J. Am. Chem. Soc. **2000,** *122,* 8305−8306

Photodetachment of the First Zwitterionic Anions in the Gas Phase: Probing Intramolecular Coulomb Repulsion and Attraction

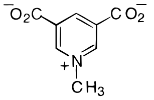
Xue-Bin Wang,[†] Katherine M. Broadus,[‡]
Lai-Sheng Wang,*[,†] and Steven R. Kass*[,‡]

Department of Physics, Washington State University
2710 University Drive, Richland, Washington 99352
W. R. Wiley Environmental Molecular Science Laboratory
MS K8-88, Pacific Northwest National Laboratory
P.O. Box 999, Richland, Washington 99352
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

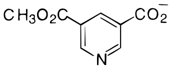
Received June 2, 2000

Zwitterions or synonymously, dipolar ions, are widely used species in many areas of chemistry. For example, they are employed as valuable reagents in organic synthesis[1] and the construction of novel materials,[2] chromatographic supports,[3] and a myriad of biological applications ranging from enzyme inhibitors to therapeutic buffers and drugs.[4−6] In nature a profusion of zwitterionic compounds can be found because amino acids exist in their dipolar form over a wide range in pH. The resulting electrostatic interactions in peptides and enzymes play a pivotal role in their structure and function.[7−9] Opposite charge interactions also are routinely assumed to be present in the gas phase and influence the characterization and analysis of many biological molecules.[10−14] Limited information on gas-phase dipolar ions is available,[15,16] however, since their independent preparation and characterization is a challenge and only just has been described.[17] In this contribution we report the first spectroscopic data on zwitterionic ions and the effect of intramolecular Coulombic forces on electron affinities and bond dissociation energies.

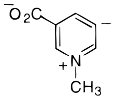
Experiments were performed with a magnetic-bottle time-of-flight (TOF) photoelectron spectrometer coupled to an electrospray ion source and an ion-trap mass spectrometer.[18] Briefly, methylated pyridinium-3,5-dicarboxylate (**1**) and the conjugate base of 5-(methoxycarbonyl)nicotinic acid (**2**) were sprayed into the gas phase using 10^{-3} M solutions of the corresponding sodium salts dissolved in methanol−water (70:30 v/v). The resulting anions produced from the electrospray source were transported into a quadrupole ion trap, where they were accumulated for 0.1 s before being passed on for mass-to-charge analyses with a TOF mass spectrometer. The main ion signals were from **1** and **2**, respectively. A small amount of the decarboxylated zwitterion (**3**) also was observed, most likely due to collision-induced dissociation during ion transport and trapping.[19] All three anions (**1**−**3**) were mass selected in the TOF mass spectrometer and decelerated before being detached by a laser beam in the interaction zone of the magnetic-bottle photoelectron spectrometer. Both an excimer laser (157 and 193 nm) and a Nd:YAG laser (266 and 355 nm) were used for photodetachment in this study. The electron kinetic energy resolution was $\Delta E/E \approx 2\%$ (i.e., 20 meV for 1 eV electrons).



1



2



3

Figure 1 shows the photoelectron spectra of **1**−**3** at a photon energy of 157 nm (7.866 eV). The inset in Figure 1c shows a vibrationally resolved spectrum for **3** at 355 nm (3.496 eV). Similar spectra were also obtained at 266 and 193 nm, but are not shown here. The spectrum of zwitterion **1** (Figure 1a) shows a broad band between 4.7 and 6.1 eV with overlapping features and a low intensity region above 6.5 eV. The spectrum of the nonzwitterionic anion **2** (Figure 1b) is similar to that of **1** with an intense broad band and overlapping features between 4 and 5.4 eV along with weaker unresolved signals above 5.5 eV. An extra lower binding energy feature is observed in the spectrum of the decarboxylated zwitterion **3** (Figure 1c). The higher energy part of the spectrum for **3** is similar to that for **1** and **2** with an intense broad band between 3.7 and 5.2 and weaker higher energy signals above 5.2 eV. The 355 nm spectrum of **3** (Figure 1c inset) yields a vibrational spacing of about 580 ± 60 cm^{-1}.

In all three spectra, the strong broad band is due to detachment from the carboxylate group. The weaker and higher binding energy features presumably are due to ionization of an aromatic ring π electron. Similar characteristics are found in the spectra of benzoate and benzene dicarboxylates, which were recently investigated.[20] The lower binding energy feature near 3 eV in the spectrum of **3** is due to detachment of a σ electron from the carbon atom lone pair. All of the measured and computed (B3LYP/6-31+G(d)) electron binding energies, both adiabatic (ADE) and vertical (VDE), are given in Table 1. The calculated energies are systematically too small but reproduce the experimental values to within 0.2 eV (ADEs) and 0.3 eV (VDEs) if one accounts for the error in nicotinate (m-pyrCO_2^-).

Consideration of the electrostatic interactions in the two zwitterions (**1** and **3**) relative to those in their nonzwitterionic analogues (**2** and phenyl anion, respectively) accounts for the relative electron binding energies. In the zwitterions the electron binding energies are determined by the combined effects of Coulomb repulsion between the two negative charges and the

---

[†] Department of Physics, Washington State University and Pacific Northwest National Laboratory.

[‡] Department of Chemistry, University of Minnesota.

(1) Gothelf, K. V.; Jorgensen, K. A. *Chem. Rev.* **1998**, *98*, 863−909.

(2) (a) Spencer, T. A.; Onofrey, T. J.; Cann, R. O.; Russel, J. S.; Lee, L. E.; Blanchard, D. E.; Castro, A.; Gu, P.; Jiang, G.; Shechter, I. *J. Org. Chem.* **1999**, *64*, 807−818. (b) Biegle, A.; Mathis, A.; Galin, J.-C. *Macromol. Chem. Phys.* **1999**, *200*, 1393−1406.

(3) Hu, W.; Haddad, P. R.; Hasebe, K.; Tanaka, K. *Anal. Commun.* **1999**, *36*, 97−100.

(4) Ramos, M. J.; Melo, A.; Henriques, E. S.; Gomes, J. A. N. F.; Reuter, N.; Maigret, B.; Floriano, W. B.; Nascimento, M. A. C. *Int. J. Quantum Chem.* **1999**, *74*, 299−314.

(5) Caron, G.; Pagliara, A.; Gaillard, P.; Carrupt, P.-A.; Testa, B. *Helv. Chim. Acta* **1996**, *79*, 1683−1695.

(6) Theodore, T. R.; Van Zandt, R. L.; Carpenter, R. H. *Cancer Biother. Radiopharm.* **1997**, *12*, 351−353.

(7) Warshel, A. *Acc. Chem. Res.* **1981**, *14*, 284−290.

(8) Honig, B.; Nicholls, A. *Science* **1995**, *268*, 1144−1149.

(9) (a) Wu, N.; Mo, Y.; Gao, J.; Pai, E. F. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 2017−2022. (b) Miller, B. G.; Hassell, A. M.; Wolfenden, R.; Milburn, M. V.; Short, S. A. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 2011−2016. (c) Appleby, T. C.; Kinsland, C.; Begley, T. P.; Ealick, S. E. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 2005−2010.

(10) Wyttenbach, T.; Witt, M.; Bowers, M. T. *J. Am. Chem. Soc.* **2000**, *122*, 3458−3464.

(11) Freitas, M. A.; Marshall, A. G. *Int. J. Mass. Spectrom.* **1999**, *182/183*, 221−231.

(12) Ewing, N. P.; Cassady, C. J. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 928−940.

(13) Schnier, P. D.; Price, W. D.; Jockusch, R. A.; Williams, E. R. *J. Am. Chem. Soc.* **1996**, *118*, 8, 7178−7189.

(14) Campbell, S.; Rodgers, M. T.; Marzluff, E. M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 12840−12854.

(15) Patrick, J. S.; Yang, S. S.; Cooks, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 231−232.

(16) Strittmatter, E. F.; Wong, R. L.; Williams, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 1247−1248.

(17) Broadus, K. M.; Kass, S. R. *J. Am. Chem. Soc.*, accepted for publication.

(18) (a) Wang, L. S.; Ding, C. F.; Wang, X. B.; Barlow, S. E. *Rev. Sci. Instrum.* **1999**, *70*, 1957- 1966. (b) Wang, L. S.; Wang, X. B. *J. Phys. Chem. A* **2000**, *104*, 1978−1990.

(19) Photodetachment of the methyl-d_3 species gives the same spectrum.

(20) Wang, X. B.; Nicholas, J. B.; Wang, L. S. *J. Chem. Phys.* **2000**, *113*, 653−661.

10.1021/ja001943z CCC: $19.00

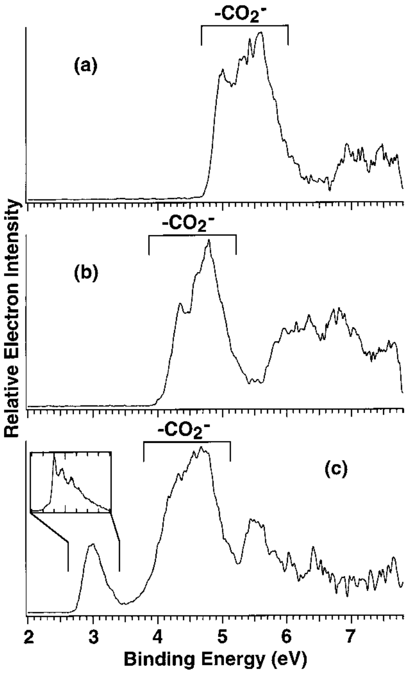


Figure 1. Photoelectron spectra at 157 nm (7.866 eV) for (a) 1-methylpyridinium-3,5-dicarboxylate (**1**), (b) 5-methoxycarbonylpyridine-3-carboxylate (**2**), and (c) (**3**) The inset in (c) shows a vibrationally resolved spectrum at 355 nm (3.496 eV). The labels indicate the origin of the detachment bands.

Table 1. Measured and Calculated Adiabatic (ADE) and Vertical (VDE) Electron Binding Energies for **1**−**3** in eV[a]

ion	ADE(C^-)	ADE(CO_2^-)	VDE(CO_2^-)
m-pyrCO_2^- [b]		3.95 ± 0.10[c] (3.69)	4.30 ± 0.10[c] (4.22)
1		4.85 ± 0.05[c] (4.65)[d]	5.02 ± 0.05[c] (4.66)
2		4.17 ± 0.07[c] (4.11)[d]	4.38 ± 0.06[c] (4.40)
3	2.905 ± 0.020[e] (2.77)[g]	3.8 ± 0.1[f]	4.2 ± 0.1[f]

[a] Computed values are at the B3LYP/6-31+G(d) level and are given in parentheses. [b] Wang, X.-B.; Wang, L.-S., unpublished results. [c] The VDEs were determined from the maxima of the first resolved features. The ADEs were determined from the detachment threshold. Uncertainties were evaluated by considering the instrumental resolution and by considering reproducibiltiy for data taken at different times and laser wavelengths. [d] The calculated ADE has been corrected by 0.26 eV, the computed error in the nicotinate value. [e] The accurate ADE is determined from the vibrationally resolved data at 355 nm. [f] The ADE and VDE for **3** are estimates due to the lack of a sharply resolved threshold feature for detachment from the carboxlate. [g] This value was corrected by 0.04 eV, the computed error for phenyl radical. See: Reed, D. R.; Kass, S. R. *J. Mass Spectrom.* **2000**, *35*, 534−539.

Coulomb attraction between the positive and two negative charges. In **1**, the distance between the positively charged nitrogen center and the negatively charged carboxylates is shorter (4.28 Å) than between the two negative charges (6.18 Å).[21] Thus, the attractive forces experienced by both negative charges are greater than their mutual repulsion, and the binding energy of zwitterion **1** is significantly higher (0.68 eV or 15.7 kcal/mol) than for nonzwitterionic **2**; a simple point charge model in conjunction with Coulomb's law leads to a stabilization of 1.04 eV or 23.9 kcal/mol. For **3**, detachment from both the carbanion center and the carboxylate is clearly observed and distinguished (Figure 1c). The vibrationally resolved lower energy feature is due to the carbon lone pair and has a spacing of 580 cm^{-1}, which agrees well with a computed value of 542 cm^{-1}. The observed 2.905 eV binding energy is considerably higher than the experimental value for phenyl anion (1.096 ± 0.006 eV)[22] and represents a remarkable electrostatic effect. One can qualitatively account for this difference (1.81 eV or 41.7 kcal/mol) by examining the distances between the charged centers in the computed structure ($N-CO_2^-$ 4.28 Å, $N-C^-$ 2.46 Å, and $CO_2^- - C^-$ 4.47 Å),[21] and if one scales the Coulomb energy (2.63 eV or 60.6 kcal/mol) by the error found for **1** (15.7/23.9), then quantitative accord is obtained (i.e., 39.8 vs 41.7 kcal/mol). On the other hand, the smaller ADE for the carboxylate in **3** relative to that in **2** indicates that the repulsive interaction between the carbanion center and the carboxylate is larger than the latter's attraction to the positively charged nitrogen. This contrasts with the simple point charge model, which apparently is too crude in this case since it indicates that there should be little effect (<3 kcal/mol) on the carboxylate's electron binding energy.

Table 2. Experimental and Computed Proton Affinities (PA) and Bond Dissociation Energies (BDE) for **1**−**3** in kcal/mol[a]

ion	PA	BDE
$C_6H_5^-$ [b]	401.7 ± 0.5	113.5 ± 0.5 (110.5)
$C_6H_5CO_2^-$	340.1 ± 2.2[c]	112 ± 3[d] (107.3)[e]
1	310 ± 5 (311.0)	108 ± 5 (109.3)[e]
2	328 ± 5 (327.4)	111 ± 5 (109.8)[e]
3	− (361.5)	115[f] (114.7)[e]

[a] Computed values are at the B3LYP/6-31+G(d) level and are given in parentheses. [b] Experimental data from Davico, G. E.; Bierbaum, V. M.; Depuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590−2599. [c] See: Bartmess, J. E. *Negative Ion Energetics Data in Secondary Negative Ion Energetic Data*; National Institute of Standards and Technology: Gaithersburg MD 20899, February 2000, (http://webbook.nist.gov). [d] The BDE was determined from the proton affinity and the ADE (3.70 ± 0.1 eV). For the latter quantity, see: ref 20. [e] The calculated BDEs make use of the exact electronic energy for H (0.5 Hartrees) and have been corrected by the errors in the directly computed electron affinities; if isogyric reactions are used, similar results (±1 kcal/mol) are obtained except for **2** where the BDE becomes 113.4 kcal/mol. [f] This value comes from the computed PA and the experimental ADE.

The experimentally determined electron binding energies can be combined with previously measured proton affinities for **1** and **2**,[17] and the computed value for **3**, in a thermodynamic cycle to provide the corresponding homolytic O−H (**1** and **2**) and C−H (**3**) bond dissociation energies. Our experimental and computational results are summarized in Table 2, and there is good agreement between the two if one accounts for the errors in the computed electron binding energies. Little, if any, effect on the bond energies is seen by the presence of a zwitterionic site, in contrast to the electron binding energies and the proton affinities.

Acknowledgment. Support from the National Science Foundation, the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, and the Minnesota Supercomputer Institute is gratefully acknowledged. This work was performed in part at the W. R. Wiley Environmental Molecular Science Laboratory, a national scientific user facility sponsored by Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for the U.S. Department of Energy by Battelle. L.S.W. is an Alfred P. Sloan Foundation Research Fellow.

Supporting Information Available: Computed structures and energies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001943Z

---

(21) Distances were determined by using B3LYP/6-31+G(d) structures, and taking the nitrogen (or carbon) atom and the midpoint between the carboxylate oxygen atoms as the charge centers.

(22) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom.* **1992**, *117*, 601−620.