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The estimation of electron affinities from *ab initio* 1*s* orbital energies

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Summary. It has been found that the electron affinities of alkoxy-radicals can be estimated using a correlation with the 1*s* orbital energy of the oxygen on the associated alkoxy-anion, $EA = -0.64503 * (1s \text{ orbital energy}) - 351.58$. The method assumes that the species of interest accepts the electron into an orbital which is localized on the oxygen.

Key words: Alkoxy – Electron affinity

Introduction

The accurate calculation of electron affinities has long been a problem of interest to computational chemists, due in part to their usefulness in the calculation of certain thermodynamic and electrochemical cycles (for example, in the calcualtion of gas-phase acidities [1]). The two most common methods for calculating electron affinities are the use of Koopmans' theorem [2] or the calculation of adiabatic electron affinities [3] (by taking the difference in energy between the neutral species and the resulting anion). One should note that, while Koopmans' theorem assumes that the electron affinity will be equal to the orbital energy of the LUMO (lowest unoccupied molecular orbital), for neutral radicals it is often assumed that the electron affinity of the neutral radical is equal to the ionization potential of the associated anion, which according to Koopmans' theorem is the energy of the HOMO (highest occupied molecular orbital) in the anion. This assumption obviates the need to do calculations on open-shell species.

In an earlier study [4], it was found that neither application of Koopmans' theorem nor the calculation of energy differences between the radical and the associated anion could be used to calculate the electron affinities of certain alkoxy-radicals to within the reported experimental error, utilizing the semi-empirical AM1 method [5] for the calculations. Novoa and Mota have done a study on calculating the *ab initio* adiabatic electron affinity of certain small molecules [6] using various basis sets and the MP2 [7] method for inclusion of electron correlation. Their results show that, even with basis sets as large as 6-31 + G*, the experimental electron affinity of methoxy-radical could not be reproduced to within 10 kcal/mol. The results also showed that very large basis sets (such as double zeta with polarization and diffuse functions) were required to obtain accurate electron affinities for the molecules that were studied.

Recently, it was found that a correlation exists between the electron affinities of oxy-radicals and the charge on the oxygen in the associated oxy-anions [4]. It was proposed that, for these systems, the electron which is accepted is placed in an orbital which is centered mainly on the oxygen. One would expect that, the easier it is for the charge which is accepted to be delocalized throughout the remainder of the molecule (through either induction or resonance), the more readily the charge would be accepted. Further, the charge on the oxygen should serve as an indirect measure of the amount of delocalization of the charge from the oxygen into the remainder of the molecule. Indeed, it was observed that molecules in which the charge on the oxygen in the oxy-anion was lower had a higher electron affinity for the associated oxy-radical. While this method could be used to obtain estimates of electron affinities for oxy-radicals, usually to within 2–3 kcal/mol of the experimental value, the method is not without disadvantages. The first is that the charges, and thus the correlations which were obtained, were highly dependent on the computational method chosen. One can see in Fig. 1 that the variation in charge from one computational technique to another is as much as two tenths of a charge unit for any given molecule. One must also note that the geometries used in the *ab initio* calculations in Fig. 1 were the AM1 geometries. If one tries to do the same correlation with geometries which are optimized using the basis sets for which the charges are derived, the correlation is not adequate if the basis set is small (e.g. 3-21 + G*, see Fig. 2). Thus, it was found that a method was needed which would both resolve the ambiguity caused by using charge in the correlation and that would work for the small basis set calculations.

It has been found that *ab initio* 1*s* orbital energies of the oxy-anions can be used, instead of charge, in the estimation of the electron affinities of the associated oxy-radicals. This method has two advantages over the previous method. The first is that 1*s* orbital energies are not an ambiguous quantity like partial charges on atoms and can be readily measured experimentally for comparison with the computed values. The second is that for small basis sets the correlation still holds, thus allowing one to do calculations on relatively large molecules.

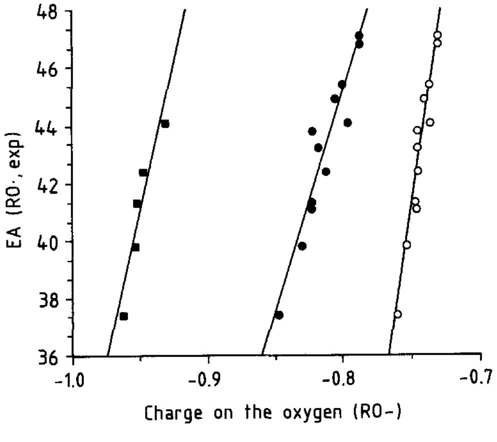

Fig. 1. Experimental electron affinities of selected oxy-radicals versus the charge on the oxygen in the associated oxy-anion for various computational techniques, ●, PM3 (EA = 164.66 + 149.69q; R^2 = 0.893); ○, AM1 (EA = 273.47 + 310.10q; R^2 = 0.932); ■, 6-31G (EA = 232.41 + 201.74q; R^2 = 0.888)

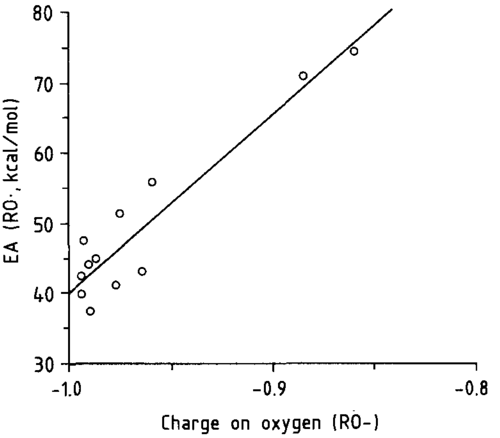

Fig. 2. Experimental electron affinities of selected oxy-radicals versus the charge on the oxygen in the associated oxy-anion. Charges are calculated using a 3-21 + G* basis set both for the geometry optimization and to determine the molecular properties ($EA = 293.93 + 254.07q$; $R^2 = 0.876$)

Theory

The core orbital energies are expected to be a direct measure of the charge distribution near an atom in a molecule. Correlations have previously been performed between 1*s* orbital energies and partial atomic charges [8]. To the first approximation the core orbitals are not very polarizable, so their energy can be adequately estimated by first order perturbation theory applied to the Fock operator. That is,

$$\varepsilon_A(1s) = \langle \phi_A(1s) | F | \phi_A(1s) \rangle, \qquad (1)$$

where $\phi_A(1s)$ is the free atom atomic 1*s* orbital. The Fock operator is given by

$$F = T + \sum_B \frac{-Z_B}{r_B} + J - K. \qquad (2)$$

For the change in orbital energy, $\Delta\varepsilon_A$, between two molecules the kinetic energy and attraction to nucleus A cancels and the exchange can be neglected. Hence,

$$\Delta\varepsilon_A = \langle \phi_A | \Delta \sum_{B \neq A} \frac{-Z_B}{r_B} + \Delta J | \phi_A \rangle. \qquad (3)$$

The difference in Coulomb potential, ΔJ, is just

$$\Delta J(1) = \int \frac{\Delta\varrho(2)\, d\tau_2}{r_{12}}, \qquad (4)$$

where $\Delta\varrho$ is the difference in charge density between the molecules.

In the CNDO (complete neglect of differential overlap) approximation, $\Delta\varrho$ would be partitioned into a sum of spherical atomic pieces,

$$\Delta\varrho = \sum \Delta\varrho_B, \qquad (5)$$

and the integral $\langle f_A | \Delta J_B | f_A \rangle$, would be approximated by $\gamma_{AB} \int \Delta\varrho_B \, d\tau$ where

$$\gamma_{AB} = \int f_B^2 r_A^{-1} \, d\tau = \int f_A(1)^2 f_B(2)^2 r_{12}^{-1} \, d\tau_1 \, d\tau_2 \qquad (6)$$

for any valence orbital. This can be assumed to also hold for the core orbital ϕ_A, for $A \neq B$. The one center Coulomb integral $\langle f_A | \Delta J_A | f_A \rangle$ would be $\gamma'_{AA} \int \Delta\varrho_A \, d\tau$

where

$$\gamma'_{AA} = \int \phi_A(1)^2 f_A(2)^2 r_{12}^{-1}\, d\tau_1\, d\tau_2, \tag{7}$$

which would be nearly the same as the nuclear attraction integral $\int f_A^2 r_A^{-1}\, d\tau$ and would differ from the CNDO γ_{AA} valence-valence interaction.

With these approximations, for a family of molecules in which the neighbors, B, to the atom A, differ only in charge and not in the value of γ_{AB},

$$\Delta\varepsilon_A = \gamma'_{AA}\, \Delta q_A + \sum_{B \neq A} \Delta q_B \gamma_{AB} \tag{8}$$

where Δq_x is the difference in net charge on atom x between two molecules. Because $\sum \Delta q_B = -\Delta q_A$, and $\gamma_{AA} \gg \gamma_{AB}$, this shift in ε_A is likely to be proportional to Δq_A. This expression is also the formula for the shift in the electrostatic potential at the nucleus.

The Koopmans' theorem ionization energy of the closed-shell anion (i.e. the electron affinity of the associated radical) is given by the orbital energy of the highest occupied molecular orbital. For the molecules considered here, this orbital is fairly localized on one oxygen. The shift in the orbital energy as the rest of the molecule is varied is given to the first order by

$$\Delta\varepsilon_{HOMO} = \langle \phi | F | \phi \rangle. \tag{9}$$

In the CNDO approximation, this reduces to

$$\Delta\varepsilon_{HOMO} = \gamma_{AA}\, \Delta q_A + \sum_{B \neq A} \Delta q_B \gamma_{AB} \tag{10}$$

if ϕ is localized on center A. Again, $\Delta q_A = -\sum \Delta q_B$, and $\gamma_{AA} \gg \gamma_{AB}$, so this should be linear in Δq_A. Also, if the γ_{AA} term dominates, one might expect that $\Delta\varepsilon_{HOMO} = (\gamma_{AA}/\gamma'_{AA})\, \Delta\varepsilon(1s)$.

Computational method

The *ab initio* calculations were performed using HONDO 7.0 [9] on an IBM 3090. A 3-21 + G* basis set was used for all calculations unless otherwise noted, and the geometries were optimized with the same basis set used to determine the 1*s* orbital energies. All calculations on the oxy-anions were done using the closed-shell RHF (restricted Hartree–Fock) method, and no perturbation (such as MP2) or CI (configuration interaction) methods were used. The basis sets used were those contained in the HONDO package supplemented with both diffuse and polarization functions from the literature [10] for all atomic species except hydrogen. For hydrogen, the standard basis set was used.

Results and discussion

The experimental electron affinities for various oxy-radicals, the *ab initio* 1*s* orbital energies for the associated oxy-anions, and estimated electron affinities based on the 1*s* orbital energies are shown in Table 1. As one can see from Fig. 3, the correlation between the calculated 1*s* orbital energies for the oxy-anions and the experimental electron affinities for the associated oxy-radicals is excellent, as opposed to the correlation of charge versus electron affinity for the same basis set.

Table 1. Experimental and calculated electron affinities

Species	EA(exp, eV)	1*s* orbital energy[a] (calculated, eV)	EA[b] (calculated, eV)	Absolute error	
				eV	kcal/mol
MeO$^{\bullet}$	1.62 ± 0.13[c]	−547.526	1.59	0.03	0.69
EtO$^{\bullet}$	1.73 ± 0.04[c]	−547.736	1.73	0.00	0.00
iPrO$^{\bullet}$	1.84 ± 0.03[c]	−547.943	1.86	0.02	0.46
nPrO$^{\bullet}$	1.79 ± 0.04[c]	−574.879	1.82	0.03	0.69
nBuO$^{\bullet}$	1.78 ± 0.15[c]	−547.879	1.82	0.04	0.92
sBuO$^{\bullet}$	1.95 ± 0.14[d]	−548.042	1.92	0.02	0.56
iBuO$^{\bullet}$	1.87 ± 0.16[c]	−548.013	1.90	0.03	0.69
tBuO$^{\bullet}$	1.91 ± 0.05[c]	−548.097	1.96	0.05	1.15
$FCH_2CH_2O^{\bullet}$	2.06 ± 0.21[e]	−548.217	2.04	0.02	0.46
$F_2CHCH_2O^{\bullet}$	2.23 ± 0.17[c]	−548.440	2.18	0.05	1.15
$F_3CCH_2O^{\bullet}$	2.42 ± 0.20[c]	−548.660	2.32	0.10	2.30
$HCOO^{\bullet}$	3.23 ± 0.19[f]	−549.962	3.16	0.07	1.61
$CH_3COO^{\bullet}$	3.07 ± 0.19[f]	−549.981	3.17	0.10	2.30
Average error				0.04	0.92

[a] 3-21 + G*//3-21 + G* *ab initio* calculation
[b] Calculated using EA = −0.64503 * (1*s* orbital energy) −351.58 (see Fig. 3)
[c] Bartmess JE, Scott JA, McIver RT (1979) J Am Chem Soc 101:6047
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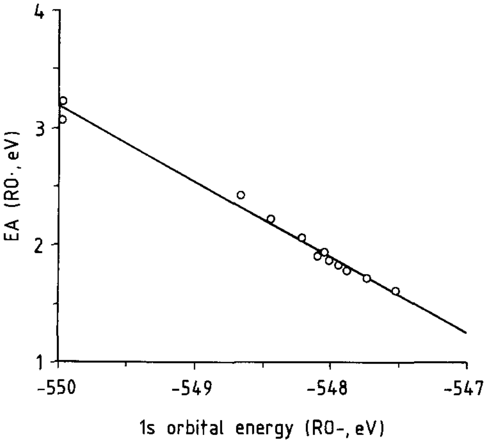

Fig. 3. Experimental electron affinities of selected oxy-radicals versus the 1*s* orbital energy of the oxygen in the associated oxy-anion. 1*s* orbital energies calculated using a 3-21 + G* basis set (EA = −351.58 − 0.64503ε; $R^2 = 0.989$)

One should note that methyl-enolate ($[CH_3COCH_2]^-$) does not fall on the same correlation curve as the alkoxides and carboxylates. This is the same phenomenon that was observed for enolates and phenolates in the charge versus electron affinity correlations. The following rational may be used to explain this phenomenon. AM1 molecular orbital calculations were used in the charge versus electron affinity study to show that the orbital which was accepting the electron in the alkoxy-radicals was centered on the oxygen (for the carboxylates, the orbital was concentrated between the two equivalent oxygens). For the case of the enolates and phenolates, the HOMO in the radical is not centered on the oxygen. Rather, AM1 and *ab initio* calculations of the molecular orbitals showed that the HOMO in the enolates and phenolates is an orbital which includes the oxygen and the carbon-carbon double bond, with most of the electron density in the area of the carbon-carbon double bond. Thus, the assumptions made in deriving (8) and (10) do not apply to these systems.

It has been suggested that using the experimental electron affinity of 1.572 eV for the methoxy-radical reported by Engleking, Ellison, and Lineberger [11], which was obtained using laser photodetachment electron spectroscopy, would give a more accurate correlation than using the value of 1.62 eV reported by Bartmess, Scott, and McIver [12], which was obtained indirectly using the ΔH_{acid} of methanol. We have found that using the experimental value reported by Engleking and coworkers does not significantly change the final correlation. In fact, the average change observed was less than 0.01 eV when using the value reported by Bartmess and coworkers. This suggests that the correlation is accurate to within the experimental error in the reported electron affinities.

Conclusion

It has been shown that electron affinities for alkoxy-radicals can be estimated by using the 1*s* orbital energies of the associated oxy-anions. The advantage of this method over the previously reported charge versus electron affinity method is that the method resolves some of the ambiguities present in the previous method (most notably the charge discrepancy seen between computational techniques). One can also see that relatively small basis sets can be utilized effectively using the 1*s* orbital energy method, enabling relatively large molecules to be able to be examined by this method.

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