JOURNAL OF MASS SPECTROMETRY, VOL. 31, 333–335 (1997)

JMS Letters

Dear Sir,

Estimation of Ionization Energies of Polycyclic Aromatic Hydrocarbons Using the Kinetic Method

We report the application of the kinetic method[1,2] to the estimation of ionization energies (IE) of polycyclic aromatic hydrocarbons (PAHs). PAHs are an important class of compounds in the environment, many having been shown to be potent carcinogens and/or mutagens.[3] The determination of their fundamental properties is therefore important. Although ionization energies of PAHs can be obtained by photoelectron spectroscopy[4] and electron-transfer equilibria,[5] such methods are often limited in scope and are difficult to apply to higher PAHs or to samples which contain impurities. This study was intended to test the applicability of the kinetic method in this measurement.

The kinetic method is an approximate method for thermochemical determinations, based on the rates of competitive dissociations of mass-selected cluster ions.[1,2] It has been used to determine proton affinities as well as affinities towards various other ions.[2] The method is sensitive to small thermochemical differences [often below 1 kcal mol^{-1} (1 kcal = 4.184 kJ)] and is applicable to polar and non-volatile compounds, even when they are not available in pure form.[2] In work closely related to this, it has been used to estimate electron affinities[6–8] by examining the dissociation of anion radical cluster ions, $[M_1M_2]^{-\cdot}$ [Eqn (1)]. When determination of ionization energies is of interest, one examines the fragmentation of the mass-selected dimeric radical cations to give the individual radical cations shown as Eqn (2).

$$M_1^{-\cdot}\cdot M_2 \rightleftharpoons M_1 M_2^{-\cdot} \rightarrow M_1 \text{---} e^- \text{---} M_2 \begin{cases} \xrightarrow{k_1} M_1^{-\cdot} + M_2 \\ \xrightarrow{k_2} M_1 + M_2^{-\cdot} \end{cases} \quad (1)$$

$$M_1^{+\cdot}\cdot M_2 \rightleftharpoons M_1 M_2^{+\cdot} \rightarrow [M_1M_2]^{+\cdot} \begin{cases} \xrightarrow{k_1} M_1^{+\cdot} + M_2 \\ \xrightarrow{k_2} M_1 + M_2^{+\cdot} \end{cases} \quad (2)$$

The weakly bound cluster ion which is the fragmenting species is formally a solvated radical cation ($M_1^{+\cdot}.M_2$ or $M_2^{+\cdot}.M_1$). However, if the difference in ionization energies of M_1 and M_2 is small, the charge can be transferred between M_1 and M_2, probably via the equilibrium shown in Eqn (2);[9] this suggests that ionization energy determinations can be made using competitive dissociations. The entropic effects associated with such competitive dissociations need not be considered since fragmentation simply involves competition for the charge.[10,11] Stevenson's rule, well known in mass spectrometry, qualitatively expresses the principle of kinetic control of fragment ion abundance in such a circumstance.[12,13] This rule states that for a simple bond cleavage in a radical cation, the fragment with the lower ionization energy will preferentially take the charge. A quantitative expression, later given by Audier,[14] further states that the difference in the activation energies for the two competitive dissociation of $[M_1M_2]^{+\cdot}$ is equal to the difference in the ionization energies of M_1 and M_2. Note that Stevenson's rule refers to strong bonds within a single molecule.

Theoretical treatments of the kinetic method, given elsewhere, lead to an approximate expression of the form[2]

$$\ln([\text{fragment}_1^{+\cdot}][\text{fragment}_2^{+\cdot}]) \approx [\Delta(\Delta E)]/(RT_{eff}) \quad (3)$$

where $[\text{fragment}_1^{+\cdot}]$ and $[\text{fragment}_2^{+\cdot}]$ are the abundances of the two monomeric fragments, $\Delta(\Delta E)$ is the difference in critical energies of the two competing reactions and T_{eff} is the effective temperature of the parent dimeric ion. In this study, the rates of competitive dissociation of heterodimeric cluster cations to form the individual radical cations can be expressed in the following analogous equation in terms of the ionization energy difference (ΔIE) between the two compounds:

$$\ln([M_1^{+\cdot}][M_2^{+\cdot}]) \approx [\Delta IE]/(RT_{eff}) \quad (4)$$

Previous studies on atomic cluster ions,[15,16] such as aluminum cluster ions, have suggested correlations between the difference in ionization energies of complementary fragment ions and their measured abundance ratios. A recent study on dimeric cluster ions established that molecular ionization energies can be measured by the kinetic method and demonstrated that the natural logarithm of the fragment ion abundance ratio correlates well with the difference in ionization energies of substituted benzenes.[11] The approach used in the present study is to generate the heterodimeric radical cations of PAHs (viz. the solvated radical cations) in the ion source by desorption chemical ionization (DCI). A reagent gas of low ionization energy (carbon disulfide, IE = 10.0685 ± 0.0020 eV[4]) was chosen in order to minimize the internal energy deposited upon charge exchange and so to maximize the possibility of generating the weakly bound cluster ions. The resulting dimeric radical cations are mass selected and fragment competitively upon collisional activation under mild conditions to yield the intact monomeric molecular radical cations as the only products. The ratio of the abundances of these two ions is examined for a correlation with the difference in ionization energies of the PAHs expressed in Eqn (4).

All experiments were performed using a Finnigan TSQ-700 triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA, USA). In pairwise fashion, PAHs (Aldrich Chemical, Milwaukee, WI, USA) were dissolved in carbon disulfide solvent to give solutions of ~1 M. A 1 μl aliquot of each solution was placed on the rhenium wire filament of a direct evaporation probe and allowed to dry. The probe was then introduced into the ion source of the instrument under carbon disulfide chemical ionization (CI) conditions and the direct evaporation filament was resistively heated from ambient to 800 °C at 500 °C min^{-1}. The desorbed PAHs were ionized in the carbon disulfide chemical ionization plasma at an estimated pressure of 0.5 Torr (1 Torr = 133.3 Pa).

The heterodimeric radical cations, $[M_1.M_2]^{+\cdot}$, generated in the ion source in relatively low abundances, were mass selected using the first quadrupole mass analyzer. Collisional activation of the dimer was achieved in the second quadrupole under very mild conditions, viz. a nominal 2 eV collision energy and an argon target gas at a nominal pressure of 0.05 mTorr. Typical main beam attenuations were ~10%, well within the single collision limit. The abundances of the fragment ions were then measured from the product ion mass spectrum generated by scanning the third quadrupole. All peak ratio measurements were recorded in triplicate and displayed relative standard deviations of <15%. Each set of

CCC 1076–5174/97/030333–03 $17.50

Received 4 November 1996
Accepted 25 November 1996

peak ratios was measured from an average of 15 or more scans.

Mass selection and collision-induced dissociation of the heterodimer, under very mild activation conditions, produced just two fragment ions, those due to the competing dissociation reactions shown in Eqn (2). Figure 1 shows a typical product ion mass spectrum, that of the heterodimeric radical cation composed of anthracene and pyrene. The fragments at 178 and 202 Thomson correspond to the anthracene and pyrene radical cations, respectively (Thomson = dalton/unit charge[17]).The ratio of the ion abundances indicates that pyrene has a slightly greater ionization energy than anthracene. This observation is consistent with the literature values, 7.50 ± 0.04 eV (pyrene) and 7.45 ± 0.04 eV (anthracene), although the difference of just 0.05 eV is close to the uncertainty of the literature determinations.[5] The ready fragmentation strongly suggests a weakly bound structure for the dimeric radical cation. Different amounts of sample and different source conditions in the same experiments led to the same results, including identical product ion abundance ratios. This implies that the composition and fragmentation of the dimeric radical cation is independent of the order in which the constituent molecules are assembled, justifying the equilibrium description in Eqn (2).

Figure 2 summarizes the results of nine measurements of $\ln(k_1/k_2)$ values made for a group of PAHs. The stair-step method was used to cross-check the results by examining different pairs of PAHs. It can be seen that the set of data is internally consistent. These results demonstrate the reliability of the kinetic method for determining the relative ordering of ionization energies for these PAHs. The order of relative ionization energies is 1,2-benzanthracene < azulene < anthracene < pyrene < biphenylene < acenaphthene, although the differences in IE and experimental uncertainties in some cases are small enough to change the order. In an attempt to obtain numerical values for the ionization energy of the PAHs, we utilized Eqn (4) to derive the effective temperature for the heterodimeric radical cation composed of the reference compounds acenaphthene (IE = 7.74 ± 0.04 eV)[5], biphenylene (IE = 7.55 ± 0.04 eV)[5], pyrene (IE = 7.50 ± 0.04 eV)[5], anthracene (IE = 7.45 ± 0.04 eV)[5] and azulene (IE = 7.42 ± 0.04 eV)[5]. Note that all the IE values for the reference compounds were obtained from the same electron-transfer equilibrium measurements in order to maintain the internal consistency of the literature IE values used. A plot of ln(abundance ratio) vs IE has a correlation coefficient of 0.940 and yields an average

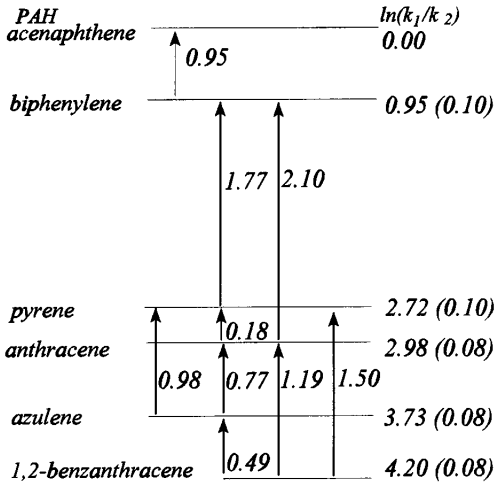

Figure 2. Measured $\ln(k_1/k_2)$ ratios and derived ΔIE values from dissociations of heterodimeric radical cations of a series of PAHs. The $\ln(k_1/k_2)$ data are the average cumulative values expressed relative to biphenylene. Data in parentheses are the estimated errors in the abundance ratio.

effective temperature of 1000 K with an estimated uncertainty (which arises mainly from uncertainties in the literature values) of ±200 K (Fig. 3). If one assumes that the effective temperatures of all the activated dimers are the same under the same ionization conditions (an assumption made in numerous applications of the kinetic method where similar compounds are being compared[1,2,6,7,11]), the ionization energy value for 1,2-benzanthracene, a test compound for this application of the method, can be estimated from the linear regression line (Fig. 3). The estimated IE value is 7.35 ± 0.07 eV. The uncertainties in both the measured ion abundance ratios and in the literature values for ionization energies of reference compounds lead to a combined estimated uncertainty of about 0.07 eV for the measured ionization energy value. This value is within 0.08 eV of the literature value (7.43 ± 0.03 eV), with which it agrees within error.[4]

The effective temperature is a measure of the internal energy of the activated dimer ion.[2] The calculated effective temperature (1000 K) is much higher than the values associated with proton-bound dimers using the same instrument and similar experimental conditions, but similar to values

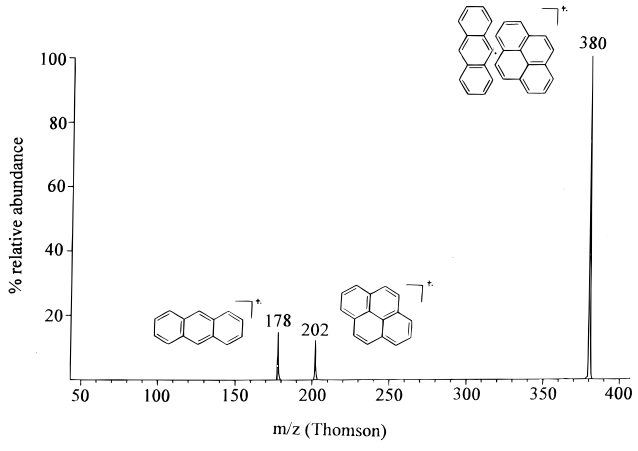

Figure 1. Product ion tandem mass spectrum of the mass-selected heterodimeric radical cations composed of pyrene and anthracene. Activation was achieved with 2 eV collisions using argon as target gas under single collision conditions.

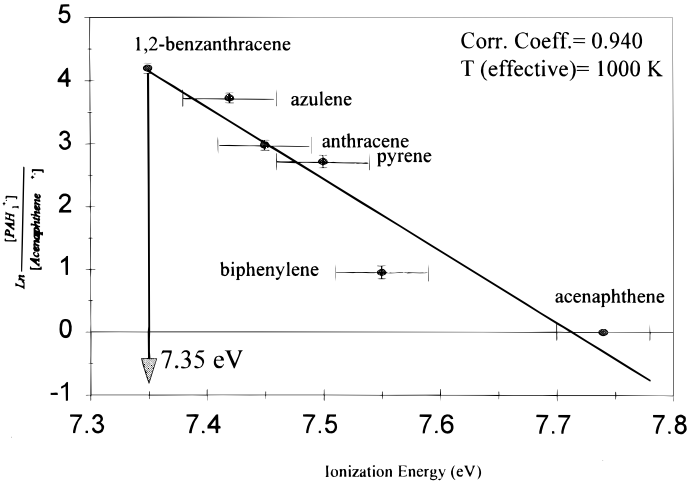

Figure 3. Linear correlation between $\ln([PAH_1^{+\cdot}][acenaphthene^{+\cdot}])$ and the ionization energies of the PAHs.

found for electron-bound dimers of PAHs which have a high effective temperature ($\sim$1250 K).[7] The relatively weak bonds in these systems and the fact that a relatively energetic method of desorption CI was used to generate the cluster ions account qualitatively for these results. Lee and Beauchamp[18] and Brauman and co-workers[19] have both recently re-derived, using RRK and RRKM theory, the kinetic method equation.Both groups demonstrated that the effective temperature is a measure of the excess average number of quanta per degree of freedom in the activated cluster ion. Brauman and co-workers suggested that the effective temperature is given by the following expression in the special case where all oscillators are degenerate:

$$T_{eff} = (n - \bar{m})/s \quad (5)$$

where n is the total number of quanta, m is the averaged number of quanta required to cause dissociation of a bond of interest and s is the total number of degrees of freedom. Clearly, the effective temperature can be increased by increasing the total number of quanta (because of the energetic ionization process) or by decreasing the number of oscillators or by decreasing the bond energy (the low binding energies in both the anionic and cationic PAH clusters). The proposed weakly bound structure in the heterodimeric radical cations is also supported by studies on bond dissociation energies of dimeric radical cations comprised of benzene and substituted benzenes, which range from 0.38–0.66 eV.[20–22] Another relevant result is Meot-Ner's measurement of the bond dissociation energies of dimeric radical cations of PAHs in which the measured bond dissociation energies for several PAHs were less than 0.80 eV.[9] These studies are consistent with the present results and with the proposed weakly bound structures for the heterodimeric radical cations.

This study has demonstrated the applicability of the kinetic method for the estimation of ionization energies of PAHs. Note that the compounds examined were chosen to have a narrow range of ionization energies; compounds with substantially different ionization energies do not readily form cluster ions and this is a limitation of the method. A strength of the method is the simplicity of the procedure and its ready implementation.

Acknowledgements. This work was supported by the National Science Foundation, CHE 92-23791.

Yours,

GUODONG CHEN and R. GRAHAM COOKS
Department of Chemistry,
Purdue University,
1393 Herbert C. Brown Laboratory,
West Lafayette,
IN 47907-1393,
USA

References

1. R. G. Cooks and T. L. Kruger, *J. Am. Chem. Soc.* **99**, 1279 (1977).
2. R. G. Cooks, J. S. Patrick, T. Kotiaho and S. A. McLuckey, *Mass Spectrom. Rev.* **13**, 287 (1994).
3. T. Vo-Dinh, in *Chemical Analysis of Polycyclic Aromatic Compounds*, edited by T. Vo-Dinh, p. 1. Wiley, New York (1989).
4. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17** (Suppl. 1), 1 (1988).
5. M. Meot-Ner (Mautner), *J. Phys. Chem.* **84**, 2716 (1980).
6. D. J. Burinsky, E. K. Fukuda and J. E. Campana, *J. Am. Chem. Soc.* **106**, 2770 (1984).
7. G. Chen and R. G. Cooks, *J. Mass Spectrom.* **30**, 1167 (1995).
8. G. Chen, R. G. Cooks, E. Corpuz and L. T. Scott, *J. Am. Soc. Mass Spectrom.* **7**, 619 (1996).
9. M. Meot-Ner (Mautner), *J. Phys. Chem.* **84**, 2724 (1980).
10. J. B. Lambert, H. F. Shurvell, D. A. Lightner and R. G. Cooks, *Introduction to Organic Spectroscopy*. Macmillan, New York (1987).
11. P. S. H. Wong, S. Ma and R. G. Cooks, *Anal. Chem.* **68**, 4254 (1996).
12. D. P. Stevenson, *Discuss. Faraday Soc.* **10**, 35 (1951).
13. K. Levsen, *Fundamental Aspects of Organic Mass Spectrometry*. Verlag Chemie, Weinheim (1978).
14. H. E. Audier, *Org. Mass Spectrom.* **2**, 283 (1969).
15. M. F. Jarrold and J. E. Bower, *J. Chem. Phys.* **86**, 3876 (1987).
16. L. H. Hanley, J. L. Whitten and S. L. Anderson, *J. Phys. Chem.* **92**, 5803 (1992).
17. R. G. Cooks and A. L. Rockwood, *Rapid Commun. Mass Spectrom.* **5**, 93 (1991).
18. H. N. Lee and J. L. Beauchamp, *J. Phys. Chem.* in press.
19. J. L. Brauman, personal communication.
20. B. Ernstberger, H. Krause, A. Kiermeier and H. J. Neusser, *J. Chem. Phys.* **92**, 5285 (1990).
21. J. T. Snodgrass, R. C. Dunbar and M. T. Bowers, *J. Phys. Chem.* **94**, 3648 (1990).
22. H. Krause, B. Ernstberger, J. J. BelBruno and H. J. Neusser, *J. Chem. Phys.* **95**, 3302 (1991).