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Substituent effects on the second ionization energies of hydroxy- and methoxy benzenes

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In memory of Sharon G. Lias.

Abstract

The second ionization energies of phenol and the isomeric dihydroxybenzenes as well as their methyl ethers are determined by means of charge-stripping mass spectrometry. Compared to the parent molecule benzene, introduction of a hydroxy substituent lowers the second ionization energy by ca. 0.6 eV, whereas a methoxy substituent exerts a much more pronounced effect of about 1.6 eV. With regard to disubstitution, the effects behave almost completely additive for the *para*-derivatives, whereas the *ortho*-compounds are stabilized only about half that much by the second substituent, and for the *meta*-derivatives the influence of a second donor substituent is even smaller. The trends observed highlight the role of quinoid resonance structures for the stabilization of the dicationic compounds.

Keywords: Dication; Electron transfer; Ionization energy; Phenol; Quinone

1. Introduction

Hydroxybenzenes form an important class of redox-active molecules, and phenolates are often referred to as non-innocent ligands in coordination chemistry [1,2]. The origin of this particular behavior is that oxygen substituents can support various charge- as well as open-shell states via resonance with the benzene skeleton. The effects are particularly pronounced in the cases of *ortho*- and *para*-disubstitution which allow for quinoid structures, whereas two substituents in *meta*-arrangement cannot efficiently support mesomeric resonances [3]. One of the prerequisites for the understanding of role of these molecules as redox-active ligands in coordination complexes is, however, a basic knowledge of the associated thermodynamic properties of the free molecules, such as bond-dissociation energies, ionization energies, and electron affinities. In this respect, the NIST chemistry webbook [4,5] provides a rather rich and extremely useful source of knowledge about intrinsic thermochemical properties, which was much inspired by the contributions of Sharon G. Lias.

With regard to the gas-phase chemistry of mono- and disubstituted hydroxy- and methoxy benzenes, inspection of the ionization energies (IEs) listed in Table 1 reveals the following trends. Relative to benzene as the parent molecule, introduction of a hydroxy substituent lowers the IE of the arene by about 0.7 eV, which can be attributed to the electron-donation ability of this group. Consistent with this view, the methoxy substitution in anisole decreases the IE even somewhat further. Although not complete and in part also with considerable error margins, the data of the disubstituted compounds demonstrate that a second donor substituent further lowers the IEs, where the effect is most pronounced for the *para*-derivatives and weakest for *meta*-substitution. As a general rule, it appears that the IEs follow the order *para* < *ortho* < *meta*. In this contribution, the second ionization energies of these compounds are determined by means of energy-resolved charge-stripping measurements in order to probe to which extent substituent effects are operative in doubly ionized hydroxy- and methoxybenzenes.

2. Experimental

The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE confi-

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Table 1
Ionization energies (in eV) of benzene derivatives C_6H_4XY (X, Y = H, OH, OCH_3) taken from the NIST webbook [4]

X	Y	IE (eV)		
H	H	9.24378[a]		
OH	H	8.49 ± 0.02		
OCH_3	H	8.20 ± 0.05		
		ortho	*meta*	*para*
OH	OH	8.15[b]	8.2[a]	7.94[b]
OH	OCH_3	–[c]	–[c]	7.5[b]
OCH_3	OCH_3	7.8[b]	8.1 ± 0.1[b,d]	7.56 ± 0.11

[a] Highly accurate value evaluated from threshold photoelectron measurements.
[b] No error evaluation given in Ref. [4].
[c] No value given in Ref. [4].
[d] Error estimated from the two independent values given in Ref. [4].

guration (B stands for magnetic and E for electric sector), which has been described in detail previously [6]. The ions of interest were generated by electron ionization of the corresponding neutral precursor molecules and accelerated to a kinetic energy of 8 keV. The ionization energies of the corresponding monocations were determined by energy-resolved charge-stripping experiments [7–9]. By virtue of the superior energy resolution of E(1), these experiments were conducted with B(1)-only mass-selected ions. To this end, the mono- and dication signals were scanned at energy resolutions $E/\Delta E \geq 4000$, and the $Q_{\min}$ values were determined from the differences between the high-energy onsets of the mono- and the dication peaks using a multiplicative calibration scheme [8]. The kinetic energy scale was calibrated using charge stripping of the molecular ion of toluene, $C_7H_8{}^+$, with applying the recently revised value for the second ionization energy, that is: $Q_{\min}(C_7H_8{}^+) = 14.8 \pm 0.1$ eV [10]. Final data were derived from at least six independent measurements, and the experimental errors given below represent the standard deviation of the data.

3. Results and discussion

In two previous articles, we already addressed the fragmentation reactions of the metastable dications of the title compounds including extensive explorations of the associated potential-energy surfaces by means of density functional theory [11,12]. Here, we report a merely experimental study on the thermodynamics of these dications.

3.1. Energy-resolved charge stripping

For the determination of the second ionization energies of phenol, anisole, and their disubstituted analogs, we apply energy-resolved charge-stripping (CS) of mass-selected monocations [13,14]. At the outset, some introductory remarks about this method are indicated, because charge stripping is not used that often anymore [15], and moreover some recent results have led to a new view of the energetic values deduced from this kind of experiments [10]; for charge stripping of anions see ref. [16]. In CS, a beam of fast-moving monocations M^+ is generated in an ion source, mass-selected, and then submitted to a high-energy collision with a neutral target gas T, in which inter alia charge stripping according to Eq. (1) can occur; note that the observation of M^{2+} requires, of course, that the dication is sufficiently stable to reach the detector and thus must bear a lifetime in the range of several microseconds [17].

$$M^+ + T \rightarrow M^{2+} + T + e \tag{1}$$

In the CS process, the energy required for the ionization of M^+ to the dication M^{2+} is taken from the kinetic energy of the projectile monocation $T(M^+)$. Energy-resolved measurements of the peak profiles of M^+ and M^{2+} can be used to extract the this energetic quantity, the so-called $Q_{\min}$ values (Eq. (2)), which represent the lowest amount of energy required for the occurrence of the CS process [14,18].

$$Q_{\min}(M^+) = T(M^+) - T(M^{2+}) \tag{2}$$

Moreover, the experimental energy scale does not perfectly match the true physical values for various instrumental reasons. Usually, conversion to absolute values is achieved by means of a reference compound R^+ for which $IE(R^+)$ is known from independent measurements. The required calibration can be done using either a multiplicative or an additive scheme, of which the former is applied in this work, Eq. (3) [8,18].

$$Q_{\min}(M^+) = f \cdot [T(M^+) - T(M^{2+})] \quad \text{with :} \quad f = \frac{IE(R^+)}{T(R^+) - T(R^{2+})} \tag{3}$$

In organic ion chemistry, charge stripping of the molecular ion of toluene $C_7H_8{}^+$ has widely been used as a convenient reference within the last 30 years. Recently, however, a detailed analysis of the Franck-Condon envelopes in the photo-double ionization threshold of toluene led to the conclusion that the previously used reference value of $IE(C_7H_8{}^+) = 15.7$ eV [19] is by almost 1 eV too high, in that the correct value amounts to $IE(C_7H_8{}^+) = (14.8 \pm 0.1)$ eV [10]; note that the revised value has recently been confirmed in independent experiments [20]. Due to the use of toluene as a reference for the calibration of energy-resolved CS, many dication energetics determined in the last decades are therefore likely to be overestimated by about 1 eV, where the precise deviation also depends on the calibration scheme actually used [10]. Moreover, because not only the resulting Q_{min} values, but already the differences of T(M^+) and T(M^{2+}) somewhat depend upon focusing, a first principle adjustment of previous measurements to the new reference value for toluene would require a complete re-analysis of the original raw data. Nevertheless, one good news from the revision of the reference value for toluene is that the correction factors f are generally closer to unity than before, thus also rendering the debate between the correctness of multiplicative versus additive calibration schemes somewhat obsolete. In the experiments reported here, typical correction factors varied between $f = 1.02$ and 1.08 for CS of mass-selected $C_7H_8{}^+$.

The second important conclusion from the Franck-Condon analysis of dication formation is that due to the way Q_{min} values are determined, they are most likely to sample adiabatic ionization energies, even though CS in these high-energy collisions can certainly assumed to occur as a vertical process [10]. The origin of this seeming paradox lies in the method of data analysis. Thus, the kinetic energies T(M^+) and T(M^{2+}) mentioned above are not determined from the peak maxima (which are additionally shifted to lower kinetic energies due to collisional broadening), but rather from an extrapolation of the high-energy onsets of the mono- and dication peaks to the base line. Provided that the corresponding $0 \rightarrow 0$ transition has a finite efficiency, this extrapolation procedure thereby leads to the adiabatic ionization energy of the monocation $\mathrm{IE_a}(M^+)$, rather than the vertical value $\mathrm{IE_v}(M^+)$. In contrast, $Q_{\mathrm{min}} = \mathrm{IE_v}(M^+)$ was generally assumed before by reference to the vertical nature of the CS process [18]. Hence, in addition to the change in the reference value, further adjustment of some dication energetics derived from earlier CS measurements might be required.

Table 2
Second ionization energies (IE in eV) of C_6H_4XY compounds (X, Y = H, OH, OCH_3) determined by charge-stripping measurements of the corresponding mass-selected monocations

X	Y	$\mathrm{IE}(C_6H_4XY^+)$[a]	ΔIE[b]	$\mathrm{IE_{est}}(C_6H_4XY^+)$[c]
H	H	15.35 ± 0.10[d,e]		
OH	H	14.75 ± 0.30	−0.60	14.75
OCH_3	H	13.74 ± 0.20	−1.61	13.75
OH	*ortho*-OH	14.45 ± 0.25	−0.90	14.48
	meta-OH	14.65 ± 0.22	−0.70	14.63
	para-OH	14.24 ± 0.27	−1.11	14.21
OCH_3	*ortho*-OH	13.39 ± 0.22	−1.96	13.48
	meta-OH	13.77 ± 0.25	−1.58	13.63
	para-OH	12.97 ± 0.30	−2.38	13.21
OCH_3	*ortho*-OCH_3	13.07 ± 0.22	−2.28	13.03
	meta-OCH_3	13.32 ± 0.22	−2.03	13.43
	para-OCH_3	12.38 ± 0.27	−2.97	12.31

[a] It is assumed that the Q_{min} values coincide with the adiabatic ionization energies $\mathrm{IE_a}$, see text.

[b] Differences between the second ionization energies and that of benzene (X = Y = H) as the parent compound.

[c] Second ionization energies estimated via an additivity approach with the increments ΔIE = −0.6 and −1.6 eV for X = OH and X = OCH_3, respectively, and factors of $\phi_i = 0.45$, 0.2, and 0.9, respectively, for *ortho*-, *meta*-, and *para*-disubstitution; see text for further explanation.

[d] Reference value from threshold-photoelectron measurements taken from Ref. [21]; also see text.

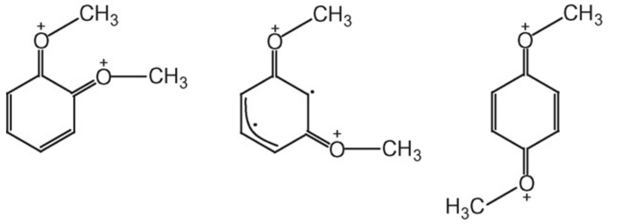
[e] After re-adjustment to the new reference value for toluene (see text), charge stripping yields $Q_{\mathrm{min}}(C_6H_6{}^+) = (15.3 \pm 0.2)$ eV, Ref. [22].

3.2. *Second ionization energies of hydroxy- and methoxybenzenes*

For the parent compound benzene, Hall et al. [21] have determined the double ionization energy of neutral molecule as ${}^2\mathrm{IE_a}(C_6H_6) = (24.6 \pm 0.1)$ eV by means of threshold-photoelectron measurements. Combined with the first ionization energy given as $\mathrm{IE_a}(C_6H_6) = (9.24378 \pm 0.00007)$ eV in the NIST database [4], a second ionization energy of $\mathrm{IE_a}(C_6H_6{}^+) = (15.35 \pm 0.1)$ eV can be derived. Note that this quantity agrees nicely with $Q_{\mathrm{min}}(C_6H_6{}^+) = (15.3 \pm 0.2)$ eV determined in energy-resolved charge-stripping measurements of Rabrenovic et al. when the original value of 16.2 eV [22] is corrected using the new reference value for CS of toluene (see above). Based on this excellent agreement, we therefore assume in the following that the measured Q_{min} values of the hydroxy- and methoxy-substituted benzenes correspond to the adiabatic IEs of the corresponding monocations.

Table 2 summarizes the Q_{min} data for the hydroxy- and methoxybenzenes examined in this work. Prior to a more detailed analysis, the general trends observed are considered. Introduction of one hydroxy group to benzene in the case of phenol (X = OH, Y = H) lowers the IE of the monocation by about ΔIE = −0.6 eV. Like for the first ionization energies (Table 1), this effect can be ascribed to the electron-donating character of the oxygen substituent. Interestingly, the effect is considerably more pronounced in the case of anisole (X = OCH_3, Y = H) with ΔIE = −1.6 eV. The fact that the difference between X = OH and OCH_3 is significantly larger in the second ionization energies than for the first IEs can be attributed to the larger amount of positive charge which can be accommodated by the methyl group and finds an experimental reflection in the unimolecular loss of a methyl cation from doubly ionized anisole [11]. Upon disubstitution, the second ionization energies are lowered further with a maximal difference of ΔIE = −3.0 eV in case of *para*-dimethoxybenzene. However, the influences of the second group are more moderate and very much depend on the position of second substituent relative to the first one. With regard to the substitution pattern, the second IEs behave as *para* < *ortho* < *meta*, as already found for the first IEs, but the differences are more pronounced in double ionization.

Additivity approaches are an often helpful concept in estimating the thermodynamics of organic compounds [23,24]. Accordingly, let us attempt to semi-quantitatively correlate the measured second IEs for the disubstituted compounds using the values of ΔIE found for phenol and anisole as reference points. In order to acknowledge for the effects of regiochemistry, coupling factors ϕ_i are introduced for substituents in *ortho*-, *meta*-, and *para*-positions, respectively, which indicate the amount to which the second substituents can further lower the ionization energy of the monocations. Accordingly, the estimated values $\mathrm{IE_{est}}(C_6H_4XY^+)$ can be derived. As an example, Eq. (4) shows



Scheme 1. Sketches of the Quinoid resonance structures for doubly ionized *ortho*-, *meta*-, and *para*-dimethoxybenzenes, when considering them as neutral $C_6H_4O_2$ entities interacting with two methyl cations via the oxygen atoms.

this approach for *ortho*-methoxy phenol; note that the methoxy substituent having the larger effect on ΔIE is introduced in the first term of the equation, while ΔIE of the second substituent is weighted with ϕ_i.

$$\begin{aligned}&\mathrm{IE_{est}}(o-\mathrm{C_6H_4(OCH_3)(OH)^+})\\&\quad=\mathrm{IE}(\mathrm{C_6H_6^+})+\Delta\mathrm{IE(OCH_3)}+\phi_{\mathrm{ortho}}\cdot\Delta\mathrm{IE(OH)}\\&\quad=15.35\,\mathrm{eV}-1.6\,\mathrm{eV}-0.45\cdot0.6\,\mathrm{eV}=13.48\,\mathrm{eV}\qquad(4)\end{aligned}$$

With respect to the uncertainty of the experimental values, a reasonably satisfying agreement with experiment is achieved for the parameters: $\Delta\mathrm{IE(OH)}=-0.6$ eV, $\Delta\mathrm{IE(OCH_3)}=-1.6$ eV, $\phi_{ortho}=0.45$, $\phi_{meta}=0.2$, and $\phi_{para}=0.9$; the largest deviation of 0.24 eV observed for *para*-methoxy phenol is covered well by the error margins of the experiments.

The major implication of these results is the importance of the role of quinoid resonance structures in the dications. The hydroquinone dication (X = Y = OH in *para*-arrangement), for example, bears a resonance structure in which it can be considered as a doubly protonated *para*-benzoquinone [12]. Hence, both oxygen-donor substituents can contribute to the stabilization of the dication and thereby lower the IE in comparison to the parent compound benzene. Much like for neutral quinones [3], the effect is much less pronounced for the *ortho*-compounds, and almost vanishes in the case of *meta*-disubstitution, for which the value of $\phi_{meta}=0.2$ may also well be accounted for by the mere polarization effect of the second substituent.

As an illustration, these quinoid resonances are sketched in Scheme 1 terms of the associated electronic structures of the corresponding doubly ionized dimethoxy derivatives. In the *para*-compound (right), both charge centers bear a large distance and the $C_6H_4O_2$ unit can adopt the favorable structure of *para*-benzoquinone. The situation is similar for the *ortho*-derivative (left), but the two positively charged methyl cations are in closer proximity, thereby disfavoring this mesomeric structure. In the case of the *meta*-compound (middle), a similar situation can only be realized for the triplet state of *meta*-quinone as the backbone, which energetically disfavors this particular resonance structure and consequently leads to a higher ionization energy.

4. Conclusions

Introduction of oxygen substituents significantly lowers the second ionization energy of benzene. For the set of substances investigated, the corresponding differences are $\Delta\mathrm{IE(OH)}=-0.6$ eV and $\Delta\mathrm{IE(OCH_3)}=-1.6$ eV, respectively. In the case of *para*-disubstitution, the ΔIE values behave almost additively ($\phi_{para}=0.9$), whereas the cooperative effects are much reduced in the *ortho*- ($\phi_{ortho}=0.45$) and *meta*-derivatives ($\phi_{meta}=0.2$). Despite the insight in the dication energetics achieved in this work, it is worth to point out that due to the particular importance of oxygen-substituted arenes as redox-active compounds, further investigations of the thermochemistry of the title compounds would be desirable, particularly with respect to the limited knowledge about the first ionization energies (Table 1).

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