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Binding Energy of Oxygen 1*s* Electrons. Substituent Effects of O-Centered Radical Cations and Related Electron-Deficient Systems

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Abstract—The binding energies of oxygen 1*s* electrons, measured by X-ray photoelectron spectroscopy and calculated by quantum-chemical methods were analyzed. The example of twelve series of oxygen-containing compounds was used to show for the first time that electron-deficient systems of three types (O-centered radical cations formed by release of an inner or a valent electron and H-complexes of the PhO–H···O type) have a common feature. In all the systems, the effect of substituents on the reaction centers combines of the inductive, resonance, and polarization effects.

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Spectroscopy and quantum chemistry are finding ever-widening application in research on electron-deficient systems $R_c^{\cdot+}BX$ and $R_c^{\delta+}BX$ (X is substituent and B is bridge) with a positively charged reaction center R_c. Correlation analysis of spectral parameters P and chemical properties shows that substituent effects in such systems radically differ from those in electroneutral systems R_cBX (see, for example, [1–5]). At the same time, the information on electron-deficient systems is fragmentary, and electronic interactions in them are scarcely explored.

The aim of the present work was compare substituent effects in *O*-centered radical cations formed by release of an inner or a valence electron, H-complexes of the PhO–H···O type, and neutral oxygen-containing molecules. To this end, we considered the binding energies E_b in the X-ray photoelectron (XPE) spectra and ionization potentials IP in the photo-electron (PE) spectra of molecules and the frequency shifts Δν in the *IR* spectra of H complexes of the PhO–H···O type, and also performed quantum-chemical calculations of resonance interactions in oxygen-containing molecules. Let us dwell briefly on the question what information of the effects of substituents X in the $R_c^{\cdot+}BX$ and $R_c^{\delta+}BX$ series can be gained from the properties *P* (E_b, *IP*, Δν). These series meet a rigid requirement: In XPE and PE spectral experiments, electron is always abstracted from the reaction center; H-complex formation, too, involves exclusively the reaction center R_c, rather than substituents X.

The XPE and PE methods are both underlain by gas-phase reaction (1).

$$R_cBX \xrightarrow{h\nu} R_c^{\cdot+}BX + \bar{e}. \quad (1)$$

The ionization energy *E* has Eq. (2).

$$E = E_{tot}(R_c^{\bullet+}BX) - E_{tot}(R_cBX). \quad (2)$$

Here $E_{tot}(R_c^{\cdot+}BX)$ and $E_{tot}(R_cBX)$ are the total energies of the radical cation and molecule, respectively.

In the XPE spectroscopy, the energy *E* is called the binding energy E_b, reaction (1) relates to an inner (core) electron (for example, oxygen 1*s* electron), and the quantum energy *hν* is several hundreds eV.

In the PE spectroscopy, the energy *E* is the ionization potential *IP*, reaction (1) relates to an outer (valent) electron, the quantum energy *hν* is no higher than several tens eV [6–8]. The Gibbs-Helmholtz equation for the standard free energy $\Delta_rG^0(T)$ of reaction (1) takes form (3).

$$\Delta_r G^0(T) = \Delta_r H^0(T) - T\Delta_r S^0(T). \quad (3)$$

Here $\Delta_r H^0(T)$ and $\Delta_r S^0(T)$ are the standard enthalpy and entropy of reaction (1). By definition [9], the ionization energy E is the standard enthalpy $\Delta_r H^0(T)$ of reaction (1). Furthermore, it was shown that the entropy contribution $T\Delta_r S^0(T)$ into $\Delta_r G^0(T)$ is no more than 5% [2]. Therefore, Eq. (3) can be written to a good approximation in form (4).

$$\Delta_r G^0(T) \approx E. \quad (4)$$

As follows from Eq. (4), the changes in the free energy $\Delta_r G^0(T)$ of reaction (1) under the action of substituents X is linearly related to changes in the ionization energy E (and, consequently, E_b and IP) under the action of X (the LFER principle). It is well known [2, 3, 5] that this principle is valid in the case of ionization potentials that obey Eq. (5).

$$\Delta_r G^0(T) \approx IP. \quad (5)$$

With E_b, the general equation (4) takes form (6).

$$\Delta_r G^0(T) \approx E_b. \quad (6)$$

To our knowledge, the LFER principle has never been applied to binding energies E_b. Let us briefly discuss this issue. The LFER principle is commonly applied as Hammett–Taft correlation equations. We previously showed [2–5], using the example of ionization potentials and H-complexes, that the form of these equations depends on the nature of bridge B in electron-deficient systems R_c^+BX and $R_c^{\delta+}BX$ [2–5]. In so-called classical systems, the bridge is the *para*-phenylene group. If there is no direct polar conjugation between X and R_c, then the effect of X on the property P ($\Delta\nu$, IP) of systems 1,4-$R_c^{\delta+}C_6H_4X$ and 1,4-$R_c^+C_6H_4X$ is described by an equation like (7).

$$P = a + b\sigma_I + c\sigma_R(\sigma_R^+). \quad (7)$$

Here σ_I is the inductive constant of X and the parameters σ_R and σ_R^+ measure the resonance effect of X at a small and a large positive positive charge on R_c.

In nonclassical systems, bridges B (such as –CH=CH–, –C≡C–, etc.) are either smaller than *para*-phenylene or lacking. The properties P ($\Delta\nu$, IP) of such systems are described [2–5] by a three-parameter equation (8).

$$P = a + b\sigma_I + c\sigma_R(\sigma_R^+) + d\sigma_\alpha. \quad (8)$$

Here σ_α is the polarization constants of X and the other denotations are the same as in Eq. (7).

It can be expected from Eqs. (6)–(8) that the effect of substituents X on the binding energies E_b of inner electrons should be described by the parameters σ_I, σ_R, and σ_R^+, which relate to the electronic effects of valent electrons. The latter statement is seemingly inconsistent with the fact that there is a weak overlap between the wave functions of inner electrons of R_c and valent electrons of X, and, consequently, inner electrons of X are scarcely involved in chemical bonding between R_c and X.

The concepts that explain the experimentally observed [6, 8, 10] dependence of E_b on X are based on the following reasoning [6–8, 11].

Let X_1–O–X_2 is the reaction series in which R_c is oxygen. Valent electrons of O create the electrostatic potential V_O (9).

$$V_O = q_O e^2/r_O. \quad (9)$$

Here q_O is the effective charge of O and r_O, mean distance between the nucleus of O and its valent electrons.

Electrons of substituents X create the electrostatic potential V_X (10).

$$V_X = q_X e^2/r_{OX}. \quad (10)$$

Here q_X are the effective charges on X and r_{OX}, mean distance between electrons of X and the O nucleus.

Internal (core) electrons of O are affected by the V_O and V_X potentials, and the binding energy E_b is described by Eq. (11).

$$E_b = q_O e^2/r_O + q_X e^2/r_{OX}. \quad (11)$$

It is well known [6, 7, 11] that experimental binding energies E_b values are linearly related calculated charges q. As an inner electron is abstracted from R_c [Eq. (1)], the effective charge q changes. This fact should be taken into account for correct q values.

As follows from the aforesaid, the binding energy E_b of inner electrons depends on the charge on the considered atom in R_c, and, consequently, on the electron density on R_c. In its turn, the electron density on R_c depends on the interaction of valence electrons of the reaction center and substituent X. Consequently, we can suggest that Eqs. (7) and (8) are valid for the binding energy, i.e. at $P = E_b$. Evidence for this suggestion was obtained by considering series **I–IX** (Tables 1–6) in which the reaction center is oxygen. It is seen from Tables 1–6 that the bonding energy E_b of

Table 1. Binding energies E_b (eV) for series **I–III**[a]

X	Series **I**, HOX, E_b (**I**)	Series **II**, CH_3OX, E_b (**II**)	Series **III**, HO(O)CX, E_b (**III**)[b]
H	539.90	539.13	540.60
Me	539.13	538.62	540.09
Et	538.82	–	540.04
i-Pr	538.51	538.09	–
t-Bu	538.39	–	–
Ph	539.23	538.70	539.79
CF_3	–	–	541.28
COH	540.65	539.88	–
$COCF_3$	541.28	540.48	–

[a]The E_b values are taken from [8]. [b] Binding energies E_b of the oxygen 1*s* electrons in the OH groups.

Table 2. Experimental E_b (eV) and calculated E_b^{calc} (eV) for molecules OX_2 (series **IV**)[a]

X_2	E_b (**IV**)	E_b^{calc} (**IV**)
H_2	539.90	540.01
HMe	539.11	539.14
HEt	538.82	538.87
H(COMe)	540.12	540.24
Me_2	538.74	538.70
Me(COMe)	539.46	539.58

[a] The E_b and E_b^{calc} (calculated by the DFT [ΔE_{KS}(PW86-PW91) + Crel/QZ4P]) values are taken from [12].

Table 3. Binding energies E_b (eV) for molecules H(O)CX (series **V**)

X	E_b (**V**) [13]
H	539.43
Me	538.40
$CH{=}CH_2$	538.03
Ph	537.52
NH_2	537.60
NMe_2	536.81

oxygen 1*s* electron depends on substituent X in all the series. To study the interaction between the reaction center and substituents, we applied correlation analysis. The correlation equations were calculated by standard programs Statgraphics 3.0. The least-squares treatment was performed at a 95% confidence level. The standard inductive, resonance, and polarization constants of substituents are listed in Table 7.

Comparison of the statistical parameters of the two- and three-parameter equation for E_b shows that in going from equations like (7) to equations like (8), the standard approximation error S_Y decreases and the correlation coefficient r increases (Table 8). This result provides evidence to show that, first, the parameters σ_I and σ_R (σ_R^+) are suitable for assessing the inductive and resonance effects of substituents X on E_b and, second, the E_b values in nonclassical series **I–IX** depend on the polarization effect of substituents.

In correlation analysis, the polarization effect is measured by substituent constants σ_α [1–5] and relates to the electrostatic interaction of the charge q_R on the electron-deficient center $R_c^{\cdot+}$ or $R_c^{\delta+}$ with a dipole which this charge induces on X. This interaction energy E_{es} is defined by Eq. (12).

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

Here α is the polarizability of X; ε, dielectric constant; r_q, and distance between q_R and induced dipole. the polarization effect is a characteristic feature of nonclassical charged systems which differ from classical by a small r_q value [1–5].

Using the equations in Table 8 we calculated the $Ind = b\Sigma\sigma_I$, resonance $Res = c\Sigma\sigma_R(\sigma_R^+)$, and polarization $Pol = d\Sigma\sigma_\alpha$ contributions in the total change of the binding energies E_b under the action of substituents X (Table 9). The series type and sample volume N (i.e. the nature and number of substituents in series **I, VI,** and **VII**) control the ratio of *Ind, Res*, and *Pol*.

Contemporary quantum-chemical methods provide quite accurate E_b^{calc} values [12]. Therefore, the *Ind, Res,* and *Pol* contributions calculated by the equations for the experimental E_b and calculated E_b^{calc} binding energies are equal to each other (Tables 8 and 9, series **IV** and **IX**).

We compared the effects of substituents on the binding energies E_b and other properties P (*IP* and $\Delta\nu$) for series **X** and **XI** ketones $O{=}CX_2$ (Tables 10 and 11). The ionization potentials *IP* (**X**) and *IP* (**XI**) corresponding to release of oxygen *n* electrons obey Eq. (8). As follows from Tables 8 and 9, conjugation only slightly affects *IP*, and at $N = 11$ in series X the *Res* contribution is completely lacking.

At the same time, polarization strongly affects *IP* and E_b (Table 9). At a constant sample volume (N = 11) the *Pol* contributions in the total changes of *IP* (**X**) and E_b (**X**) are 44 and 36%, respectively.

Table 4. Binding energies E_b (eV) for molecules $O{=}CX_2$ (series **VI** and **VII**)

X_2	Series **VI**, E_b (**VI**)[a]	Series **VII**, E_b (**VII**) [13]	X_2	Series **VI**, E_b (**VI**)[a]	Series **VII**, E_b (**VII**) [13]
H_2	539.44 [10]	539.43	EtPr	537.66	–
Me_2	538.05 [10]	537.91	EtPr-*i*	537.62	–
MeEt	537.85	–	EtBu	537.61	–
MePr	537.75	–	Pr_2	537.57	–
MePr-*i*	537.73	–	PrPr-*i*	537.59	–
MeBu	537.71	–	*i*-Pr_2	537.52	–
MeBu-*i*	537.71	–	$(CF_3)_2$	540.65 [10]	540.51
MeBu-*s*	537.66	–	$(NH_2)_2$	537.19 [10]	537.05
$Me(C_5H_{11})$	537.72	–	F_2	540.77 [10]	540.60
$Me(C_5H_{11}$-*i*)	537.64	–	Cl_2	539.72 [10]	539.55
$Me(CH_2t$-Bu)	537.67	–	Me(Ph)	–	537.16
$Me(C_6H_{13})$	537.72	–	Ph_2	–	536.80
Et_2	537.72	–	(*t*-Bu)Cl	–	538.65
			$(MeO)_2$	–	537.88

[a] The E_b values are taken from [14], unless otherwise specified.

Table 5. Binding energies E_b (eV) for molecules $O{=}CX_2$ (series **VIII**)[a]

X_2	E_b (**VIII**) [15]	X_2	E_b (**VIII**) [15]
H(OMe)	538.45	CF_3(OMe)	539.03
H(OEt)	538.26	CF_3(OEt)	538.83
H(OPr)	538.27	CH_2Cl(OEt)	538.10
Me(OMe)	537.92	CH_2Br(OEt)	538.01
Me(OEt)	537.78	$(MeO)_2$	538.06

[a] The E_b and E_b^{calc} (calculated by the DFT [ΔE_{KS}(PW86-PW91) + Crel/QZ4P]) values are taken from [12].

Table 6. Experimental E_b (eV) and calculated E_b^{calc} (eV) for molecules $O{=}CX_2$ (series **IX**)[a]

X_2	E_b (**IX**)	E_b^{calc}(**IX**)
H_2	539.48	539.47
$H(NH_2)$	537.74	537.71
$H(NMe_2)$	536.95	536.99
Me(OH)	538.33	538.19
Me(OMe)	537.92	537.81

[a] Binding energies E_b of the oxygen 1*s* electrons in the C=O groups.

Table 11 lists the Δν(OH) shifts in the IR spectra of unassiciated phenol, induced by the formation of the Ph–O–H···$O{=}CX_2$ H-complexes. The complex formation forms a partial charge δ+ on the ketone oxygen atom and thus gives rise to the polarization effect [3, 4]. The Δν values for various H complexes obey the LFER principle [3, 4]. Therefore, the property Δν (**XI**) at $N = 22$ obeys Eq. (8) whose coefficients are listed in Table 8, and the *Ind, Res*, and *Pol* contributions are listed in Table 9.

The Δν values for the IR spectra of the Ph–O–H···$O{=}CX_2$ complexes are contributed not only by the inductive, resonance, and polarization but also steric effects [3]. The latter effect can be characterized by the E'_s constants of substituents X [22, 23]. The E'_s constants are only known for a limited number of substituents. In this connection we could obtain a four-parameter corrlation $\Delta\nu = f(\sigma_I, \sigma_R, \Delta\nu, E'_s)$ for ten H complexes only ($N = 10$). The statistical parameters S_Y and r of this correlation (Table 8) are better than for a three-parameter correlation $\Delta\nu = f(\sigma_I, \sigma_R, \Delta\nu)$ for 22 H complexes ($N = 22$). It follows from Table 9 (series **XI**, $N = 10$) that the *Pol* contributions into the total changes of Δν (**XI**) and *IP* (**XI**) are 24 and 46%, respectively.

Thus, the polarization effect is a common characteristic feature of all the electron-deficient systems studied. At the same time, the strength of this effect in O-centered radical cations formed by release of an outer or an inner electron and in H complexes is different.

Table 7. Inductive Δν, resonance σ_R^0, σ_R, and σ_R^+, and polarization Δν parameters of substituents X for series **I–XII**[a]

X	σ_I	σ_R (σ_R^0)	σ_R^+	σ_α	X	σ_I	σ_R (σ_R^0)	σ_R^+	σ_α
H	0	0	0	0	COH	0.33	0.09	0.40	–0.46
Me	–0.05	–0.12 (–0.08)	–0.26	–0.35	COMe	0.33	0.17	~0.20	–0.55
Et	–0.05	–0.10	–0.25	–0.49	CN	0.51	0.5 (0.09)	0.15	–0.46
Pr	–0.05	–0.10	–0.25	–0.54	CF_3	0.38	0.16 (0.04)	0.23	–0.25
i-Pr	–0.03	–0.12	–0.25	–0.62	CCl_3	0.38	0.09	–0.16	–0.70
Bu	–0.05	–0.10	–0.25	–0.57	NH_2	0.08	–0.74 (–0.47)	–1.38	–0.16
i-Bu	–0.03	–0.10	–0.25	–0.61	NMe_2	0.15	–0.98	–1.85	–0.44
s-Bu	–0.03	–0.10	–0.25	–0.68	NEt_2	0.01	–0.73	–2.08	–0.56
t-Bu	–0.07	–0.13	–0.19	–0.75	OH	0.33	–0.70 (–0.41)	–1.25	–0.03
C_5H_{11}	–0.05	–0.10	–0.25	–0.58	OMe	0.29	–0.56	–1.07	–0.17
i-C_5H_{11}	–0.03	–0.10	–0.25	–0.61	OEt	0.26	–0.50	–1.07	–0.23
C_6H_{13}	–0.05	–0.10	–0.25	–0.59	OPr	0.26	–0.51	–1.09	–0.26
$CH{=}CH_2$	0.13	–0.17 (–0.05)	–0.29	–0.50	$COCF_3$	0.54	0.26	0.31	–0.51
C≡CH	0.22	0.01 (–0.01)	0.00	–0.60	SH	0.30	–0.15 (–0.25)	–0.33	–0.55
Ph	0.12	–0.13	–0.30	–0.81	SMe	0.23	–0.23	–0.83	–0.68
CH_2OMe	0.13	–0.12	–0.18	–0.42	SEt	0.26	–0.23	–0.83	–0.74
CH_2Cl	0.13	–0.01	–0.14	–0.54	F	0.45	–0.39 (–0.30)	–0.52	0.13
CH_2Br	0.14	0.00	–0.12	–0.61	Cl	0.42	–0.19 (–0.22)	–0.31	–0.43
$CHCl_2$	0.31	0.01	–0.15	–0.62	Br	0.45	–0.22	–0.30	–0.59

[a] The σ constants are taken from [1–5, 16].

Table 8. Coefficients and their standard deviations ($a\pm S_a$, $b\pm S_b$, $c\pm S_c$, $d\pm S_d$) in the equations $P = (a\pm S_a) + (b\pm S_b)\Sigma\sigma_I + (c\pm S_c)\Sigma\sigma_R(\sigma_R^+) + (d\pm S_d)\Sigma\sigma_\alpha$, standard approximation errors S_Y, correlation coefficients r, and sample volume N for series **I–XII**

Property P	$a\pm S_a$	$b\pm S_b$	$c\pm S_c$	σ	$d\pm S_d$	S_Y[c]	r[c]	N
E_b (**I**)	539.86±0.11	5.54±0.89	–2.04±1.45	σ_R	1.98±0.32	0.13 (0.37)	0.992 (0.934)	8
E_b (**I**)	539.89±0.02	7.87±0.33	–5.40±0.50	σ_R	2.87±0.12	0.03 (0.38)	0.999 (0.929)	6
E_b (**II**)	539.15±0.04	6.42±0.60	–4.08±0.91	σ_R	2.16±0.22	0.05 (0.29)	0.998 (0.944)	6
E_b (**III**)	540.65±0.06	–	4.32±0.35	σ_R	0.33±0.14	0.07 (0.09)	0.993 (0.989)	5
E_b (**IV**)	539.85±0.11	7.22±2.46	–4.94±2.91	σ_R	2.36±0.64	0.13 (0.29)	0.975 (0.861)	6
E_b^{calc} (**IV**)	539.94±0.11	7.01±2.42	–4.28±2.86	σ_R	2.34±0.63	0.12 (0.29)	0.980 (0.889)	6
E_b (**V**)	539.35±0.08	–	1.79±0.11	σ_R	1.98±0.15	0.10 (0.56)	0.994 (0.783)	6
E_b (**VI**)	539.39±0.04	2.06±0.04	0.77±0.02	σ_R^+	1.14±0.04	0.05 (0.34)	0.999 (0.940)	23
E_b (**VI**)[a]	539.42±0.08	2.02±0.10	0.78±0.04	σ_R^+	1.14±0.10	0.10 (0.62)	0.998 (0.900)	6
E_b (**VII**)	539.44±0.29	1.96±0.34	0.89±0.13	σ_R^+	1.39±0.22	0.36 (0.92)	0.967 (0.760)	10
E_b (**VII**)[a]	539.38±0.09	1.93±0.10	0.80±0.04	σ_R^+	1.20±0.11	0.10 (0.66)	0.997 (0.887)	6
E_b (**VIII**)	538.73±0.08	1.62±0.10	0.64±0.05	σ_R^+	0.70±0.08	0.05 (0.18)	0.992 (0.886)	10
E_b (IX)	539.46±0.06	6.20±0.57	1.30±0.08	σ_R^+	2.45±0.36	0.07 (0.31)	0.998 (0.941)	5
E_b^{calc} (IX)	539.44±0.11	5.14±0.99	1.25±0.13	σ_R^+	2.20±0.64	0.11 (0.29)	0.992 (0.948)	5
IP (**X**)	10.97±0.16	2.46±0.14	0.16±0.09	σ_R^+	1.37±0.13	0.21 (0.45)	0.983 (0.920)	35
IP (**X**)	10.87±0.09	2.58±0.09	–	–	1.37±0.10	0.09 (0.44)	0.998 (0.956)	11
E_b (**X**)	539.58±0.32	1.94±0.26	0.92±0.19	σ_R^+	1.35±0.28	0.24 (0.48)	0.982 (0.929)	11
Δν (**XI**)	100±23	–247±21	–204±15	σ_R	–32±22	21 (22)	0.961 (0.959)	22
Δν (**XI**)[b]	40±35	–259±19	–194±30	σ_R	–118±36	5 (9)	0.986 (0.954)	10
IP (**XI**)	10.89±0.15	2.19±0.25	0.16±0.13	σ_R^+	1.29±0.10	0.07 (0.34)	0.993 (0.828)	10
q_π (**XII**)	–0.485±0.002	–	0.291±0.09	σ_R^0	–	0.005	0.996	10
q_I (**XII**)	–1.110±0.008	0.045±0.022	0.234±0.020	σ_R^0	–	0.012	0.970	10

[a] X = H, Me, CF_3, NH_2, F, Cl. [b] Steric contribution $k\Sigma E_s' = (37\pm10)\Sigma E_s'$. [c] Values in parentheses are the S_Y and r values for the correlation equations $P = (a\pm S_a) + (b\pm S_b)\Sigma\sigma_I + (c\pm S_c)\Sigma\sigma_R(\sigma_R^+)$ (the polarization effect on P is not included).

Table 9. The *Ind, Res*, and *Pol* contributions (%) into the substituent-induced changes of the binding energies E_b, ionization potentials *IP*, and frequency shifts in H complexes Δν for series **I–XI**

Series no.	Property *P*	Sample volume *N*	*Ind*	*Res*	*Pol*
I	E_b (**I**)	8	58±9	14±10	28±4
	E_b (**I**)	6	51±2	23±2	26±1
II	E_b (**II**)	6	53±5	22±5	25±2
III	E_b (**III**)	5	–	82±7	18±8
IV	E_b (**IV**)	6	43±15	28±16	29±8
	E_b^{calc} (**IV**)	6	44±15	25±17	31±8
V	E_b (**V**)	6	–	52±3	48±4
VI	E_b (**VI**)	23	33±1	40±1	27±1
	E_b (**VI**)	6	35±2	43±2	22±2
VII	E_b (**VII**)	10	26±5	39±6	35±6
	E_b (**VII**)	6	33±2	44±2	23±2
VIII	E_b (**VIII**)	10	36±2	41±3	23±3
IX	E_b (**IX**)	5	32±3	44±3	24±4
	E_b^{calc} (**IX**)	5	30±6	47±5	23±7
X	*IP* (**X**)	35	47±3	8±5	45±4
	IP (**X**)	11	56±2	–	44±3
	E_b (**X**)	11	35±5	29±6	36±8
XI	Δν (**XI**)	22	46±4	47±3	7±5
	Δν (**XI**)[a]	10	32±2	21±3	24±7
	IP (XI)	10	48±5	6±5	46±4

[a] Steric contribution $k\Sigma E_s' = 23\pm6\%$.

Table 10. Ionization potentials *IP* (eV) and binding energies E_b (eV) for molecules $O{=}CX_2$ (series **X**)[a]

X_2	*IP* (**X**)[b]	E_b (**X**)[c]	X_2	*IP* (**X**)[b]
Me_2	9.71	538.05	$Me(CH_2OMe)$	9.66
MeEt	9.56	537.85	$Me(CH_2Cl)$	9.88
MePr	9.38	537.75	$Me(CH_2Br)$	9.73
MePr-*i*	9.29	537.73	$Me(CF_3)$	11.00
Et_2	9.30	537.72	$Me(NEt_2)$	9.20
i-Pr_2	8.95	537.52	Me(SEt)	9.65
Me(Ph)	9.57	537.16	(Me)F	11.80
$(CF_3)_2$	12.09	540.65	(Me)Cl	11.08
Me(OEt)	10.45	537.78	(Me)Br	10.68
F_2	13.60	540.77	$Ph(CH_2Cl)$	9.60
Cl_2	11.90	539.72	$Ph(CH_2Br)$	9.60
MeBu-*t*	9.11	–	$(CH{=}CH_2)F$	11.70
i-PrBu-*t*	8.79	–	(C≡CH)F	11.81
i-Bu_2	8.98	–	$(CH_2Cl)Cl$	10.30
t-Bu_2	8.67	–	$(CH{=}CH_2)Cl$	10.90
$Me(CH{=}CH_2)$	9.66	–	(C≡CH)Cl	11.25
$Et(CH{=}CH_2)$	9.50	–	$(CH{=}CH_2)Br$	10.51
Me(C≡CH)	10.18	–		

[a] The IP values relate to oxygen *n* electrons and E_b, to oxygen 1*s* electrons. [b] The *IP* values are taken from [8, 17–19]. [c] The E_b values are taken from Tables 4 and 5.

Table 11. Frequency shifts Δν (cm^{-1})[a] in the IR spectra and ionization potentials *IP* (eV) for molecules $O{=}CX_2$ and sums of the steric constants $\Sigma E_s'$ of substituents X (series **XI**)

X_2	Δν (**XI**)[b]	*IP* (XI)[c]	$\Sigma E_s'$[d]	X_2	Δν (**XI**)[b]
Me_2	193	9.71	0.00	$Me(NEt_2)$	338
MeEt	202	9.56	–0.08	$Et(NMe_2)$	325
MePr	210	9.38	–0.31	$Et(NEt_2)$	324
MePr-*i*	200	9.29	–0.48	Et(OMe)	176
MeBu-*t*	200	9.11	–1.43	Et(OEt)	174
t-Bu_2	195	8.67	–2.86	$(CH_2Cl)_2$	125
$Me(CH_2Cl)$	142	9.88	–0.18	$CH_2Cl(NMe_2)$	272
Me(OEt)	173	10.45	–0.07	$CH_2Cl(OEt)$	131
Me(SEt)	150	9.65	–0.96	$CHCl_2(NEt_2)$	227
$CH_2Cl(MeO)$	125	10.70	0.02	$CCl_3(NMe_2)$	171
$Me(NMe_2)$	340	–	–	SMe(Cl)	58

[a] The shifts of the stretching vibration frequency of phenolic OH, induced by Ph–OH···$O{=}CX_2$ H-complex formation. [b] The Δν values are taken from [20, 21]. [c] The *IP* values are taken from [8] and Table 10. [d] The E_s' values are taken from [22, 23].

Table 12. Total charges q_t (e) and their *p*-contributions q_π (e) on the oxygen atoms in molecules $CH_3(O)CX$ (series **XII**)[a]

X	q_t	q_π	X	q_t	q_π
Me	–1.140	–0.507	NH_2	–1.207	–0.624
$CH{=}CH_2$	–1.119	–0.495	OH	–1.206	–0.609
C≡CH	–1.093	–0.487	SH	–1.143	–0.551
CN	–1.070	–0.469	F	–1.170	–0.576
CF_3	–1.083	–0.472	Cl	–1.126	–0.543

[a] The q_t and q_π values calculated by the ab initio MP2/6-31G method are taken from [24].

In electroneutral systems, the polarization effect is absent by definition. Therefore, the oxygen qt charge in molecules $CH_3(O)CX$ of series **XII** (Table 12) depends exclusively on the inductive and resonance effects of substituents measured by their σ_I and σ_R^0 constants (Table 8). The resonance contribution q_π into this charge is determined by the σ_R^0 constants of substituents X (Table 8).

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