J. Am. Chem. Soc. 1984, 106, 2770–2771

Electron Affinities from Dissociations of Mixed Negative Ion Dimers

David J. Burinsky,[†] Elaine K. Fukuda,[†] and Joseph E. Campana*

Contribution from the Naval Research Laboratory, Chemistry Division, Washington, DC 20375.

Received October 14, 1983

Abstract: This study demonstrates that radical negative ion dimers can be formed in a high-pressure ion source of a mass spectrometer, and the dissociations of these negative ion complexes can be used to determine the gas-phase electron affinities of the monomeric species. The technique, which yields results of precision comparable to other methods, uses a kinetic approach for the determination of a gas-phase thermochemical quantity. Strengths of this method include the simplicity of the procedure and its potential application to a variety of compounds.

We report a new method for the determination of gas-phase electron affinities. The basis of this method is the comparison of the rates of competitive dissociation reactions for mixed negative ion dimers,

$$[M_1M_2]^{-\cdot} \xrightarrow{k_1} [M_1]^{-\cdot} + M_2 \tag{1a}$$

$$[M_1M_2]^{-\cdot} \xrightarrow{k_2} [M_2]^{-\cdot} + M_1 \tag{1b}$$

These mixed negative ion dimers are formed in a high-pressure ion source,[1] where they undergo many thermalizing collisions with the neutral monomer bath species. The ensemble of mixed dimer anions is kinetically sampled, and the dissociations of the dimers are observed mass spectrometrically.

This method is analogous to the method of Cooks et al. for the determination of relative proton affinities and gas-phase acidities from proton-bound dimers.[2] The dissociation rate constants for eq 1 can be approximated from the absolute rate theory or the equivalent RRKM theory in the high-pressure limit[3]

$$k_i = \mathbf{k}T/\mathbf{h}(Q_i^+/Q_i)\exp(-E_0/\mathbf{k}T) \tag{2}$$

where Q_i^+ is the partition function of the activated complex, Q_i is the partition function of the reactant mixed dimer ion, and E_0 is the critical energy. The ratio of the rates k_1/k_2 can be obtained by using eq 2 and simplified, because both reactions proceed from the same reactant (i.e., $Q_1 = Q_2$), so

$$\ln(k_1/k_2) = \Delta\epsilon/\mathbf{k}T + \ln(Q_1^+/Q_2^+) \tag{3}$$

where $\Delta\epsilon$ is the difference between the electron affinity of M_1 and M_2 and T is the average effective temperature of the mixed negative ion dimer. We emphasize that T is the average effective temperature of those dimer ions that dissociate after sampling from the ion source, and this temperature reflects the ion structure and the time scale of the dissociation with respect to sampling.[2,4]

The partition functions of the activated complexes should be quite similar for eq 1, because the transition states must be nearly identical. This is a reasonable assumption, because the mobile electron can be viewed to reside with some probability on each of the two similar moieties (monomers) composing the activated complex of the dimer. In other words, we assume the activated complex of eq 1 is identical and the resultant product species is a function only of the residence time of the mobile electron on each moiety. Furthermore, the ratio Q_1^+/Q_2^+ could vary over an order of magnitude (0.5–5.0) without adversely affecting the usefulness of the method, because of the semiquantitative nature of many reported electron affinity values.[5] With the assumption $Q_1^+ \simeq Q_2^+$, eq 3 reduces to

$$\ln(k_1/k_2) = \Delta\epsilon/\mathbf{k}T \tag{4}$$

which we use to demonstrate the method.

Method

In this technique, the mixed dimer anion radical ($[M_1M_2]^{-\cdot}$) is formed in a modified high-pressure chemical ionization source[6] of a VG Analytical Ltd ZAB-2F reverse-geometry double-focusing mass spectrometer. The dimer is mass selected, and its collision-induced dissociation (CID) spectrum (helium collision gas) or unimolecular dissociation spectrum are obtained by ion kinetic energy analysis. This technique is referred to as mass-analyzed ion kinetic energy spectrometry (MIKES).[7] The relative ion abundance $[I(M_1^{-\cdot})/I(M_2^{-\cdot})]$ of the resulting fragment species, $M_1^{-\cdot}$ and $M_2^{-\cdot}$, is a measured of the fraction of time the electron spends on each of the two species in the complex. Therefore, their relative electron affinity is obtained by,

$$\ln(k_1/k_2) = \ln[I(M_1^{-\cdot})/I(M_2^{-\cdot})] = \Delta\epsilon/\mathbf{k}T \tag{5}$$

Plots (Figure 2), relating the electron affinities of several species, are constructed in a stepwise fashion with use of semiquantitative electron affinity data[5] having errors on the order of ±2 kcal/mol.

Results and Discussion

A mixture of nitrobenzene and *p*-nitrotoluene gives a negative ion chemical ionization mass spectrum that displays intense signals at *m/z* 123 and *m/z* 137 due to the molecular anions ($M^{-\cdot}$) and minor peaks at *m/z* 246, 260, and 274 corresponding to the three possible negative ion complexes. Figure 1 shows the CID/MIKES spectrum of the mixed dimer ion of interest $[(C_6H_5NO_2)(CH_3C_6H_4NO_2)]^{-\cdot}$ at *m/z* 260. The two competing decomposition reactions correspond to the elimination of one or the other of the neutral molecules from the complex (eq 1a and 1b). From the ratio of the ion abundances we infer that nitrobenzene has a greater electron affinity than *p*-nitrotoluene. This observation is confirmed by the literatures value, reported as a difference of 1.4 kcal/mol.[8]

[†] National Research Council Research Associate.

(1) Previous reports of negative ion dimer radicals have been limited to relatively small species from molecular beam experiments [Klots, C. E.; Compton, R. N. *J. Chem. Phys.* **1977**, *67*, 1779–1780. Armbruster, M.; Haberland, H.; Schindler, H. G. *Phys. Rev. Lett.* **1981**, *47*, 323–326. Bowen, K. H.; Liesegang, G. W.; Sanders, R. A.; Herschbach, D. R. *J. Phys. Chem.* **1983**, *87*, 557–565] and some larger species produced by ion cyclotron resonance mass spectrometry [Bowie, J. H.; Williams, B. D. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *17*, 395–401].

(2) Cooks, R. G.; Kruger, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1279–1281. McLuckey, S. A.; Cameron, D.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1313–1317.

(3) Robinson, P. J.; and Holbrook, K. A. "*Unimolecular Reactions*"; Wiley-Interscience: New York, 1972.

(4) McLafferty, F. W.; Wachs, T.; Lifshitz, C.; Innorta, G.; Irving, P. *J. Am. Chem. Soc.* **1970**, *92*, 6867–6880.

(5) Fukuda, E. K.; Doctorate Dissertation, University of California, Irvine, 1983. It should be noted that the absolute electron affinity values used in Figure 2 are in disagreement with previous determinations by about +1 eV.[9] However, the relative electron affinity values are in agreement with recent high-pressure mass spectrometry results (Caldwell G.; Kebarle, P. *J. Chem. Phys.* **1984**, *80*, 577–579).

(6) Burinsky, D. J.; Campana, J. E., unpublished work. The source pressure was about 100 mtorr of reactants measured with a capacitance manometer.

(7) Beynon, J. H.; Cooks, R. G.; Amy, J. W.; Baitinger, W. E.; Ridley, T. Y. *Anal. Chem.* **1973**, *45*, 1031A. McLafferty, F. W. *Science*, **1981**, *214* 280–287.

(8) Fukuda, E. K.; McIver, R. T., Jr. *J. Phys. Chem.* **1983**, *87*, 2993–2995.

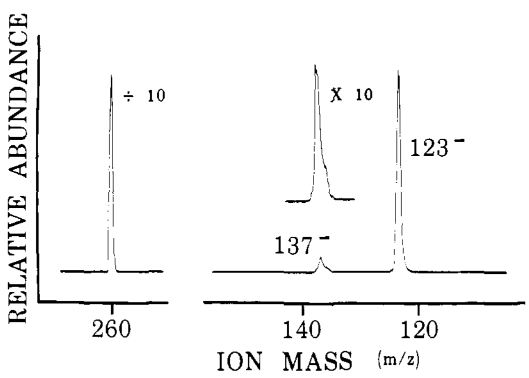

Figure 1. The CID/MIKES spectrum of the mixed negative ion dimer of nitrobenzene and *p*-nitrotoluene (*m/z* 260). The peak at *m/z* 137 corresponds to the negative ion of *p*-nitrotoluene, and its lower intensity is indicative of its lower electron affinity with respect to nitrobenzene (*m/z* 123).

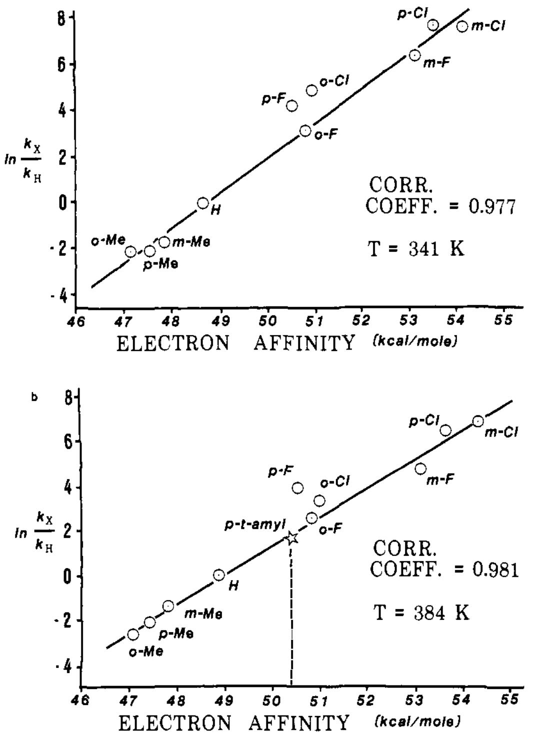

Figure 2. (a) The logarithm of the relative rates of unimolecular dissociation from mixed negative ion dimers of substituted nitrobenzenes vs. the electron affinity.[5] All rates k_x (x = substituent) are relative to nitrobenzene. (b) The logarithm of the relative rates of collision-induced dissociation from mixed negative ion dimers of substituted nitrobenzenes vs. the electron affinity.[5] All rates k_x (x = substituent) are relative to nitrobenzene. The electron affinity of the unknown *p-tert*-amylnitrobenzene is determined to be 50 ± 4 kcal/mol.

The results of the unimolecular and collision-induced fragmentations for a series of substituted nitrobenzenes are plotted in Figure 2a,b, respectively. The ratio of the substituted nitrobenzene peak height over the peak height of the unsubstituted compound ($C_6H_5NO_2$ = H) $[M_x]^{-}\cdot/[M_H]^{-}\cdot$ yields a value ln (k_x/k_H) for each reaction pair. Compounds with relatively large electron affinity differences cannot be compared directly in a single experiment, because large differences in ion abundances cannot be measured accurately. Consequently, the plot is constructed in a stepwise fashion, as is true for equilibrium methods.[9] A plot of the ln (k_x/k_H) values vs. the electron affinity of each of the substituted nitrobenzenes gives a straight line with a correlation coefficient of 0.98. The average effective temperature of the dissociating dimer ions is 341 K for those unimolecularly dissociating and 384 K for the collision-induced dissociations, as calculated from the slope of the line ($1/\mathbf{k}T$). The higher temperature of the dimer ions that undergo CID is consistent with the fact that the internal energy of the reactant ion is increased upon collision.[2,10]

The electron affinity of *p-tert*-amylnitrobenzene was determined by using the data in Figure 2b and serves as an illustrative case for the determination of an unknown electron affinity. In the CID/MIKES experiment the ratio of the peak height of the negative ion of *p-tert*-amylnitrobenzene to that of nitrobenzene was 7.23. Therefore, the electron affinity is assigned the value of 50 ± 4 kcal/mol (95% confidence interval), which is consistent with the size and structure of the substituent. This rather large uncertainty in the absolute electron affinity is a consequence of the scatter of the data points about the line (deviation of the correlation coefficient from unity) and the uncertainty of the reported values of absolute electron affinity.[5] However, our experiments show that relative electron affinities can be obtained reproducibly with a precision of a few tenths of a kcal/mol.[11]

Conclusions

This study indicates that abundant radical negative ion dimers can be formed in a high-pressure ion source of a mass spectrometer, and the dissociations of these mixed negative ion complexes are useful for the determination of the relative gas-phase electron affinities of the monomer components. Previously, this information had been available only by more complex methods. The technique, which appears to yield results of comparable precision to other methods,[8,9,13] uses an approximate kinetic approach for the determination of a gas-phase thermochemical quantity.

Strengths of this method include the simplicity of the procedure and its potential applicability to a variety of compounds that are not handled easily by other experimental techniques such as photoelectron spectroscopy[12] and charge-exchange reactions.[13] The study of a series of substituted substrates is particularly suitable, because of the ease and accuracy of constructing the stepwise plot. Intractable compounds could be studied in a high-pressure fast-atom bombardment ion source,[14] where the desorbed negative ion dimer species could be stabilized collisionally and the desorbed monomers could form mixed dimers by ion/molecule reactions.

Acknowledgment. We wish to thank Professor R. Graham Cooks (Purdue University) for valuable discussions during the conceptual stages of this work.

Registry No. *o*-Nitrotoluene, 88-72-2; *p*-nitrotoluene, 99-99-0; *m*-nitrotoluene, 99-08-1; 1-fluoro-2-nitrobenzene, 1493-27-2; 1-fluoro-4-nitrobenzene, 350-46-9; 1-chloro-2-nitrobenzene, 88-73-3; 1-fluoro-3-nitrobenzene, 402-67-5; 1-chloro-4-nitrobenzene, 100-00-5; 1-chloro-3-nitrobenzene, 121-73-3; nitrobenzene, 98-95-3; *p-tert*-amylnitrobenzene, 6284-98-6.

---

(9) Fukuda, E. K.; McIver, R. T., Jr. *J. Phys. Chem.* **1982**, *77*, 4942–4948.

(10) Cooks, R. G. "Collision Spectroscopy"; Cooks, R. G., Ed.; Plenum Press: New York, 1978; Chapter 7.

(11) Cooks et al.[2] have shown also that the technique is capable of reproducibly differentiating relative proton affinities that differ by only a few tenths of a kcal/mol.

(12) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1975**, *4*, 539–576.

(13) Janousek, B. K.; Brauman, J. I. "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapter 10.

(14) Freas, R. B.; Campana, J. E., unpublished results.