Effect of substituents on ionization potentials of phosphorus compounds. Conjugation in radical cations

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The first vertical ionization potentials (I) of phosphorus compounds $P(X_i)_3$, $OP(X_i)_3$, $SP(X_i)_3$, $(4\text{-}XC_6H_4)_3P$, and P≡CX are related to the inductive, resonance, and polarizability parameters of inorganic, organic, and organometallic substituents X by dependences of the type $I = I_H + a\Sigma\sigma_I + b\Sigma\sigma_R^+ + c\Sigma\sigma_\alpha$, where I_H is the I value for X = H. The I values are also affected by hyperconjugation. The ratio of the contributions of the resonance ($b\Sigma\sigma_R^+$) and polarizability ($c\Sigma\sigma_\alpha$) effects to the I value is determined by the degree of delocalization of the unpaired electron and the positive charge in the radical cations formed upon ionization of neutral molecules. The σ_R^+ resonance parameters of organosilicon, organogermanium, and organotin substituents bound to the $P^{\bullet+}$ radical cation center were calculated for the first time.

Key words: organophosphorus compounds; phosphorus compounds containing P—Si, P—Ge, and P—Sn bonds; ionization potential; radical cation; conjugation; polarizability of substituents.

In quantum chemistry, the ionization potentials (IP) I are usually determined in the Koopmans approximation[1]

$$I_i^0 = -E_i, \quad (1)$$

where E_i is the MO energy. If i is the highest occupied MO (HOMO), we get a relationship for the first IP:

$$I_1^0 = -E_{HOMO}. \quad (2)$$

Equation (1) seems to be more valid for the HOMO rather than for other MOs owing to strong redistribution of the electron density in the case of ionization of deeper molecular energy levels.[1—3] Therefore, we consider below mainly the first IPs.

Until recently, the use of IP values in physical organic chemistry was hampered by the absence of a substantiated and simple quantitative model of the influence of inorganic, organic, and organometallic substituents bound to the reaction (indicator) centers of the π-type (R_π) or n-type (Y). In the simplest case (X_iR_π and X_iY molecules), the HOMO is mainly localized on the R_π or Y fragments. It was found that for X_iR_π (R_π = Ar, Het, CH=CH_2, C≡CH, *etc.*)[4—6] and X_iY (Y = S—)[7] molecules the overall change in the I values caused by the effects of substituents X_i includes not only the inductive (In) and resonance (Res) contributions, but also the polarizability contribution (Pol)

$$I = I_H + In + Res + Pol, \quad (3)$$

where I_H is the ionization potential of unsubstituted molecule (X_i = H). The Pol contribution characterizes the electrostatic interaction between the positive charge of the radical cation $X_iR_\pi^{\bullet+}$ or $X_iY^{\bullet+}$ with the induced dipole moment of the substituent X_i.[4—7]

Particular forms of the dependences described by Eq. (3) are determined by the nature of substituents and the type of the indicator center. The obtaining of correlation equations for different reaction series allows quantitative estimation of the ratio of the In, Res, and Pol contributions and, hence, investigation of the substituent effects in radical cations (*e.g.*, conjugation, interrelation between conjugation and the polarizability of substituents, resonance interaction of poorly studied substituents R_i, *etc.*). Using the IP values for five series of organophosphorus compounds, in this work we found quantitative relationships between the ionization potentials and the properties of substituents bound to the P atom and studied the resonance and electrostatic interactions in radical cations, as well as conjugation between substituents containing the atoms of the silicon subgroup elements and the radical cation center $P^{\bullet+}$.

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Table 1. First vertical ionization potentials of $P(X_i)_3$ ($I(n_P)$), $O{=}P(X_i)_3$ ($I(n_O)$), and $S{=}P(X_i)_3$ molecules ($I(n_S)$) and the sums of σ parameters of substituents $(X_i)_3$

Compound	$(X_i)_3$	$I(n_P)$	$I(n_O)$	$I(n_S)$	$\Sigma\sigma_I$	$\Sigma\sigma_R^+$	$\Sigma\sigma_P^+$	$\Sigma\sigma_\alpha$
		eV						
1	H_3	10.6	—	—	0	0	0	0
2	H_2Me	9.63	—	—	−0.05	−0.26	−0.31	−0.35
3	H_2Bu^t	9.32	—	—	−0.07	−0.19	−0.26	−0.75
4	H_2CF_3	11.15	—	—	0.38	0.23	0.61	−0.25
5	HMe_2	9.10	10.32	8.78	−0.10	−0.52	−0.62	−0.70
6	HBu^t_2	8.35	—	—	−0.14	−0.38	−0.52	−1.50
7	HPh_2	8.3	—	—	0.24	−0.60	−0.36	−1.62
8	$H(CF_3)_2$	11.43	—	—	0.76	0.46	1.22	−0.50
9	$H(OMe)_2$	—	11.10	—	0.58	−2.14	−1.56	−0.34
10	$H(OEt)_2$	—	10.86	—	0.52	−2.14	−1.62	−0.46
11	HF_2	11.00	—	—	0.90	−1.04	−0.14	+0.26
12	Me_3	8.62	9.9	8.48	−0.15	−0.78	−0.93	−1.05
13	Et_3	8.28	—	—	−0.15	−0.75	−0.90	−1.47
14	Bu^t_3	7.68	—	—	−0.21	−0.57	−0.78	−2.25
15	$Et_2(CH{=}CH_2)$	—	9.66	—	0.03	−0.79	−0.76	−1.48
16	$Bu_2(CH{=}CH_2)$	8.25	—	—	0.03	−0.79	−0.76	−1.64
17	Me_2Ph	8.32	—	—	0.02	−0.82	−0.80	−1.51
18	Bu_2Ph	8.03	—	—	0.02	−0.80	−0.78	−1.95
19	$MePh_2$	8.3	—	—	0.19	−0.86	−0.67	−1.97
20	Ph_3	7.92	—	—	0.36	−0.90	−0.54	−2.43
21	$Bu_2(CH_2Ph)$	8.09	—	—	0.07	−0.95	−0.88	−1.84
22	Me_2CN	9.80	—	—	0.41	−0.37	0.04	−1.16
23	$Me(CN)_2$	10.85	—	—	0.97	0.04	1.01	−1.27
24	$(CN)_3$	12.04	—	—	1.53	0.45	1.98	−1.38
25	$Me_2(CF_3)$	9.7	—	—	0.28	−0.29	−0.01	−0.95
26	$(CN)_2CF_3$	11.81	—	—	1.40	0.53	1.93	−1.17
27	$Me(CF_3)_2$	10.80	—	—	0.71	0.20	0.91	−0.85
28	$CN(CF_3)_2$	11.72	—	—	1.27	0.61	1.88	−0.96
29	$(CF_3)_3$	11.60	—	—	1.14	0.69	1.83	−0.75
30	$(NMe_2)_3$	—	—	8.05	0.45	−5.55	−5.10	−1.32
31	$(CH{=}CH_2)_2OEt$	—	10.23	—	0.52	−1.65	−1.13	−1.23
32	$(CH_2Cl)_2OEt$	—	10.19	—	0.52	−1.35	−0.83	−1.31
33	$Me(OMe)_2$	—	10.53	—	0.53	−2.40	−1.87	−0.69
34	$Ph(OEt)_2$	8.53	—	—	0.64	−2.44	−1.80	−1.27
35	$(OMe)_3$	9.25	10.81	9.16	0.87	−3.21	−2.34	−0.51
36	$(OEt)_3$	9.0	10.54	8.96	0.78	−3.21	−2.43	−0.69
37	Me_2SMe	8.6	—	—	0.13	−1.35	−1.22	−1.38
38	Et_2SEt	8.38	—	—	0.13	−1.33	−1.20	−1.72
39	Me_2F	9.35	—	—	0.35	−1.04	−0.69	−0.57
40	Bu^t_2F	8.5	—	—	0.31	−0.90	−0.59	−1.37
41	MeF_2	10.33	12.35	—	0.85	−1.30	−0.45	−0.09
42	Bu^tF_2	9.65	—	—	0.83	−1.23	−0.40	−0.49
43	$(CN)F_2$	11.90	—	—	1.41	−0.89	0.52	−0.20
44	F_3	12.23	13.52	11.05	1.35	−1.56	−0.21	+0.39
45	Me_2Cl	9.15	10.77	9.12	0.32	−0.83	−0.51	−1.13
46	$Et(CH{=}CH_2)Cl$	—	10.62	—	0.50	−0.85	−0.35	−1.42
47	$(CF_3)_2Cl$	11.13	—	—	1.18	0.15	1.33	−0.93
48	$(CH_2Cl)_2Cl$	9.85	10.75	9.54	0.68	−0.59	0.09	−1.51
49	$(NMe_2)_2Cl$	—	—	8.75	0.72	−4.01	−3.29	−1.31
50	$(OMe)_2Cl$	9.76	—	—	1.00	−2.45	−1.45	−0.77
51	$(OEt)_2Cl$	—	10.96	9.41	0.94	−2.45	−1.51	−0.89
52	$(OPr)_2Cl$	—	10.89	—	0.94	−2.49	−1.55	−0.95
53	$MeCl_2$	9.86	11.49	9.73	0.79	−0.88	−0.09	−1.21
54	$(CH{=}CH_2)Cl_2$	9.84	11.24	9.70	0.97	−0.91	0.06	−1.36
55	$PhCl_2$	9.63	—	9.47	0.96	−0.92	0.04	−1.67
56	$(CF_3)Cl_2$	10.70	—	—	1.22	−0.39	0.83	−1.11
57	$(CH_2Cl)Cl_2$	10.17	11.50	—	0.97	−0.76	0.21	−1.40

(*to be continued*)

Table 1 (*continued*)

Compound	$(X_i)_3$	$I(n_P)$	$I(n_O)$	$I(n_S)$	$\Sigma\sigma_I$	$\Sigma\sigma_R^+$	$\Sigma\sigma_P^+$	$\Sigma\sigma_\alpha$
		eV						
58	$(NMe_2)Cl_2$	—	—	9.35	0.99	−2.47	−1.48	−1.30
59	$(OMe)Cl_2$	10.26	—	—	1.13	−1.69	−0.56	−1.03
60	$(OEt)Cl_2$	—	11.46	9.81	1.10	−1.69	−0.59	−1.09
61	Cl_3	10.52	11.89	10.11	1.26	−0.93	0.33	−1.29
62	Me_2Br	9.24	—	—	0.35	−0.82	−0.47	−1.29
63	F_2Br	—	—	10.58	1.35	−1.34	0.01	−0.33
64	$MeBr_2$	9.66	—	9.53	0.85	−0.86	−0.01	−1.53
65	$(CF_3)Br_2$	10.23	—	—	1.28	−0.37	0.91	−1.43
66	FBr_2	—	—	10.23	1.35	−1.12	0.23	−1.05
67	Br_3	9.96	11.02	9.89	1.35	−0.90	0.45	−1.77

Note. The $I(n_P)$, $I(n_O)$, and $I(n_S)$ values were taken from Refs. 1, 2, and 8—11. The values of the σ_I, σ_R^+, and σ_α parameters of substituents X_i and the sums $\sigma_P^+ = \sigma_I + \sigma_R^+$ were taken from Refs. 4—7 and 12.

Calculation Procedure

The experimental values of the first vertical IPs corresponding to detachment of an electron from the HOMO for five series of molecules of the types $P(X_i)_3$ (***A***), $O{=}P(X_i)_3$ (***B***), $S{=}P(X_i)_3$ (***C***), $(4\text{-}XC_6H_4)_3P$ (***D***), and $P{\equiv}CX$ (***E***) are listed in Tables 1—3. The IP values were determined by photoelectron spectroscopy with an accuracy of 0.01 eV. The IP notations and the preferred HOMO localization according to the published data[1,2,8—11,13,14] for different series of the molecules are given in parentheses. They are as follows: series ***A*** ($I(n_P)$, n-orbital of P atom), series ***B*** ($I(n_O)$, n-orbital of O atom of the O=P fragment), series ***C*** ($I(n_S)$, n-orbital of S atom of the S=P fragment), series ***D*** ($I^P(n_P)$, n-orbital of P atom), and series ***E*** ($I(\pi)$, the $\pi(P{\equiv}C)$ MO). For the compounds of series ***E*** we also list the second IPs, $I_2(n_P)$, which correspond to detachment of an electron from the n-orbital of P atom.

Irradiation of neutral molecules (*e.g.*, $P(X_i)_3$) by photons with the energy $h\nu$ results in the formation of $P^{\bullet+}(X_i)_3$ radical cations

$$P(X_i)_3 + h\nu \rightarrow P^{\bullet+}(X_i)_3 + e^- . \qquad (4)$$

Table 2. First vertical ionization potentials $I^P(n_P)$ of $(4\text{-}XC_6H_4)_3P$ molecules and the sums of σ parameters of substituents X

Compound	X	$I^P(n_P)$ /eV	$\Sigma\sigma_I$	$\Sigma\sigma_R^+$	$\Sigma\sigma_P^+$	$\Sigma\sigma_\alpha$
68	H	7.92	0	0	0	0
69	Me	7.6	−0.15	−0.78	−0.93	−1.05
70	Pr^i	7.53	−0.09	−0.75	−0.84	−1.86
71	Bu^t	7.52	−0.21	−0.57	−0.78	−2.25
72	CF_3	8.30	1.14	0.69	1.83	−0.75
73	NMe_2	6.95	0.45	−5.55	−5.10	−1.32
74	OMe	7.48	0.87	−3.21	−2.34	−0.51
75	F	8.12	1.35	−1.56	−0.21	0.39
76	Cl	8.18	1.26	−0.93	0.33	−1.29

Note. The $I^P(n_P)$ values were taken from Ref. 13. The σ_I, σ_R^+, and σ_α parameters of substituents X and the $\sigma_P^+ = \sigma_I + \sigma_R^+$ sums were taken from Refs. 4—7 and 12.

The ionization potential is equal to the difference between the total energies of the radical cation and the corresponding neutral molecule

$$I = E_n^{\bullet+} - E_n, \qquad (5)$$

and can also be expressed in the form[1]

$$I = I^0 - R + C. \qquad (6)$$

The relaxation energy R and correlation energy C characterize changes in the composition of the wave function of the neutral molecule due to its transformation into the radical cation. The Koopmans approximation (2), which ignores the R and C contributions to the I value, was found to be invalid for both X_iR_π molecules[4—6] and X_iY sulfides.[7] For these series of molecules, relationship (3) takes the form

$$I = I_H + a\sigma_I + b\sigma_R^+ + c\sigma_\alpha, \qquad (7)$$

where σ_I, σ_R^+, and σ_α are the parameters characterizing the inductive, resonance, and polarizability effects of substituents X_i, respectively; and a, b, and c are coefficients dependent on the nature of the reaction center.

Judging from the magnitudes of the resonance ($Res = b\sigma_R^+$) and polarizability ($Pol = c\sigma_\alpha$) contributions to the I values, the Koopmans approximation is invalid for the series of compounds studied previously.[4—7] Indeed, for neutral molecules, the reso-

Table 3. The $I(\pi)$ and $I_2(n_P)$ ionization potentials of $P{\equiv}CX$ molecules and the σ parameters of substituents X

Compound	X	$I(\pi)$	$I_2(n_P)$	σ_I	σ_R^+	σ_P^+	σ_α
		eV					
77	H	10.79	12.86	0	0	0	0
78	Me	9.89	12.19	−0.05	−0.26	−0.31	−0.35
79	Bu^t	9.61	11.44	−0.07	−0.19	−0.26	−0.75
80	Ph	9.87	11.76	0.12	−0.30	−0.18	−0.81
81	F	10.57	13.55	0.45	−0.52	−0.07	0.13

Note. The $I(\pi)$ and $I_2(n_P)$ values were taken from Refs. 2 and 14. The σ_I, σ_R^+, and σ_α parameters of substituents X and the $\sigma_P^+ = \sigma_I + \sigma_R^+$ sums were taken from Refs. 4—7 and 12.

nance effect of substituents X_i on the E_{HOMO} (and, hence, the I value, provided that the Koopmans relationship is valid) is quantitatively characterized by the σ_R^0 constants. In the radical cations $X_iR_\pi^{\bullet+}$ and $X_iY^{\bullet+}$, the reaction centers carry large positive charges and conjugation of substituents X_i with such electron-deficient centers is characterized by the σ_R^+ constants. The values of the σ_R^0 and σ_R^+ constants differ appreciably, especially for those substituents which are typical +M-resonance donors (NMe_2, OMe, *etc.*).[12] Therefore, conjugation in neutral molecules and in radical cations cannot be equal in magnitude.

The polarizability contribution, Pol = $c\sigma_\alpha$, which is absent for neutral molecules, can be rather large for radical cations.[4—7] Consideration of substituent effects on the I value without taking into account this contribution (*i.e.*, in the Koopmans approximation (2)) leads to severe problems.[4—7] This contribution is due to electrostatic stabilization of the positive charge q of the radical cation by the dipole moment induced in the substituent X_i. The stabilization energy is defined by the following expression

$$E_{st} = -q^2\alpha/(2\varepsilon r^4), \quad (8)$$

where α is the polarizability of substituent X_i, ε is the dielectric constant, and r is the distance between the charge and the induced dipole. Considerable difficulties in the calculations of E_{st} values arise if the charge and the induced dipole are parts of the same ion.[15] It is possible to circumvent these difficulties by introducing a parameter σ_α, which quantitatively characterizes stabilization of the charge q owing to the polarizability of the substituents X_i. The σ_α constants of a large number of substituents were calculated by *ab initio* quantum-chemical methods and are used in the studies of the gas-phase ionic reactions[12,16] including process (4). The origin of the scale of the σ_α parameters was chosen in such a way that $\sigma_\alpha = 0$ for X_i = H (see Tables 1—3). This provides a standard use of these constants in the correlation equations similar to the Hammett—Taft relationship (7). The larger the negative σ_α value, the stronger the stabilization of the charge q and, thus, the lower the energy of the radical cation $E_n^{\bullet+}$, and the ionization potential I.

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

Assume that the influence of substituent X_i on the corresponding I value involves only inductive and resonance effects. The correlation equations obtained in this case have usually such low correlation coefficients that they cannot even be used for qualitative estimates. Taking into account the polarizability of substituents, *i.e.*, passage to three-parameter correlations

$$I(n_P) = 10.30 + 1.55\Sigma\sigma_I + 0.62\Sigma\sigma_R^+ + 0.94\Sigma\sigma_\alpha, \quad (9)$$

$$S_a = 0.10,\ S_b = 0.07,\ S_c = 0.04,\ S_d = 0.06,\ S_Y = 0.24,\ r = 0.980,\ n = 52;$$

$$I(n_O) = 11.79 + 1.62\Sigma\sigma_I + 0.55\Sigma\sigma_R^+ + 1.16\Sigma\sigma_\alpha, \quad (10)$$

$$S_a = 0.13,\ S_b = 0.08,\ S_c = 0.05,\ S_d = 0.08,\ S_Y = 0.16,\ r = 0.982,\ n = 23;$$

$$I(n_S) = 9.43 + 1.22\Sigma\sigma_I + 0.26\Sigma\sigma_R^+ + 0.48\Sigma\sigma_\alpha, \quad (11)$$

$$S_a = 0.11,\ S_b = 0.07,\ S_c = 0.02,\ S_d = 0.06,\ S_Y = 0.13,\ r = 0.982,\ n = 20;$$

$$I^P(n_P) = 7.87 + 0.37\Sigma\sigma_I + 0.18\Sigma\sigma_R^+ + 0.07\Sigma\sigma_\alpha, \quad (12)$$

$$S_a = 0.06,\ S_b = 0.05,\ S_c = 0.01,\ S_d = 0.04,\ S_Y = 0.07,\ r = 0.985,\ n = 9;$$

$$I(\pi) = 10.78 + 2.10\sigma_I + 2.34\sigma_R^+ + 0.65\sigma_\alpha, \quad (13)$$

$$S_a = 0.12,\ S_b = 0.69,\ S_c = 0.68,\ S_d = 0.21,\ S_Y = 0.13,\ r = 0.969,\ n = 5;$$

$$I_2(n_P) = 12.85 + 1.60\sigma_I + 0.37\sigma_R^+ + 1.52\sigma_\alpha, \quad (14)$$

$$S_a = 0.12,\ S_b = 0.66,\ S_c = 0.65,\ S_d = 0.20,\ S_Y = 0.12,\ r = 0.990,\ n = 5$$

makes the statistical characteristics of the correlation equations much better. It is noteworthy that Eq. (13) has a relatively low correlation coefficient (0.969). This can be explained by low accuracy of determination of the $I(\pi)$ value for the P≡CPh molecule, for which this is the third (not the first!) ionization potential.[14]

In the P≡CX molecules conjugation involving the lone electron pair of the P atom is impossible. By applying the method of statistical testing of hypothesis[17] and the Palm criteria[18] to the data described by Eq. (14) we found that the term $0.37\sigma_R^+$ is statistically insignificant. After exclusion of the Res contribution from Eq. (14) we get a new relationship

$$I_2(n_P) = 12.81 + 1.27\sigma_I + 1.58\sigma_\alpha, \quad (15)$$

$$S_a = 0.08,\ S_b = 0.27,\ S_c = 0.13,\ S_Y = 0.10,\ r = 0.993,\ n = 5,$$

which has better statistical characteristics.

From Eqs. (9)—(13) and (15) it follows that ignoring the polarizability contribution to the overall change in the I values caused by substituents X_i in the molecules of series ***A—E*** would be erroneous. Correlation equations (9)—(13) show again that relationships of the type (7) are valid for both the X_iR_π (R_π is a π-electron fragment)[4—6] and X_iY, systems with Y = S—[7] or P< (original data obtained by the authors). Therefore, the σ_R^+ constants quantitatively characterize the resonance interaction between substituents X_i and the radical cation centers $R_\pi^{\bullet+}$ and $Y^{\bullet+}$.

Consider the inductive, resonance, and polarizability contributions to the overall change in the IP value caused by the influence of substituents X_i in more detail. The mean values of these contributions in series ***A—E*** are different (Table 4); however, the differences between them depend on both the sample size (n) and the type of X_i and can therefore hardly be used for comparing the electronic interactions in the molecules. A more rigorous approach involves the inclusion of the In, Res, and Pol contributions to the I value, which are due to passage from PH_3 to PMe_3, $P(OMe)_3$, and PBr_3 in series ***A—D***.

Table 4. Inductive (In), resonance (Res), and polarizability (Pol) contributions (%) to the changes in the ionization potentials, caused by replacement of H atoms by substituents X in the PH_3, OPH_3, and SPH_3 molecules (series ***A*—*C***) and in the Ph_3P and P≡CH molecules (series ***D***, ***E***)

Substituent	$P(X_i)_3$ (***A***)			$O{=}P(X_i)_3$ (***B***)			$S{=}P(X_i)_3$ (***C***)			$(4\text{-}XC_6H_4)_3P$ (***D***)			P≡CX (***E***)		
X	In	Res	Pol	In	Res	Pol	In	Res	Pol	In	Res	Pol	In	Res	Pol
Me	14	28	58	13	23	64	20	23	57	22	52	26	11 (10)	65 —	24 (90)
MeO	35	52	13	37	47	16	50	39	11	34	62	4	19 (58)	78 —	3 (42)
Br	48	13	39	46	11	43	61	8	31	64	21	15	46 (38)	35 —	19 (62)
Mean values*	35	31	34	38	23	39	44	31	25	31	60	9	37 (31)	42 —	21 (69)

Note. For series ***E***, figures given without parentheses denote the contributions to the changes in the $I(\pi)$ values. The contributions to the changes in the $I_2(n_P)$ values are given in parentheses.
* Mean contributions to the IP values calculated for full series ***A*—*E***.

Equations (9)—(13), (15) also allow calculations of these contributions for uninvestigated or hypothetical compounds. For instance, the use of correlation equations for the molecules of series ***E*** makes it possible to evaluate the In, Res, and Pol contributions on going from P≡CH to P≡CMe, P≡COMe, and P≡CBr in spite of the absence of the I values for the last-mentioned two molecules.

The data listed in Table 4 indicate the following tendencies of changes in these contributions to the I values. On going from series ***A*** to series ***B*** the first term (In) changes slightly, the second term (Res) decreases, while the third term (Pol) increases. The last-mentioned two contributions were found to be interrelated. For instance, in series ***A*** conjugation between substituents X_i and the radical cation center $P^{\bullet+}(X_i)_3$ leads to delocalization of both the unpaired electron and the positive charge q. This corresponds to a change in the q and r values in formula (8) and, hence, in the Pol contribution. Stereoelectronic conditions for such a delocalization in the $^{\bullet+}O{=}P(X_i)_3$ radical cations seem to be less favorable. Therefore, despite a longer distance between the X_i substituents and the radical cation center, the Pol contribution in the molecules of series ***B*** is larger than in those of series ***A***. Additionally, the conditions for conjugation between the X_i substituents and the radical cation center in the molecules of series ***B*** are also less favorable than in those of series ***A***.

Conjugation in the molecules of series ***C*** is weak. This is indicated by the smaller value of the Res/In ratio compared to that for the molecules of series ***B***. Nevertheless, the Pol contribution for series ***C*** is also lower than for series ***B***. This is likely due to the greater P=S bond length as compared to the P=O bond length and, as hence, to an increase in the distance r between the X_i substituents and the radical cation center (see formula (8)).

In the molecules of series ***D***, the distances from the X substituents to the radical cation center $P^{\bullet+}$ are maximum. The degree of delocalization of both the unpaired electron and the charge q over three aromatic rings seems to be higher than for the molecules of series ***A*—*C***. That is why series ***D*** is characterized by the smallest Pol and the largest Res contributions.

In the molecules of series ***E***, conjugation between the X substituents and the radical cation center $R_\pi^{\bullet+}$ is strong. The Res contribution to a change in the $I(\pi)$ value is larger than similar contributions in series ***A*—*D***. (For strong conjugation in radical cations of acetylene derivatives, see Ref. 5) The molecules of series ***E*** are yet another example of interrelation between the contributions of different electronic effects. Here, with the largest Res contribution, the contribution Pol is as small as that for the molecules of series ***D***. Just the opposite is the effect of X substituents on the ionization potentials $I_2(n_P)$ of the molecules of series ***E***. The Res contribution is zero, but the Pol contribution is the largest for all the five series of compounds.

Consider the correlation equation (9) for series ***A*** in more detail. The absolute term of Eq. (9) differs from the IP of the PH_3 molecule (*cf.* 10.30 and 10.60 eV, respectively). Series ***A*** includes compounds which may or may not contain P—H bonds. A separate consideration of the first type of molecules (**1—8** and **11**) leads to the following relationship:

$$I(n_P) = 10.55 + 1.36\Sigma\sigma_I + 1.06\Sigma\sigma_R^+ + 1.16\Sigma\sigma_\alpha, \quad (16)$$

$$S_a = 0.08,\ S_b = 0.13,\ S_c = 0.10,\ S_d = 0.08,\ S_Y = 0.13,\ r = 0.994,\ n = 9.$$

A similar relationship for the second type of compounds (**12—14**, **16—29**, **34—45**, **47**, **48**, **50**, **53—57**, **59**, **61**, **62**, **64**, **65**, and **67**) has the form

$$I(n_P) = 10.21 + 1.57\Sigma\sigma_I + 0.59\Sigma\sigma_R^+ + 0.89\Sigma\sigma_\alpha, \quad (17)$$

$$S_a = 0.16,\ S_b = 0.08,\ S_c = 0.05,\ S_d = 0.08,\ S_Y = 0.24,\ r = 0.981,\ n = 43.$$

Equations (16) and (17) have higher correlation coefficients than the general relationship for the whole

series ***A*** (see Eq. (9)). It is noteworthy that (i) the absolute term of the former equation is somewhat larger while that of the latter equation is smaller than the absolute term of Eq. (9) and (ii) the absolute term of Eq. (16) is nearly equal to the $I(n_P)$ value of the PH_3 molecule. Previously,[7] comparison of the $I(n_S)$ ionization potentials of the H_2S and HSX molecules with those of the $S(X_i)_2$ molecules containing no S—H bonds revealed a similar picture.

It seems likely that, as in the case of sulfides,[7] the difference between the absolute terms of Eqs. (16) and (17) is due to the dependence of hyperconjugation on the number of alkyl groups R bound to the radical cation center $P^{\bullet+}$. According to commonly accepted concepts,[19] hyperconjugation is an additional resonance donor effect of substituents R, which increases (i) if the reaction center (in particular, $S^{\bullet+}$ or $P^{\bullet+}$) is positively charged and (ii) with increasing number of R groups. In this case, an increase in hyperconjugation considered as a +M-donor effect must decrease both the $I(n_P)$ value and, hence, the absolute term of Eq. (17). Indeed, the $P(X_i)_3$ compounds described by Eq. (17) contain a larger number of R groups (and therefore hyperconjugation makes the larger contribution to the $I(n_P)$ value) than the corresponding compounds containing one, two, or three P—H bonds, which are described by Eq. (16).

We used Eqs. (9), (16), and (17) for calculations of unknown values of the $\sigma_R^+(P)$ parameters of organoelement substituents MR_3 (M = Si, Ge, Sn) bound to the radical cation center $P^{\bullet+}$ (Table 5).

Consider the $\sigma_R^+(P)$ parameters according to modern concept of conjugation in compounds of the silicon subgroup elements.[24] In the $R_\pi MR_3$ and YMR_3 (M = Si, Ge, Sn, Pb; R is an organic substituent) molecules, the overall resonance effect of substituents involves both acceptor and donor components. The acceptor properties of the MR_3 substituents toward the reaction centers of the π-type (R_π) and n-type (Y) are due to d,π- and d,n-conjugation (interactions of the vacant nd-orbitals of the M atom and the antibonding σ^*-orbitals of the M—C bonds with the orbitals of R_π and Y, respectively). These types of conjugation decrease with increasing atomic number of the M element. The donor properties of the MR_3 substituents toward the above-mentioned reaction centers are due to σ,π- and σ,n-conjugation (interactions of the σ-orbitals of the M—C bonds with the orbitals of R_π and Y, respectively). These types of conjugation increase with increase in both the atomic number of the M element and the positive charge on the R_π and Y fragments. The charges on the reaction centers in the neutral $R_\pi MR_3$ and YMR_3 molecules and in the corresponding radical cations differ appreciably. Therefore, the $\sigma_R^+(P)$ parameters quantitatively characterizing the overall resonance effect of the MR_3 substituents toward the radical cation center $P^{\bullet+}$ (see Table 5) are of importance not only for understanding conjugation in systems containing the $M—P^{\bullet+}$ fragments, but also for the development of a general concept of resonance interactions in compounds of the silicon subgroup elements.

For most of the MR_3 substituents, the values of the $\sigma_R^+(P)$ constants are appreciably different from the

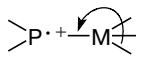
Table 5. Calculated $\sigma_R^+(P)$ parameters of MR_3 (M = Si, Ge, Sn) substituents

Compound	MR_3	$I(n_P)$/eV	$\Sigma\sigma_I$	$\Sigma\sigma_\alpha$	$\Sigma\sigma_R^+(P)$	$\sigma_R^+(P)$	$\sigma_R^+(B)$
H_2PMR_3 (**82**)	SiH_3	9.9	−0.04	−0.59	0.08	0.08	0.03
$HP(MR_3)_2$ (**83**)	SiH_3	9.62	−0.08	−1.18	0.52	0.26	
$P(MR_3)_3$ (**84**)	SiH_3	9.3	−0.12	−1.77	1.46	0.49	
					(1.37)	(0.46)	
H_2PMR_3 (**85**)	$SiMe_3$	9.1	−0.15	−0.72	−0.39	−0.39	0.02
$HP(MR_3)_2$ (**86**)	$SiMe_3$	8.35	−0.30	−1.44	−0.11	−0.05	
$P(MR_3)_3$ (**87**)	$SiMe_3$	7.9	−0.45	−2.16	0.54	0.18	
					(0.53)	(0.18)	
H_2PMR_3 (**88**)	SiF_3	11.06	0.43	−0.25	0.21	0.21	0.27
Me_2PMR_3 (**89**)	$SiCl_3$	9.1	0.29	−1.4	−0.02	−0.02	−0.23
					(−0.01)	(−0.01)	
H_2PMR_3 (**90**)	GeH_3	9.7	−0.04	−0.6	−0.09	−0.09	0.00
$P(MR_3)_3$ (**91**)	GeH_3	9.0	−0.12	−1.8	0.98	0.33	
					(0.94)	(0.31)	
$P(MR_3)_3$ (**92**)	$SnMe_3$	7.81	−0.39	−1.8	−0.32	−0.11	−0.21
					(−0.32)	(−0.11)	

Note. The $\sigma_R^+(P)$ parameters of MR_3 substituents in the PH_2MR_3 and $PH(MR_3)_2$ molecules were calculated by Eq. (16) and those in the $P(MR_3)_3$ and $PMe_2(MR_3)$ molecules were calculated by Eq. (17) and Eq. (9) (see figures in parentheses). The $I(n_P)$ values of compounds **82**, **90**, **91**, and **92** were taken from Refs. 8, 20, and 21; those of other compounds were taken from Ref. 22. The values of the σ_I and σ_α parameters were taken from Refs. 4—7 and the σ_α constants of the SiF_3, $SiCl_3$, and GeH_3 groups were estimated approximately from the σ_α constants of organic substituents[12,16] and their organometallic analogs.[4—7] The $\sigma_R^+(B)$ values were taken from Ref. 23.

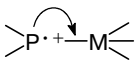
σ_R^+(B) constants characterizing conjugation between the same substituents and the positively charged benzene ring.[23] Yet another feature of conjugation with the radical cation center $P^{\bullet+}$ is the large difference between the σ_R^+(P) constants and the σ_R^0 parameters considered as a quantitative measure of conjugation in neutral molecules. The σ_R^0 constant of the SiH_3 substituent in the H_2PSiH_3 molecule is close to zero.[25] At the same time, the σ_R^+(P) constant of the SiH_3 group in the $H_2P^{\bullet+}SiH_3$ radical cation is 0.08, thus being an indicator of d,n-conjugation involving the unpaired electron of the P atom.

The effects of d,n- and σ,n-conjugation in the radical cations under study vary over a wide range (see Table 5). These effects, as well as the degree of delocalization of the unpaired electron and that of the positive charge, are interrelated. Undoubtedly, the degree of delocalization increases with increasing n in the $H_{3-n}P^{\bullet+}(MR_3)_n$ radical cations. Therefore, the most favorable stereoelectronic conditions for σ,n-conjugation in these radical cations arise if $n = 1$, which corresponds to the highest degree of localization of the positive charge on the $P^{\bullet+}$ center, since σ,n-conjugation weakens in the order $H_2PMR_3 > HP(MR_3)_2 > P(MR_3)_3$.



σ,n-conjugation

Considering d,n-conjugation as delocalization of the unpaired electron, it is easy to understand that it is maximum if $n = 3$. Therefore, the resonance acceptor effect of the MR_3 substituents increases in the order $H_2PMR_3 < HP(MR_3)_2 < P(MR_3)_3$.



d,n-conjugation

Thus, particular values of the σ_R^+(P) parameters of the MR_3 substituents are determined by competition of two resonance effects, namely, d,n- and σ,n-conjugation. For R = H, d,n-conjugation dominates over σ,n-conjugation, which is confirmed by positive values of the σ_R^+(P) constants. Since the $SiMe_3$ substituent is a stronger electron donor than SiH_3, the corresponding σ_R^+(P) parameter changes its sign as the n value in the $H_{3-n}P^{\bullet+}(SiMe_3)_n$ radical cations varies. If $n = 1$, the σ_R^+(P) parameter is negative (*i.e.*, σ,n-conjugation is dominant), while if $n = 2$ the effects of σ,n- and d,n-conjugation are comparable in magnitude. In the $P^{\bullet+}(SiMe_3)_3$ radical cation, the acceptor effect of the trimethylsilyl substituents toward $P^{\bullet+}$ is dominant.

The value of the σ_R^+ parameter of the $SiMe_3$ substituent depends on the type of the radical cation to which it is bound. In the $(4\text{-}Me_3SiC_6H_4)_3P^{\bullet+}$ radical cation, this substituent is a strong resonance acceptor ($\sigma_R^+ = 0.23$, calculated by Eq. (12) using $I^P(n_P) = 7.67$ eV [13]), whereas in the $Me_3SiC{\equiv}P^{\bullet+}$ radical cation it is not too strong an electron donor ($\sigma_R^+ = -0.04$, calculated by Eq. (13) using $I(\pi) = 9.90$ eV [22]).

The SiF_3 substituent bound to the benzene ring is the strongest resonance acceptor (σ_R^+(B) = 0.27). This is consistent with the lowest ability of the SiF_3 group to be involved in σ,π-conjugation with the benzene ring.[26] In the $H_2P^{\bullet+}SiF_3$ radical cation, d,n-conjugation also dominates over σ,n-conjugation (σ_R^+(P) = 0.21).

In contrast to the SiF_3 group, the $SiCl_3$ substituent is a resonance donor (σ_R^+(B) = −0.23) toward the positively charged benzene ring. In the $Me_3P^{\bullet+}SiCl_3$ radical cation, the donor properties of the $SiCl_3$ substituent (σ,n-conjugation) are comparable with its acceptor properties (d,n-conjugation), which is indicated by the σ_R^+(P) value, which is close to zero.

The σ_R^+(B) parameters of the SiH_3 and GeH_3 groups are close. However, these substituents possess appreciably different properties in radical cations, being respectively a resonance acceptor and a donor toward the $H_2P^{\bullet+}$ center. In the $P^{\bullet+}Y_3$ radical cations, both substituent are typical acceptors. We found that SiH_3 (σ_R^+(P) = 0.49) is a stronger resonance acceptor than GeH_3 (σ_R^+(P) = 0.33). This indicates an increase in σ,n-conjugation and a decrease in d,n-conjugation on going from SiH_3 to GeH_3 (see also Ref. 24).

The $SnMe_3$ substituents in the $P^{\bullet+}(SnMe_3)_3$ radical cations were found to be resonance donors (σ_R^+(P) = −0.11), though weaker than in the $Me_3SnR_\pi^{\bullet+}$ systems (σ_R^+(B) = −0.21). This indicates that σ,n-conjugation dominates over d,n-conjugation and confirms that the resonance donor effect changes in the order Si < Ge < Sn while the resonance acceptor effect changes in the order Si > Ge > Sn.

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