the $^{1,3}\Pi_u$ valence states of Cl_2 are in a much better energy range to serve as the virtual states for two-photon excitation than are the $^{1,3}\Pi_u$ valence states of Br_2. Less information[19] is available for the Rydberg states of ICl; however, there are numerous known vacuum UV Rydberg transitions[22] in the energy range corresponding to $V(Xe^+,ICl^-)$. The absence of two-photon excitation to the isolated Rydberg states of Cl_2 followed by reactive collisions with Xe *may* be a consequence of the diabatic curve crossing between the $^{1,3}\Pi_g$ states and a repulsive state correlating to chlorine atoms.[17]

In conclusion, we ascribe the two-photon laser-assisted reaction of Xe with Cl_2 and ICl to excitation from the van der Waals ground-state potential to the ion-pair potential that gains two-photon oscillator strength via configuration interaction with the halogen $^{1,3}\Pi_g$ Rydberg states. The one-photon-assisted reaction[4b] probably proceeds with assistance of configuration interactions of the $^{1,3}\Pi_u$ Rydberg states with $V(Xe^+,Cl_2^-)$. Further work undoubtedly will result in refinement of this view.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. The U.S. Department of Energy provided funds for purchase of the laser.

---

[22] Venkatswarlu, P. *Can. J. Phys.* **1975**, *53*, 812.

Relative Electron Affinities of Substituted Nitrobenzenes in the Gas Phase

Elaine K. Fukuda and Robert T. McIver, Jr.*

Department of Chemistry, University of California, Irvine, California 92717 *(Received: March 10, 1983)*

Using pulsed ion cyclotron resonance mass spectrometry, we have determined the relative electron affinities of 12 substituted nitrobenzenes in the gas phase by measuring equilibrium constants for electron transfer reactions of the type $C_6H_5NO_2^- + X\text{–}C_6H_4NO_2 = X\text{–}C_6H_4NO_2^- + C_6H_5NO_2$, where X is a substituent group. An excellent correlation is found between the relative electron affinities of the substituted nitrobenzenes and the relative gas-phase acidities of substituted anilines and phenols.

One of the fundamental properties of a negative ion is the lowest energy required to remove an electron. This energy is called the electron affinity (EA) and is equal to ΔE for the process

$$A^- = A + e^- \tag{1}$$

Several experimental methods have been developed for measuring electron affinities. The most precise and accurate methods are photodetachment spectroscopy[1,2] and photoelectron spectroscopy[3] which probe reactions of the type

$$A^- + h\nu \rightarrow A + e^- \tag{2}$$

In another approach, endothermic electron transfer reactions such as

$$Cl^- + NO_2 \rightarrow NO_2^- + Cl\cdot \tag{3}$$

have been studied in tandem mass spectrometers.[4] Previously we reported that a wide variety of gaseous negative ion radicals can be generated in the trapped ion analyzer cell of a pulsed ion cyclotron resonance (ICR) spectrometer.[5-7] The ions were stabilized and stored for several seconds in the ICR cell, and exothermic electron transfer reactions of the type

$$C_6H_5NO_2^- + SO_2 \rightarrow SO_2^- + C_6H_5NO_2 \tag{4}$$

were observed.[6] Ion cyclotron double resonance was used to confirm the occurrence of reaction 4. Since it is a rapid reaction, we conclude that the electron affinity of nitrobenzene is less than that for sulfur dioxide.

TABLE I: Free Energy Changes for Electron Transfer Reactions in the Gas Phase

$C_6H_5NO_2^- + X\text{-}C_6H_4NO_2 = X\text{-}C_6H_4NO_2^- + C_6H_5NO_2$

X	$\Delta G°_{380}$, kcal/mol	X	$\Delta G°_{380}$, kcal/mol
p-CH_3	+1.4	*p*-Cl	−4.7
m-$N(CH_3)_2$	+1.1	*m*-Cl	−5.4
m-CH_3	+1.0	*m*-CF_3	−8.4
H	(0.0)	*m*-CN	−12.0
p-F	−1.7	*m*-NO_2	−13.8
m-F	−4.3	*p*-NO_2	−21.2

In this Letter we discuss the results of a pulsed ICR study of electron transfer reactions involving a wide variety of substituted nitrobenzenes. The relative electron affinities of 12 substituted nitrobenzenes were determined by measuring equilibrium constants for electron transfer reactions of the type

$$C_6H_5NO_2^- + X\text{–}C_6H_4NO_2 = X\text{–}C_6H_4NO_2^- + C_6H_5NO_2 \tag{5}$$

where X is a meta or para substituent. An experiment is initiated by a low-energy (ca. < 1 eV) electron beam pulse through the ICR cell. Inelastically scattered electrons are trapped in the cell and captured by the neutral reactants to form excited negative ion radicals which can either autodetach an electron or be stabilized by spontaneous emission and ion–neutral collisions.[5-7] After many cycles of reversible electron transfer, reaction 5, the equilibrium constant and free energy change $\Delta G°$ can be calculated from the relative abundances of the two negative ions and

---

[1] Branscomb, L. M. In "Atomic and Molecular Processes"; Bates, D. R., Ed.; Academic Press: New York, 1962; p 100.

[2] Smyth, K. C.; Brauman, J. I. *J. Chem. Phys.* **1972**, *56*, 1132.

[3] Lineberger, W. C. In "Chemical and Biochemical Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1974; Vol. 1, p 71.

[4] (a) Lifshitz, C.; Hughes, B. M.; Tiernan, T. O. *Chem. Phys. Lett.* **1970**, *7*, 469. (b) Lifshitz, C.; Tiernan, T. O.; Hughes, B. M. *J. Chem. Phys.* **1973**, *59*, 3182.

[5] Rains, L. J.; Moore, H. W.; McIver, Jr., R. T. *J. Chem. Phys.* **1978**, *68*, 3309.

[6] Fukuda, E. K.; McIver, Jr., R. T. *J. Chem. Phys.* **1982**, *77*, 4942.

[7] McIver, R. T.; Fukuda, E. K. In "Ion Cyclotron Resonance Spectrometry II"; Hartmann, H., Wanczek, K.-P., Eds.; Springer-Verlag: New York, 1982; p 164.

[8] Foster, M. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1975**, *31*, 482.

0022-3654/83/2087-2993$01.50/0

the partial pressures of the neutral species. When the method of multiple overlaps was used, such as was used for the gas-phase acidity scale[9-11] and gas-phase basicity scale,[12-14] a scale of free energy changes ΔG° has been generated.[7]

A summary of the ΔG° values for reaction 5 is given in Table I. Many of these values were calculated from measurements involving other compounds of intermediate electron affinity which are not included in the table but have been reported previously.[7] For the general electron transfer reaction

$$A^- + B = B^- + A \tag{6}$$

the free energy change can be written as

$$\Delta G^\circ = -RT \ln K = \Delta E - RT \ln \left(\frac{Q_A Q_{B^-}}{Q_B Q_{A^-}} \right) \tag{7}$$

where T is the temperature, ΔE is the energy change for the reaction at 0 K, and the Q's are molecular partition functions.[15] ΔE, the energy separation between the ground states of the products and the reactants, is essentially the same as EA(A) − EA(B), the difference in their adiabatic electron affinities. In general the partition function term in eq 7 is expected to be small for reactions of this type since the ratio of partition functions is close to 1. This is clearly a good approximation for the translational partition functions for A^- and A since the mass of an electron is small compared to the mass of the molecules. In addition, since the structures of the substituted nitrobenzenes and nitrobenzene anions are similar, differential rotational and vibrational contributions to the partition functions will be quite small. Contributions to ΔG° from the electronic partition functions are also small since there is an odd-electron anion and an even-electron molecule on both sides of the equilibrium. Thus, we conclude that the ΔG° values shown in Table I are approximately equal to the electron affinities of the substituted nitrobenzenes relative to nitrobenzene.

The same conclusion can be reached by examining the entropy change for eq 7. Using the fundamental definition of entropy, $S = -(\partial G/\partial T)_p$, we can write the entropy change for reaction 6 as

$$\Delta S = R \ln \left(\frac{Q_A Q_{B^-}}{Q_B Q_{A^-}} \right) + RT \frac{\partial}{\partial T} \left[\ln \left(\frac{Q_A Q_{B^-}}{Q_B Q_{A^-}} \right) \right] \tag{8}$$

Since the ratio of the partition functions is close to 1 and has a small temperature coefficient, ΔS is expected to be very small for these reactions.

The large effect of substituents on the electron affinity of nitrobenzenes is apparent from Table I. For example, the positive ΔG° values for methyl substituents are indicative of an electron-donating effect which destabilizes the anion radical. In contrast, electron-withdrawing groups stabilize the nitrobenzene anion and increase the electron affinity in the order F < Cl < CF_3 < CN < NO_2. These trends are similar to those seen previously in our studies of gas-phase acidities and suggested that similar interaction mechanisms may be operative.

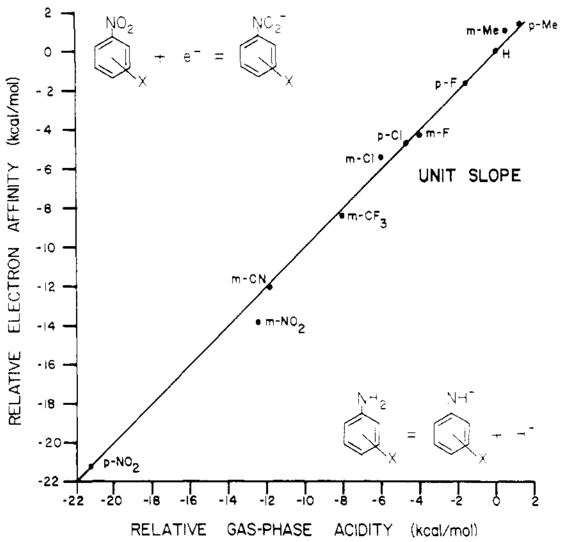

Figure 1. Comparison of substituent effects on the electron affinities of various nitrobenzenes with the corresponding gas-phase acidities of anilines. For example, *p*-dinitrobenzene has the largest electron affinity and *p*-nitroaniline is the most acidic compound shown. The gas-phase acidities were taken from ref 11.

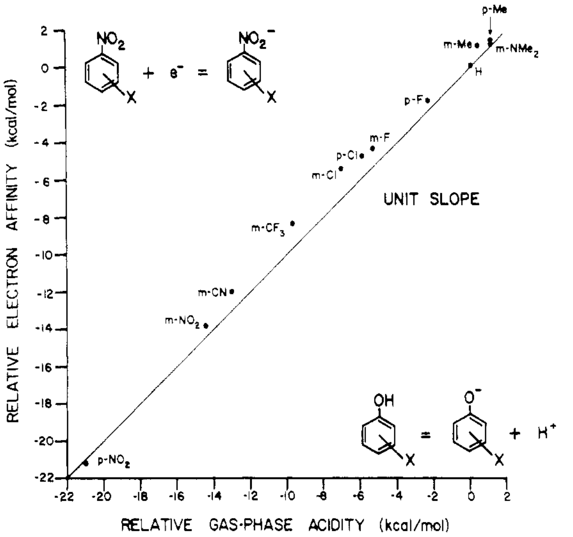

Figure 2. Comparison of substituent effects on the electron affinities of various nitrobenzenes with the corrsponding gas-phase acidities of phenols. The *m*-CF_3 substituent increases both the acidity of phenol and the electron affinity of nitrobenzene. The gas-phase acidities were taken from ref 11.

Figures 1–3 show comparisons of the relative electron affinities of the substituted nitrobenzenes with the relative gas-phase acidities of substituted anilines, phenols, and benzoic acids, respectively. A line of unit slope is drawn in all figures to show the degree of correlation. The gas-phase acidity (proton donor ability) of a molecule AH is defined as ΔG° for the process

$$AH = A^- + H^+ \tag{9}$$

The enthalpy change for this reaction is given by

$$\Delta H^\circ = DH^\circ(A\text{–}H) - EA(A\cdot) + IP(H) \tag{10}$$

where DH°(A–H) is the homolytic AH bond strength, EA(A·) is the electron affinity of the A· radical, and IP(H) is the ionization potential of hydrogen.[9-11] At first glance

---

(9) Bartmess, J. E.; Scott, J. A.; McIver, Jr., R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6046–56.

(10) Fujio, M.; McIver, Jr., R. T.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017–29.

(11) Bartmess, J. E.; McIver, Jr., R. T. In "Gas-Phase Ion Chemistry"; Bowers, M. T.; Ed.; Academic Press: New York, Vol. 2, chapter 11.

(12) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M. McIver, Jr., R. T.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417–29.

(13) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, chapter 9.

(14) Taft, R. W. In "Proton Transfer Reactions"; Caldin, E. F.; Gold, V.; Ed.; Wiley-Halsted: New York, 1975; p 31.

(15) Davidson, N. "Statistical Mechanics"; McGraw-Hill: New York, 1962; p 103.

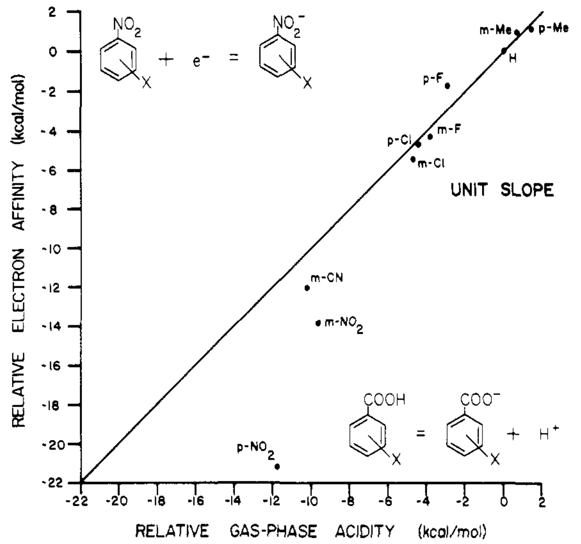

Figure 3. Comparison of substituent effects on the electron affinities of various nitrobenzenes with the corresponding gas-phase acidities of benzoic acids. No resonance interactions are possible with the benzoic acids, giving rise to a large deviation from the line of unit slope for the p-NO_2 substituent. The gas-phase acidities were taken from ref 11.

one might expect quite different energetics for substituent effects on electron affinities (reaction 5) and on gas-phase acidities (reaction 9) since the former involves an odd-electron negative ion and the latter involves a closed-shell negative ion. However, it is apparent from Figures 1 and 2 that there is an excellent correlation between the relative electron affinities of the substituted nitrobenzenes and the relative gas-phase acidities of substituted anilines and phenols.

Previously it has been shown that substituent effects on gas-phase acidities is largely determined by interactions in the anion, rather than the neutral.[16] Furthermore, since similar A–H bond strengths have been found for a homologous series of compounds such as the substituted phenols, it is apparent from eq 10 that the gas-phase acidities parallel the electron affinities of the phenoxy radicals. Therefore, Figures 1–3 essentially compare substituent effects on the electron affinities of nitrobenzenes with those on the electron affinities of the $C_6H_5NH\cdot$, $C_6H_5O\cdot$, or $C_6H_5COO\cdot$ radicals.

The best correlation is exhibited by the substituted anilines (Figure 1). The phenol series (Figure 2) is also well correlated, with the best fit line having a slope of 0.95. It is well known that O^- and NH^- groups can act as π-donors to a benzene ring, and a similar mechanism for charge delocalization must exist for the nitrobenzene, phenoxide, and anilide negative ions. In the benzoic acid series (Figure 3) there are large deviations from the line of unit slope most likely due to a lack of resonance interactions in the benzoate anion. Since the odd electron of the nitrobenzene radical anion occupies a nominally π^*-orbital, it has appropriate symmetry to interact with the benzene ring and substituent π-symmetry orbitals.

Other evidence for these resonance interactions in the nitrobenzene radical anion comes from the analysis of electron spin resonance spectra, polarographic half-wave potentials, and theoretical calculations. It has been estimated that 0.37 of an electronic charge is delocalized to the ring in the nitrobenzene anion,[17] which is quite similar to the value 0.527 for phenoxide and 0.503 for anilide. In addition, spin densities determined from ESR hyperfine constants have been found to be in agreement with those calculated by using Hückel theory, and a significant amount of spin density is located on the ortho and para ring carbons of the nitrobenzene anion.[17,18] In the case where the nitro group is forced out of plane relative to the benzene ring, large effects consistent with the reduction of resonance interactions are observed in both ESR and polarography experiments.[17,18]

Acknowledgment. We gratefully acknowledge research support from the National Science Foundation, the National Institutes of Health, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. p-$CH_3C_6H_4NO_2$, 99-99-0; m-$N(H_3)_2C_6H_4NO_2$, 100-23-2; m-$CH_3C_6H_4NO_2$, 99-08-1; $C_6H_5NO_2$, 98-95-3; p-$FC_6H_4NO_2$, 350-46-9; m-$FC_6H_4NO_2$, 402-67-5; p-$ClC_6H_4NO_2$, 100-00-5; m-$ClC_6H_4NO_2$, 121-73-3; m-$CF_3C_6H_4NO_2$, 98-46-4; m-$CNC_6H_4NO_2$, 619-24-9; m-$NO_2C_6H_4NO_2$, 99-65-0; p-$NO_2C_6H_4NO_2$, 100-25-4.

---

(16) (a) Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 818–26. (b) Kemister, G.; Pross, A.; Radom, L.; Taft, R. W. *Ibid.* **1980**, *45*, 1056–60.

(17) Geske, D. H.; Ragle, J. L.; Bambenek, M. A.; Balch, A. L. *J. Am. Chem. Soc.* **1964**, *86*, 987.

(18) Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1963**, *39*, 609.