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Note

Prediction of responses of aromatic hydrocarbons in an electron-capture detector

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In a recent paper[1] we showed that many aromatic hydrocarbons can sensitively be analysed with an electron-capture detector (ECD) and, at the same time, this method can be used for the determination of some physico-chemical parameters of electron + aromatic hydrocarbon reactions[1–4].

The capture coefficients, K, of aromatic hydrocarbons, which determine the molar responses in the ECD, are usually interpreted in terms of electron affinities, EA, on the basis of the equation derived by Wentworth *et al.*[2]

$$K = (k_L/k_D)\, AT^{-3/2} \cdot \exp\,(\mathrm{EA}/kT) \tag{1}$$

where T is the detector cell temperature, A is a fundamental constant, k is Boltzmann's constant and k_L/k_D is a constant characteristic of the detector. With this relation it is also possible to predict the detectabilities of aromatics. However, accurate EA values are known only for a rather limited number of compounds, partly because the methods commonly utilized for EA measurements are complicated and tedious, and the results are often erroneous as indicated by the large scatter of values obtained by different methods, especially with low or negative EA. It is worth noting that one of the best methods for measuring the absolute, adiabatic EA value of aromatic hydrocarbons (between EA = 0.1 and 0.9 eV) is supplied by the detector itself, utilizing the temperature dependence of the electron equilibrium[2–4]:

$$\mathrm{AB} + e^- \rightleftharpoons \mathrm{AB}^-$$

Based on theoretical and experimental investigations[3,5–7], it was found that the EA is closely correlated, among other molecular parameters, with the ionization potential, IP: this relationship can be used to predict EAs because IP values determined by different techniques for a large number (more than 100) of aromatics are available (see, *e.g.*, refs. 6, 8–12). There is, however, a problem that some of the methods (*e.g.*, electron impact, photoelectron spectroscopy) provide principally "vertical" IPs where during the ionization the nuclear coordinates do not change; in contrast, other methods (*e.g.*, photoionization) give an "adiabatic" value, *i.e.*, the energy difference between the equilibrated ground and ionized states.

In Fig. 1 the IPs were selected from the literature as "adiabatic" or "near

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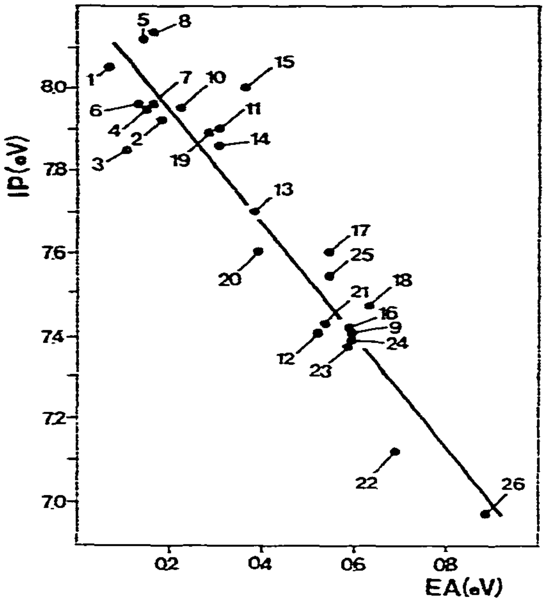

Fig. 1. IP *vs.* EA plot for aromatic hydrocarbons. The ionization potential was taken from the literature cited. Hydrocarbons: 1 = durene (1,2,4,5-tetramethylbenzene)[8]; 2 = pentamethylbenzene[8]; 3 = hexamethylbenzene[8]; 4 = biphenyl[9]; 5 = naphthalene[6]; 6 = 1-methylnaphthalene[6]; 7 = 2-methylnaphthalene[6]; 8 = indene[10]; 9 = azulene[6]; 10 = fluorene[9]; 11 = phenanthrene[11]; 12 = anthracene[12]; 13 = *trans*-stilbene[9]; 14 = diphenylacetylene[8]; 15 = 1,1-diphenylethylene[9]; 16 = pyrene[11]; 17 = benzo[*c*]phenanthrene[12]; 18 = benz[*a*]anthracene[11]; 19 = triphenylene[12]; 20 = chrysene[11]; 21 = benzo[*c*]pyrene[11]; 22 = benzo[*a*]pyrene[11]; 23 = dibenz[*a,h*]anthracene[11]; 24 = dibenz[*a,j*]anthracene[11]; 25 = picene[11]; 26 = naphthacene[12].

adiabatic" values, whereas all EAs were determined by the ECD method. The values for hydrocarbons 1–15 are from our work[1], 16–25 are from Becker and Chen[3] and 26 is from Lyons *et al.*[4].

In the case of highly conjugated polycondensed aromatics possessing large EA values, since the equilibrium internuclear positions in the ground state of the neutral molecule and the positive ion are approximately the same, the difference between the IP values determined by different techniques is not large: "vertical" IP values practically agree with the "adiabatic" values[6,11]. On the other hand, for less conjugated molecules (lower EA values), where large nuclear distance distortions may occur during ionization, the IPs determined by "vertical" and "adiabatic" techniques are considerably different[6]. From the literature [3,6] and also from our studies, it appears that EAs determined by the ECD method give a better correlation with the "adiabatic" IPs than with the "vertical" ones.

The relationship between IP and EA values (in eV) in Fig. 1 is described by:

$$\mathrm{IP} = (8.22 \pm 0.18) - (1.36 \pm 0.09)\,\mathrm{EA} \qquad (2)$$

By combining eqns. 1 and 2, the relation

$$K = (k_U/k_D)AT^{-3/2}\cdot\exp\,[1000(70.17 - 8.539\,\mathrm{IP})/T] \qquad (3)$$

allows the estimation of the approximate order of magnitude of K on the basis of known ionization potentials.

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REFERENCES

1 L. Wojnárovits and G. Földiák, *J. Chromatogr.*, 206 (1981) 511.
2 W. E. Wentworth, E. Chen and J. E. Lovelock, *J. Phys. Chem.*, 70 (1966) 455.
3 R. S. Becker and E. Chen, *J. Chem. Phys.*, 45 (1966) 2403.
4 L. E. Lyons, G. S. Morris and L. J. Warren, *J. Phys. Chem.*, 72 (1968) 3677.
5 N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, 51 (1955) 600.
6 R. P. Blaunstein and L. G. Christophorou, *Radiat. Res. Rev.*, 3 (1971) 69.
7 J. M. Younkin, L. J. Smith and R. N. Compton, *Theoret. Chim. Acta*, 41 (1976) 157.
8 V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medredev and Ye. L. Frankevich, *Bond Energies, Ionization Potentials and Electron Affinities*, St. Martin's Press, New York, 1966.
9 J. P. Maier and D. W. Turner, *J. Chem. Soc., Farad. Trans. II*, 69 (1973) 196.
10 J. H. D. Eland and C. J. Danby, *Z. Naturforsch. A*, 23 (1968) 355.
11 R. Boschi, E. Clar and W. Schmidt, *J. Chem. Phys.*, 60 (1974) 4406.
12 W. Schmidt, *J. Chem. Phys.*, 66 (1977) 828.