. no.	*Ind*	*Res*	*Pol*
P	13	37 ± 2	16 ± 3	47 ± 3
As	14	42 ± 2	5 ± 4	53 ± 4
P	15	33 ± 4	15 ± 5	52 ± 4
As	16	38 ± 3	0	62 ± 4
P	17	49 ± 3	26 ± 5	25 ± 6
As	18	52 ± 7	29 ± 10	19 ± 11
As	19	50 ± 5	7 ± 3	43 ± 6
As	20	51 ± 7	29 ± 9	20 ± 11
As	21	52 ± 6	28 ± 8	20 ± 10
As	22	62 ± 8	21 ± 7	17 ± 12
As	23	61 ± 8	22 ± 8	17 ± 11

$$I_1(n_\mathrm{P}) = 10.36 + 1.57\Sigma\sigma_I + 0.44\Sigma\sigma_R^+ + 1.17\Sigma\sigma_\alpha; \quad (15)$$

S_a 0.18, S_b 0.17, S_c 0.14, S_d 0.10, S_Y 0.25, r 0.986, n 8.

$$I_1(n_\mathrm{As}) = 10.36 + 1.66\Sigma\sigma_I + 1.28\Sigma\sigma_\alpha; \quad (16)$$

S_a 0.14, S_b 0.13, S_d 0.08, S_Y 0.19, r 0.99 3, n 8.

In going from Eqs. (13) and (14) to Eqs. (15) and (16), the free terms increase, approaching the ionization potentials of phosphine and arsine. The *Ind*, *Res*, and *Pol* contributions calculated by Eqs. (13) and (15) are, within error, almost equal to each other (Table 2). By contrast, Eqs. (14) and (16) radically differ from each other in that the latter equation has no term like $b\Sigma\sigma_R^+$. This finding implies that in the radical cations $As^{+\cdot}X_3$ formed from neutral molecules **I**–**VIII** (Table 1), there is no conjugation between X (Ph, C≡CH, CF_3, F, Cl, Br, but not Me) and the radical-cation center $As^{+\cdot}$.

Compounds **IX**–**XXII** containing, along with other substituents, Me, $CH{=}CH_2$, or $CH_2CH{=}CH_2$ groups fit correlation equations (17) and (18).

$$I_1(n_\mathrm{P}) = 10.09 + 1.57\Sigma\sigma_I + 0.77\Sigma\sigma_R^+ + 0.69\Sigma\sigma_\alpha; \quad (17)$$

S_a 0.10, S_b 0.12, S_c 0.15, S_d 0.16, S_Y 0.12, r 0.980, n 14.

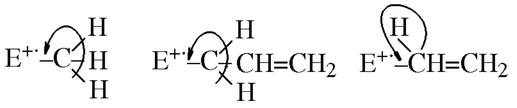
$$I_1(n_\mathrm{As}) = 9.86 + 1.43\Sigma\sigma_I + 0.72\Sigma\sigma_R^+ + 0.43\Sigma\sigma_\alpha; \quad (18)$$

S_a 0.16, S_b 0.19, S_c 0.24, S_d 0.25, S_Y 0.18, r 0.941, n 14.

Equations (17) and (18) have smaller free terms compared with Eqs. (13) and (14) and, especially, Eqs. (15) and (16). At E = As, the free terms are decreased stronger [10.36 – 9.86 = 0.50 eV, cf. Eqs. (16) and (18)] than at E = P [10.36 – 10.09 = 0.27 eV, cf. Eqs. (15) and (17)]. Unlike the *Ind*, *Res*, and *Pol* contributions calculated by Eqs. (15) and (16), those calculated by Eqs. (17) and (18) are close to each other (Table 2).

It is very important that, in the AsX_3 series, the *Res* contribution is very large for compounds **IX**–**XXII** (X = Me, $CH=CH_2$, or $CH_2CH=CH_2$) and lacking for compounds **I**–**VIII**. Moreover, the correlation coefficients for Eqs. (13) and (14), as well as (15) and (16), are comparable. However, in going from Eq. (17) to Eq. (18), the *r* value sharply decreases.

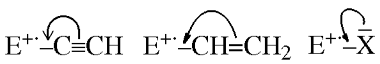
As follows from the aforesaid, conjugation of substituents X with the radical-cation center in $As^{+\cdot}X_3$ takes place only when X = Me, $CH_2CH=CH_2$, and, probably, $CH=CH_2$. In $R^{+\cdot}X_3$, this condition is not necessary. Therefore, it can be inferred that the σ,n hyperconjugation of C–H σ orbitals with the *n* orbital of the unpaired electron enhances in going from P to As.



A **B** **C**

E = P, As.

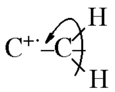
At the same time, the π,n- and n,n-conjugation effects which can be illustrated by schemes **D**–**F** take place only at E = P, whereas at E = As they are lacking.



D **E** **F**

X = F, Cl, Br.

Let us consider Eqs. (13)–(18) in light of the above assumptions. It should first be noted that in C-centered radical cations $R_\pi^{+\cdot}X$ (R_π = aryl, hetaryl, vinyl, ethynyl, etc.) at R_π = const, the free term I_1^H of equations like (10) is always equal to the ionization potential of unsubstituted neutral molecule $R_\pi H$ [1, 2]. Consequently, the hyperconjugation of alkyl groups with the radical-cation center in radical cations $R_\pi^{+\cdot}Alk$ is directly related to the standard resonance parameters σ_R^+ of these groups.



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As known [8, 21], such σ_R^+ values quantitatively characterize the hyperconjugation of alkyl groups with electron-deficient centers localized on the carbon atom.

Change of the reaction center, for instance, on passing from C-centered radical cations to P- and As-centered, changes conditions for hyperconjugation. Therefore, the standard tabulated σ_R^+ values lose their usual meaning as a universal characteristics of the properties of alkyl groups. We earlier showed that in radical cations containing $Z^{+\cdot}$–Alk fragments, the alkyl groups get stronger resonance electron donors at Z = S [3] and weaker resonance electron donors at Z = N [5] than in radical cations $R_\pi^{+\cdot}$–Alk [1, 2]. In particular, evidence for these conclusion comes from the trend in the free terms I_1^H of equations like (10) with increasing number of compounds with X = Alk in the ZX_n series. The I_1^H values decrease at Z = S and decrease at Z = N.

In the EX_3 series in study, the I_1^H values decrease. The decrease in I_1^H [0.27 eV in going from Eq. (15) for compounds containing no P–C–H fragments to Eq. (17) for compounds containing such fragments] at E = P is less significant than at E = As [0.50 eV in going from Eq. (16) to Eq. (18)]. This finding implies stronger hyperconjugation in radical cations $E^{+\cdot}X_3$ (E = P, As) compared with C-centered radical cations $R_\pi^{+\cdot}X$, enhancing in going from P to As.

The weaker hyperconjugation in radical cations $E^{+\cdot}X_3$ at E = P allows the resonance effects of alkyl groups to be characterized by tabulated σ_R^+ values with a smaller error than at E = As. Therefore, Eq. (13) for the ionization potentials of the full series (*n* 22) of neutral molecules PX_3 has better statistical characteristics compared with the similar equation [Eq. (14)] for AsX_3.

The reverse situation is observed with neutral molecules **I**–**VIII** and their radical cations (Table 1), whose substituents X are capable, by definition, for hyperconjugation with the reaction center. Therewith, Eq. (15) for the ionization potentials of PX_3 has worse statistical characteristics than Eq. (16) for AsX_3. This fact, as well as the lack of resonance term in Eq. (16), can be explained by specific features of the lone electron pair in the central atoms P and As.

Thus, in trimethyl derivatives EMe_3, as the atomic number of the Group 15 element increases, the CEC bond angle decreases (110.6, 98.6, and 96° at E = N, P, and As, respectively [23]. Hybridization of the lone electron pair of E changes simultaneously. At E = N, the hybridization is close to sp^3. As the atomic number of E increases, the *s* character of the lone electron pair enhances (for details, see [14, 24]). By symmetry reasons, the overlap integral between *s* and p_π orbitals is zero.

The considerable *s*-character of the lone electron pair of the P atom in neutral molecules **I**–**VIII** with

E = P (Table 1) results in a relatively weak conjugation with the p_π orbitals of substituents X, i.e. the *Res* values calculated by Eq. (15) are low (Table 2). As the *s*-character of the lone electron pair enhances in going from P to As, conjugation in radical cations $As^{+\cdot}X_3$ (Table 1) disappears completely, which is confirmed by the zero *Res* contribution in Eq. (16) (Table 2).

An alternative interpretation of the resonance interactions in the radical cations of **I**–**VIII** is possible. Probably, in radical cations $E^{+\cdot}X_3$, the resonance acceptor interaction of atom E (P, As) with substituents X occurs by the *d*,*n*-conjugation mechanism. This electronic effect in compounds of the silicon subgroup (M = Si, Ge, Sn, Pb) has been thoroughly studied [25]. For example, in neutral molecules R_3MX (R = Alk), there is a resonance acceptor interaction between the R_3M group and the X (F, Cl, Br, Ph, etc.) substituent having p_π orbitals, involving vacant *nd* orbitals of the M atom and antibonding σ^* orbitals of the R–M bonds (*d*,*n* conjugation). This effect weakens with increasing atomic number of M. Presumably, the *d*,*n* conjugation in compounds of the phosphorus subgroup, too, weakens in going from P to As. In this context the relatively weak *d*,*n* conjugation in phosphines **I**–**VIII** [the *Res* contribution calculated by Eq. (15) is 15±5%] vanishes in arsines **I**–**VIII**.

At present we cannot decide between the above two mechanisms of conjugation in radical cations $P^{+\cdot}X_3$ (Table 1). Apparently, both mechanisms contribute into the total resonance effect. Its intricate nature is responsible for the lower correlation coefficient *r* of Eq. (15) for phosphines **I**–**VIII** compared with the respective value for Eq. (16) for isostructural arsines **I**–**VIII** which lack conjugation.

The isostructural radical cations $P^{+\cdot}X_3$ and $As^{+\cdot}X_3$ contain substituents X (Me, $CH{=}CH_2$, $CH_2CH{=}CH_2$) capable for hyperconjugation with the radical-cation reaction center. The σ,*n* hyperconjugation between the σ orbitals of C–H bonds and the *n* orbital of the unpaired electron of the E atom in the ECH fragments.

First, the overlap integrals between σ and *n* orbitals are nonzero at any hybridization of the orbital accommodating the unpaired electron (from close to sp^3 at E = N to close to *s* at E = As, and intermediate at E = P) [11, 24, 25]. In any words, hyperconjugation is not forbidden by symmetry reasons. Unlike this, the overlap integral between the *s* orbital of the lone electron pair of As and the p_π orbital of X (C≡CH, Ph, F, etc.) in the As–X fragments is zero.

Second, the degree of mixing of σ and *n* orbitals (hyperconjugation strength) is also determined by their energy. Therefore, hyperconjugation is difficult to assess quantitatively [11, 24, 25], even though qualitatively this effect has been well studied on compounds of Group 14 elements [11]. In particular, the hyperconjugation in the M–C–H fragments was found to enhance with increasing atomic number of M.

The same regularity is observed with compounds of Group 15 elements. Their hyperconjugation, too, enhances with increasing atomic number of the element.

By analogy with compounds of Group 14 elements [11], one would expect enhancing hyperconjugation in the $E{-}C{\lessdot}H$ fragments with increasing number of hydrogen atoms and methyl groups attached to E (P, As). In isostructural radical-cation series $E^{+\cdot}X_3$, the number of E atoms and Me groups is the same, but at E = As hyperconjugation is stronger than at E = P. Therefore, as noted above, the standard tabulated σ_R^+ values worse describe the resonance effects of methyl groups in the $As^{+\cdot}$–Me fragments compared with $P^{+\cdot}$–Me. All this explains why the statistical characteristics of Eq. (18) for the ionization potentials of arsines **IX**–**XXII** are much worse compared with Eq. (17) for the ionization potentials of the isostructural phosphines. The strong hyperconjugation in radical cations $As^{+\cdot}X_3$, too, explains the significant difference between the free term of Eq. (18) and the ionization potential of AsH_3.

Thus, radical cations $As^{+\cdot}X_3$ are unique systems in which hyperconjugation is the only resonance effect. By purposively varying the properties of data set we could gain a deeper insight into this effect. To this end, we formed of the whole series [compounds **IX**–**XXII**, Eq. (18)] five narrower series of compounds whose ionization potentials are described by Eqs. (19)–(23). The *Ind*, *Res*, and *Pol* contributions and certain statistical characteristics of these compounds are listed in Tables 2 and 3.

Equations (19)–(23) have higher correlation coefficients *r* and lower standard approximation errors S_Y compared with Eq. (18). As shown above, the resonance donor properties of the Me, $CH{=}CH_2$, and $CH_2CH{=}CH_2$ groups in As-centered radical cations are stronger than in C-centered. Therefore, the use of standard tabulated σ_R^+ values to characterize the hyperconjugation in arsine derivatives is associated with inevitable errors whose magnitude depends on the number and type of groups attached to As. Therefore, for the whole series [compounds **IX**–**XXII**, Eq. (18)], there is the largest error scatter and the worst statistical characteristics (*r* and S_Y). In narrower series [for example, compounds **IX**–**XV** in which As always bears only one Me, $CH{=}CH_2$, or $CH_2CH{=}CH_2$

Table 3. Statistical characteristics of Eqs. (14), (16), and (18)–(23) and the specific contents *m*/*n* of C–H bonds in the As–C–H fragments

Eq. no.	Comp. no.	Presence of Me, $CH=CH_2$, and $CH_2CH=CH_2$, groups attached to As	I_1^H	S_Y	*r*	n^a	m^b	*m*/*n*
14	**I–XXII**	Whole data set	10.24	0.22	0.980	22	62	2.82
16	**I–VIII**	Me, $CH=CH_2$, and $CH_2CH=CH_2$ groups are lacking	10.36	0.19	0.993	8	0	0
18	**IX–XXII**	1, 2 or 3 Me groups, $CH=CH_2$ or $CH_2CH=CH_2$	9.86	0.18	0.941	14	62	4.43
19	**IX–XV**	1 Me group, $CH=CH_2$ or $CH_2CH=CH_2$	10.28	0.08	0.986	7	17	2.43
20	**IX, XII, XIII, XV–XXI**	1 or 2 Me groups	9.94	0.18	0.952	10	48	4.80
21	**IX, XII, XIII, XV–XXII**	1, 2 or 3 Me groups	9.93	0.16	0.964	11	57	5.18
22	**XVI–XXI**	2 Me groups	9.73	0.11	0.975	6	36	6.00
23	**XVI–XXII**	2 or 3 Me groups	9.76	0.11	0.977	7	45	6.43

[a] *n*, series size. [b] *m*, total number of C–H bonds in the As–C–H fragments.

group; Eq. (19)], the errors are roughly at the same level, and the statistical characteristics get better.

Among the five narrower series described by Eqs. (19)–(23), the radical cations derived from compounds **IX**–**XV** occupy a particular place. They weakest hyperconjugation in them correlates with the lowest *Res* values obtained by Eq. (19) (Table 2).

Let us now correlate I_1^H and *m*/*n* for the series described by Eqs. (14), (16), and (18)–(23). The I_1^H values are the free terms of these equations. The *m*/*n* values are the ratios of the total number of C–H bonds in the As–C–H fragments in the series *m* on the series size *n*, i.e. they characterize the specific content of C–H bonds in the series.

As follows from the aforesaid, hyperconjugation in As-centered radical cations should enhance with increasing *m*/*n*. With enhancing hyperconjugation, the free term I_1^H should decrease. The I_1^H values reflect anomalously strong resonance donor properties of the Me, $CH=CH_2$, or $CH_2CH=CH_2$ substituents. Such properties are explained by stronger hyperconjugation in As-centered radical cations compared with C-centered, and they are only partially accounted for by standard σ_R^+ constants. Therefore, the stronger hyperconjugation in a series, the smaller the free term I_1^H in the corresponding equation. The I_1^H and *m*/*n* values are interrelated by the linear equation (24).

$$I_1^H = 10.45 - 0.11m/n; \quad (24)$$

$$S_a\ 0.07,\ S_b\ 0.02,\ S_Y\ 0.09,\ r\ 0.946,\ n\ 8.$$

Its free term almost coincides with the ionization potential of AsH_3. The negative slope of Eq. (24) provides one more evidence to show that the stronger hyperconjugation in radical cations $As^{+\cdot}X_3$, the smaller the free term I_1^H in Eqs. (14), (16), and (18)–(23).

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