

## An Empirical Method for the Evaluation of Electron Affinities

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An empirical correlation involving electron affinity ( $E_{ea}$ ), first ionization potential ( $E_i$ ) and the lowest singlet excited-state energy ( $\Delta E_{0-0}^1$ ) has been obtained through a multiple regression analysis performed on the literature data of model monocyclic substituted aromatic compounds. The  $E_{ea}$  of a series of aryl alkyl sulphides has been evaluated using this correlation. The resulting data are within the expected range, when compared with those of the model compounds.

Although several methods<sup>1-3</sup> for the measurement of the electron affinities ( $E_{ea}$ ) of organic compounds have been reported in recent years, these techniques are not yet widely available. However, since  $E_{ea}$  data now find applications in many areas of condensed-phase chemistry,<sup>4,5</sup> and the number of measured  $E_{ea}$  data on organic compounds is relatively small, the development of an empirical correlation leading to their evaluation should be welcome. This correlation should be expressed by a simple equation, using readily accessible input data and providing the  $E_{ea}$  for a wide variety of species. We selected the first ionization potential ( $E_i$ ) and the energy of the lowest singlet excited state ( $\Delta E_{0-0}^1$ ) to be the parameters of the equation. These parameters should correlate with  $E_{ea}$ , according to the perturbation theory,<sup>6</sup> provided that the electron-electron interaction terms ( $E_e$ ) remain constant ( $\Delta E_{0-0}^1 = E_i - E_{ea} + E_e$ ), as is assumed to happen within a series of related compounds.

In this paper, these ideas are applied to the evaluation of the  $E_{ea}$  of a series of aryl alkyl sulphides 1-10. With this goal, eqn. (1) was obtained through a multiple regression analysis,

$$E_{ea} = 0.71E_i - 2.70\Delta E_{0-0}^1 + 5.10 \quad (1)$$

performed on the literature data of eight (out of a possible eleven†) model monocyclic substituted aromatic compounds (Table 1). The standard error of the multiple estimate ( $s$ ) and the multiple correlation coefficient ( $r$ ) for eqn. (1) are 3.5 and 97.7%, respectively, while the standard errors associated with the equation's coefficients do not exceed 10%. The accuracy of this empirical correlation [eqn. (1)] was tested by comparison of calculated and measured  $E_{ea}$  values of ten compounds (Table 2). Two of the compounds in Table 2 were intentionally not used to build the correlation, as we intended to use them to validate further the accuracy test. An analysis of the relative deviations presented in Table 2 suggests that eqn. (1) permits a fair enough evaluation of  $E_{ea}$ , even in the worst case (phenol†).

In the case of those compounds for which the values of  $E_i$  are known, the evaluation of  $E_{ea}$  was straightforward [eqn. (1)]. For compounds of unknown  $E_i$  values 3-6 (Table 3), this quantity was calculated from the measured  $E_{ox}^\ddagger$  values (Table 3), through the empirical correlation proposed by Latypova *et al.*,<sup>9</sup> the  $E_{ea}$  values were obtained from eqn. (1), as in the former case.

To summarize our results, we list the measured  $\Delta E_{0-0}^1$  and  $E_{ox}^\ddagger$  values, together with the calculated and the available literature  $E_i$  values, as well as the  $E_{ea}$  values obtained from eqn. (1) (Table 3).

The  $E_{ea}$  values obtained for the sulphides 1-10 are within the expected range, when compared with those of the model compounds. Taking benzene as a reference ( $E_{ea} = -1.15$  eV), the sulphur-containing substituent stabilizes the radical anion

Table 1 Values of the  $E_i$ ,  $E_{ea}$  and  $\Delta E_{0-0}^1$  of the model compounds

Compound	$E_i$ /eV <sup>a</sup>	$E_{ea}$ /eV <sup>b</sup>	$\Delta E_{0-0}^1$ /eV <sup>c</sup>
Benzene	9.25	-1.15	4.75
Toluene	8.81	-1.11	4.61
Anisole	8.22	-1.09	4.46
Chlorobenzene	9.07	-0.75	4.56
Fluorobenzene	9.20	-0.89	4.66
<i>o</i> -Xylene	8.56	-1.12	4.58
<i>m</i> -Xylene	8.59	-1.06	4.54
<i>p</i> -Xylene	8.44	-1.07	4.53

<sup>a</sup> Photoionization or spectroscopic values for the first ionization potentials, taken from ref. 7. <sup>b</sup> First vertical electron affinities, determined by electron transmission spectroscopy (ETS), compiled by Jordan and Burrow.<sup>1</sup> <sup>c</sup> Lowest excited singlet energy values, as compiled in ref. 8.

Table 2 Literature and calculated  $E_{ea}$  values of the test compounds

Compound	$E_{ea}$ /eV <sup>a</sup> (lit.)	$E_{ea}$ /eV <sup>b</sup> (Calc.)	Rel. Dev. (%)
Benzene	-1.15	-1.16	0.87
Toluene	-1.11	-1.09	1.80
Anisole	-1.09	-1.11	1.83
Chlorobenzene	-0.75	-0.77	2.67
Fluorobenzene	-0.89	-0.95	6.74
<i>o</i> -Xylene	-1.12	-1.18	5.36
<i>m</i> -Xylene	-1.06	-1.06	0.00
<i>p</i> -Xylene	-1.07	-1.13	5.61
Phenol <sup>c</sup>	-1.01	-0.91	9.90
Ethylbenzene <sup>d</sup>	-1.17	-1.17	0.00

<sup>a</sup> From ref. 1. <sup>b</sup> Calculated from eqn. (1). <sup>c</sup>  $E_i = 8.50$  (ref. 7).  $\Delta E_{0-0}^1 = 4.46$  eV (ref. 8). <sup>d</sup>  $E_i = 8.76$  eV (ref. 7).  $\Delta E_{0-0}^1 = 4.63$  eV (ref. 8).

in methylthiobenzene 1 and ethylthiobenzene 2 ( $E_{ea} = -0.89$  and  $-0.87$  eV, respectively) more than does oxygen in anisole ( $E_{ea} = -1.09$  eV †), an effect similar to that observed by Jordan *et al.*<sup>13</sup> in the case of halobenzenes: both chloro- and bromobenzene exhibit this stabilization, when compared with fluorobenzene. However, this stabilization diminishes on changing either the alkyl chain from methyl to propyl, or the aryl group from phenyl to tolyl. In the case of the *o*-tolyl sulphides, this fact may be due to the steric effect of the methyl ring substituent over

† The eleven compounds, for which all necessary data are available in the literature, are those ten listed in Table 2, plus aniline. However, aniline deviates very strongly from the correlation expressed by eqn. (1), a phenomenon akin to that reported by Latypova *et al.*,<sup>9</sup> in the case of a correlation between  $E_i$  and  $E_{ox}^\ddagger$ . Perhaps the 10% deviation exhibited by phenol has the same origin.

‡ 1 eV = ca.  $1.602 \times 10^{-19}$  J.

**Table 3** Experimental and calculated data for aryl alkyl sulphides

Compound <sup>a</sup>	$\Delta E_{0-0}^1$ / eV <sup>b</sup>	$E_{ox}^\ddagger$ / V <sup>c</sup>	$E_i$ /eV <sup>d</sup>	$E_{ca}$ /eV <sup>e</sup>
1 C <sub>6</sub> H <sub>5</sub> SMe	4.32	1.06	7.99 (8.07)	-0.83
2 C <sub>6</sub> H <sub>5</sub> SEt	4.32	1.10	8.03 (8.00)	-0.88
3 C <sub>6</sub> H <sub>5</sub> SPr <sup>n</sup>	4.40	1.11	8.03 (—)	-1.08
4 <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> SMe	4.34	0.98	7.92 (—)	-1.00
5 <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> SEt	4.38	0.92	7.86 (—)	-1.15
6 <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> SPr <sup>n</sup>	4.38	0.98	7.92 (—)	-1.10
7 <i>m</i> -MeC <sub>6</sub> H <sub>4</sub> SMe	4.42	0.96	7.90 (8.00)	-1.15
8 <i>m</i> -MeC <sub>6</sub> H <sub>4</sub> SEt	4.44	0.96	7.90 (7.92)	-1.27
9 <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SMe	4.33	0.94	7.88 (7.87)	-1.00
10 <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SEt	4.33	0.92	7.86 (7.85)	-1.02

<sup>a</sup> All compounds were prepared according to literature<sup>10</sup> procedures.

<sup>b</sup> The singlet state energies were calculated<sup>11</sup> from the crossing points of the normalized room-temperature absorption and emission spectra of the sulphide 1–10 in benzene solution. <sup>c</sup> The voltametric half-wave oxidation potentials were measured in acetonitrile (0.1 mol dm<sup>-3</sup> in NaClO<sub>4</sub>), at a platinum anode; the reference electrode was Ag/Ag<sup>+</sup>.

<sup>d</sup> Values calculated from the equation:<sup>9</sup>  $E_i = 0.914E_{ox}^\ddagger + 7.02$ ; lit.<sup>12</sup> values in parentheses. <sup>e</sup> Calculated from eqn. (1).

the alkylthio-chain rotameric equilibrium, which should make the sulphur/ring orbital interactions less effective. This model can also explain the observed value for compound 3, assuming the existence of steric hindrance to rotation caused by the *ortho* ring-protons over the propylthio group. On the other hand, the  $E_{ca}$  values obtained for the *m*-tolyl sulphides are a rather surprising feature.

Finally, we would like this paper to be regarded as an example of the utility of correlations involving  $\Delta E_{0-0}^1$ , which provide a versatile way of obtaining  $E_{ca}$  from  $E_i$  (as well as  $E_{red}^\ddagger$

from  $E_{ox}^\ddagger$ ) and *vice-versa*. This approach can be a shortcut to assessing data that otherwise is difficult to obtain.

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