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Linear Free Energy Relationship in Ion Thermochemistry

Dana A. Shea, Ruud J. J. M. Steenvoorden, and Peter Chen*

Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, Zürich

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We report a linear correlation between the proton affinity of 4-substituted pyridines and the hydride affinity of comparably substituted methyl cations that spans almost 30 and 120 kcal/mol, respectively. The linear correlation holds for cations bearing substituents that can stabilize an adjacent charge by a resonance interaction; cations with nonconjugating substituents fall off of the line. The cyanomethyl radical, for which a sharp, vertical ionization with $IP_{ad}[{}^{\bullet}CH_2CN] = 10.30 \pm 0.04$ eV was observed, is found to belong to the class of resonance-stabilized cations, contrary to earlier suggestions.

Introduction

Linear free energy relationships (LFER) have a long history in solution-phase chemistry in which they functioned to predict properties, quantify interactions, and classify reactions according to mechanistic type.[1] In gas-phase chemistry, the absence of solvation should remove one of the complicating factors in LFER methods, which, after all, purport to deal primarily with intrinsic electronic effects. Accordingly, a variety of applications in ion−molecule reactions have been made, usually with the goal of validating a calculation or measurement.[2] We report a linear correlation between the proton affinity of 4-substituted pyridines and the hydride affinities of substituted methyl cations that both has predictive utility and serves to classify cations according to their mode of stabilization.

In the course of photoelectron spectroscopic investigations of simple radicals, we had noticed that the literature values[3] for the ionization potential of ${}^{\bullet}CH_2CN$, the cyanomethyl radical, spread over an unacceptably large range and needed, accordingly, remeasurement. While the ionization potential of any individual species holds relatively little significance, the critical evaluation of the accuracy of the measured value has led us to a thermochemical correlation of surprisingly broad generality. Coincidentally, the value for ${}^{\bullet}CH_2CN$ constitutes one of the extrema in the correlation and, thus, gains significance in the validation of the entire scheme. Thus, the present study, which originated in an effort to check the observed ionization potential of ${}^{\bullet}CH_2CN$, resulted in a more general linear correlation of proton affinities in substituted pyridines with hydride affinities of simply substituted alkyl cations that spans a 28 kcal/mol range of proton affinities and a 120 kcal/mol range in hydride affinities.

The general linear free energy relationship, of which the Brønsted Catalysis Law[4] and the Hammett $\sigma\rho$ relationships[1] are simply the most familiar examples, reduces to the expression

$$(\Delta G - \Delta G_0) = \rho(\Delta G^0 - \Delta G_0{}^0) \quad \text{or} \quad (\Delta G^{\ddagger} - \Delta G_0{}^{\ddagger}) = \rho(\Delta G^0 - \Delta G_0{}^0)$$

depending on whether it is an equilibrium or a rate that is being correlated with the reference reaction. In either case, the change in free energy (or free energy of activation), upon substitution, varies linearly with the change in free energy for a reference reaction with the same substitution. The reaction constant, ρ, is simply the proportionality constant. The original Hammett scheme used the pK_a of para-substituted benzoic acids as the reference reaction for three reasons: (i) the substituted benzoic acids were readily available, (ii) the physical property, in that case pK_a, was easily and reproducibly measurable, and (iii) the substituent and the site of ionization were remote from each other and separated by a polarizable spacer unit (the phenyl ring), presumably isolating electronic from steric effects. The comparable reference reaction for a gas-phase linear free energy relationship is without doubt the protonation of 4-substituted pyridines. The same three considerations apply, as would be concluded by a brief perusal of any compilation of proton affinities or gas-phase basicities. It remained only to find the appropriate reaction exothermicity to plot against the pyridine proton affinities to see if any correlation would appear.

Experimental Section

The supersonic jet flash pyrolytic radical source, the magnetic bottle time-of-flight photoelectron spectrometer, and the 10.49 eV laser photoionization source have all been previously described.[5] Cyanomethyl radical was generated by the pyrolysis of commercially available chloro-, bromo-, or iodoacetonitrile (from Aldrich, Fluka, and Fluka, respectively) at temperatures $>$1200 K (10 ms contact time). Even acetonitrile itself, when pyrolyzed at temperatures above 1600 K, yielded the same radical. All pyrolyses were first checked in the TOF mass spectrometer. Only for the iodo compound was there a visible mass peak for any species other than ${}^{\bullet}CH_2CN$. In that case, $I^{\bullet}$ with $IP[I^{\bullet}] = 10.45$ eV, was also observed. The ionization potentials of all other species lay above the 10.49 eV photon energy, rendering the precursors and side products invisible. Attempts at the pyrolytic preparation of the nitromethyl radical by pyrolysis of 2-nitroethyl nitrite or the α-halonitromethane were either inconclusive or unsuccessful. Accordingly, an ab initio study at the G-2 level of theory (see below) of its IP was conducted.

Most of the proton affinities for 4-substituted pyridines were taken from the compilation by Lias, Liebman, and Levin.[6] A few taken from other compilations[7] were corrected to the same reference value of $PA[NH_3] = 204.0$ kcal/mol. The remaining proton affinities, $PA[H-C{\equiv}C-C_5H_5N]$ and $PA[Ph-C_5H_5N]$, were measured by proton-transfer bracketing in an ion cyclotron resonance spectrometer.[8] 4-Phenylpyridine (Aldrich) was used as received. 4-Ethynylpyridine was synthesized by the procedure from Whiteford, Lu, and Stang.[9] Ab initio calculations for the Franck−Condon modeling of photoelectron spectra (to

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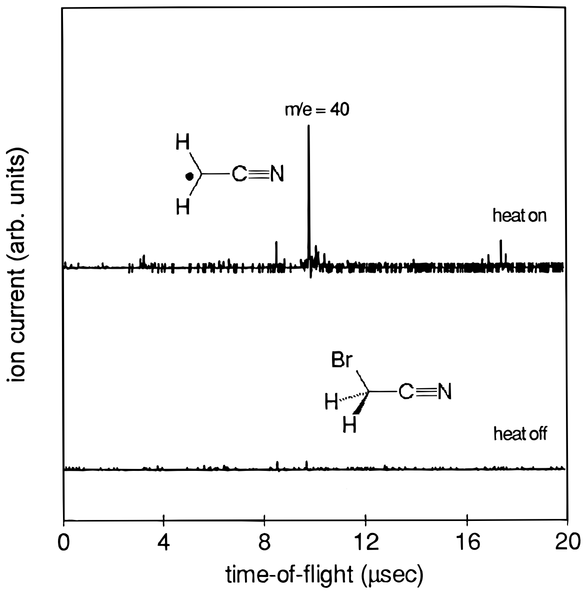


Figure 1. 10.49 eV photoionization TOF mass spectrum of unpyrolyzed and pyrolyzed bromoacetonitrile.

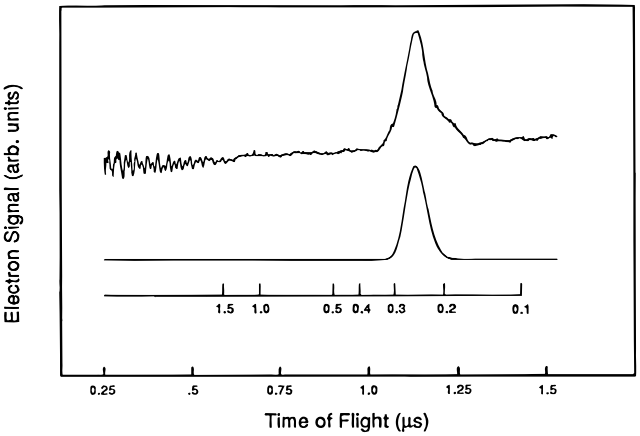
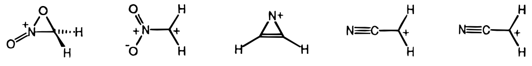


Figure 2. TOF photoelectron spectrum of the cyanomethyl radical produced by 10.49 eV laser photoionization, with a Franck–Condon simulation. A photoelectron kinetic energy scale (eV) is indicated below the spectrum.

determine the adiabatic IP) were done at the MP2/6-31G* level of theory on an IBM RS/6000-590 workstation using Gaussian 92[10] or Gaussian 94.[11] This level of theory has been shown to suffice for the geometries and force fields needed for Franck–Condon simulations.[5] Further calculations at the G-2 level of theory[12] were performed on nitromethyl radical and cation to predict the ionization potential. The claimed accuracy of the G-2 method for $\Delta H_{f,298}$ and IP's is ± 2 kcal/mol.

Results and Discussion

SCHEME 1: Heats of Formation for Nitromethyl and Cyanomethyl Cations, Computed at the G-2 Level for the Structures Found to be Minima at the MP2(full)/6-31G* Level of Theory[a]



	singlet	triplet	singlet	singlet	triplet
$\Delta H_{f,298}$ (kcal/mol)	238.5	287.8	284.2	298.3	366.6

[a] The same level of theory gives 29.1 and 63.8 kcal/mol for the nitromethyl and cyanomethyl radicals, respectively. Cartesian coordinates, energies, and frequencies for each structure are included in the Supporting Information.

The mass and photoelectron spectra of $^{\bullet}CH_2CN$ are shown in Figures 1 and 2. Franck–Condon modeling of the vibrational envelope for the photoelectron spectrum was also done to confirm the identity of the carrier of the spectrum and extract IP_{ad}. From the spectrum, the adiabatic ionization potential is read directly, yielding $IP_{ad}[^{\bullet}CH_2CN] = 10.30 \pm 0.04$ eV. Using the best available homolytic bond strengths,[13] one finds for cyanomethyl radical $\Delta H_{f,298}[^{\bullet}CH_2CN] = 60.4 \pm 2.1$ kcal/mol, which, with the ionization potential from this work, gives $\Delta H_{f,298}[^{+}CH_2CN] = 297.9 \pm 4.4$ kcal/mol for the "linear" cation. The latter number is considerably higher than the previously reported numbers[3,14] of $\Delta H_{f,298}[^{+}CH_2CN] = 287 \pm 1$ and 289 ± 1 kcal/mol, determined by electron impact appearance energies. The discrepancy was also one of the original motivations for the attempt at a correlation analysis. It should be noted that ref 3 reports an electron impact ionization energy of 10.30 ± 0.02 eV for the cyanomethyl radical but then assigns it to a nonadiabatic transition. The ab initio calculations and Franck–Condon simulation for cyanomethyl find the linear cation in a minimum on the $C_2H_2N^+$ potential surface. If there is a lower-energy cyclic isomer, as suggested in ref 3, then it is separated from the linear isomer by a potential barrier high enough to create a local minimum at the linear geometry.

The nitromethyl cation would constitute a yet more extreme case of an alkyl cation substituted by an electron-withdrawing group and was accordingly studied as well. Using again the best available bond strengths,[13] one finds $\Delta H_{f,298}[^{\bullet}CH_2NO_2] = 26.7 \pm 3.2$ kcal/mol, which compares well with the G-2 computed value of 29.1 kcal/mol.

A search for a minimum structure for the cation at the MP2(full)/6-31G* level of theory found a bridged, nonclassical singlet cation to lie below the classical triplet. $\Delta H_{f,298}[^{+}CH_2NO_2]$, computed with the G-2 method at the nonclassical singlet geometry, was predicted to be 238.5 kcal/mol. The triplet was found to lie 49.4 kcal/mol higher (see Scheme 1).

The proton-transfer bracketting experiment for 4-ethynylpyridine and 4-phenylpyridine yielded $PA[H{-}C{\equiv}C{-}C_5H_5N] = 222.3 \pm 1.1$ kcal/mol and $PA[Ph{-}C_5H_5N] = 224.6 \pm 0.5$ kcal/mol. The derived thermochemical data is listed in Table 1, along with the comparable data taken from the literature. It should be emphasized that Table 1 includes *all* of the cases for which both proton and hydride affinities have been determined. The proton and hydride affinities correspond to $-\Delta H_r$ for the two formal reactions below shown in Scheme 2. Comparison of canonical resonance structures as a basis for a correlation.

Note that cyanomethyl and nitromethyl, and 4-cyanopyridine and 4-nitropyridine, lie at the extreme end in both hydride and proton affinities. The substituted methyl cations and the last resonance structure for the protonated pyridine share a common relationship of the charge to the substituent, so it should be no surprise that a correlation can be made. If one makes the safe assumption that the entropy change in either of the two formal reactions is relatively constant as the substituent is varied, then enthalpies instead of free energies can be used in a LFER plot. Accordingly, a plot of the hydride affinity of substituted methyl cations against the proton affinity of substituted pyridines is shown in Figure 3. As is immediately evident from the plot, the points fall into two groups: the set of 11 points that fall on a straight line and the set of 6 that all lie off the line, mostly to one side. The point for cyanomethyl not only falls on the line but constitutes the most extreme point in that set by a large margin.

The principal conclusion is that, from the thermochemical point-of-view and contrary to previous suggestions,[3] $^{+}CH_2CN$ belongs in the same class of compounds as the undeniably resonance-stabilized cations such as allyl, propargyl, benzyl, and

TABLE 1: Proton and Hydride Affinities in kcal/mol

X	PA $[X-C_5H_5N]^a$	$\Delta H_{f,298}$ $[CH_3-X]^b$	$\Delta H_{f,298}$ $[^+CH_2-X]^b$	HA $[^+CH_2-X]^c$
$-N(CH_3)_2$	236.1	−5.7 ± 0.1	158	196.9
$-NH_2$	230.0	−5.5 ± 0.1	178	216.7
$-OCH_3$	227.6	−44.0 ± 0.1	157	234.2
$-C(CH_3)_3$	225.9	−40.0 ± 0.1	190	263.2
$-SCH_3$	225.9	−9.0 ± 0.1	194	236.2
$-CH_3$	225.2	−20.1 ± 0.05	215.6 ± 1.0	268.9
$-C_6H_5$	224.6 ± 0.5^d	12.0 ± 0.1	215.6 ± 2.1^e	236.8
$-CH_2CH_3$	224.6	−24.8 ± 0.1	211	269.0
$-CH{=}CH_2$	223.2	4.8 ± 0.2	226.0	254.4
$-C{\equiv}CH$	222.3 ± 1.1^d	44.6 ± 0.5	282	270.6
$-H$	220.8	−17.8 ± 0.1	261.3 ± 0.4	312.3
$-Br$	218.2	−9.1 ± 0.3	224	266.3
$-Cl$	217.8	−19.6 ± 0.1	229.2	282.0
$-F$	216.6	−59.0	199	291.2
$-CF_3$	212.8	−179.0 ± 0.7	120	332.2
$-C{\equiv}N$	210.3	17.69 ± 0.03^e	297.2 ± 2.2^d	312.7^d
$-NO_2$	208.5	−17.8 ± 0.15^e	238.5^f	289.5^f

[a] All values referenced to $PA[NH_3]$ = 204.0 kcal/mol. [b] Unless otherwise noted, data is taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. [c] Using $\Delta H_{f,298}[H^-] = 33.23 \pm 0.005$ kcal/mol from: Chase, M. W. Jr.; Davies, C. A.; Downey, J. R. Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed; ACS/AIP/NBS, 1985. [d] This work. [e] See ref 13. [f] Obtained from the G-2 calculation.

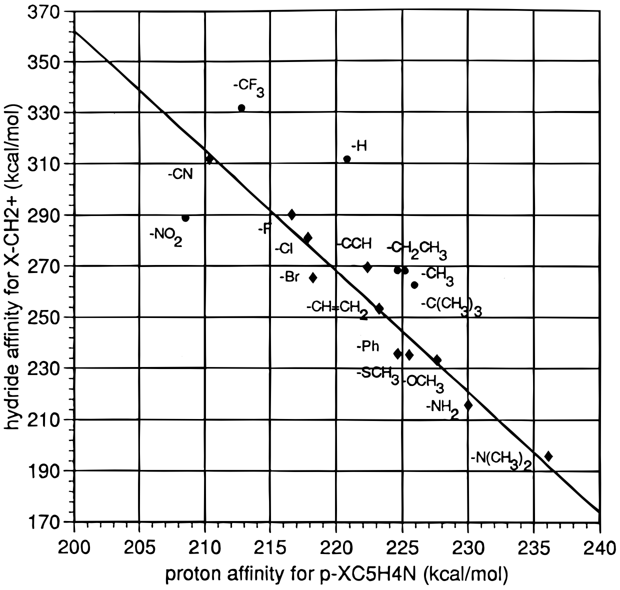
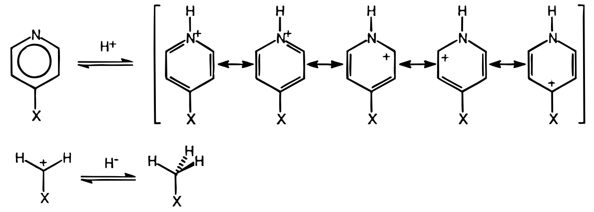


Figure 3. Plot of the hydride affinity of substituted methyl cations against the proton affinity of substituted pyridines. A least-squares fit through the 11 points representing resonance-stabilized cations is shown. The analytic expression for the line is HA = 1305 − (4.711 × PA), with 0.96 as the correlation coefficient. Points used in the regression are marked with diamonds, unused points with filled circles.

SCHEME 2: Comparison of Canonical Resonance Structures as a Basis for a Correlation



the π-donor-substituted methyl cations. Presumably, this means that cations with a −CN substituent are nevertheless resonance-stabilized despite strong inductive electron withdrawal. One could pose the counterargument that the linear correlation between hydride affinities and proton affinities says nothing about the interactions; the plot in this case would say only that whatever interactions are at work in the 4-substituted pyridinium cations work also for the substituted methyl cations, giving no information, however, about the nature of the interaction.

This counterargument founders, though, on the observation that those substituents that cannot interact by a resonance interaction, i.e., alkyl, −H, and even the strongly electron-withdrawing $-CF_3$, fall off of the line. Evidently, the charge in the heavily delocalized pyridinium cations interacts differently with a nonconjugating substituent than does a localized charge.

The final point to be made is that the correlation provides a means for the estimation of $\Delta H_{f,298}$ for a resonance-stabilized cation, which is itself often difficult to measure, starting from the proton affinity of a pyridine, which is much easier to determine. The prediction should be particularly useful for those cations that are not directly observable by dissociative ionization by virtue of fast rearrangement to a lower energy isomer. For example, 4-formylpyridine and 4-acetylpyridine have proton affinities[6] of 215.2 and 217.4 kcal/mol, respectively, which lead to predicted hydride affinities for the acyclic isomers of formylmethyl and acetylmethyl cations, which lead in turn to predicted values of $\Delta H_{f,298}[CH_2{=}CH{-}O^+] \sim 218$ and $\Delta H_{f,298}[CH_2{=}C(CH_3){-}O^+] \sim 196$ kcal/mol. Consequently, the resulting C−H and O−H homolytic dissociation energies[15] in the radical cations of acetaldehyde, acetaldehyde enol, acetone, and acetone enol are accordingly predicted to be: $\Delta H_{298}[\mathbf{H}{-}CH_2{-}CH{=}O^{\bullet+}] \sim 74$, $\Delta H_{298}[\mathbf{H}{-}O{-}CH{=}CH_2^{\bullet+}] \sim 89$, $\Delta H_{298}[\mathbf{H}{-}CH_2C(CH_3){=}O^{\bullet+}] \sim 76$, and $\Delta H_{298}[\mathbf{H}{-}O{-}C(CH_3){=}CH_2^{\bullet+}] \sim 90$ kcal/mol, which are all reasonable. Similarly, the adiabatic ionization potentials of the formylmethyl and acetylmethyl radicals are predicted to be $IP_{ad}[^\bullet CH_2CH{=}O] \sim 9.4$ and $IP_{ad}[^\bullet CH_2C(CH_3){=}O] \sim 8.9$ eV, using the radical heats of formation from Holmes and Lossing.[16] Similar estimations can be made for any radical and cation for which the appropriate pyridine is available for proton affinity measurements. One caution can be drawn from the case of nitromethyl cation. The published proton affinity for 4-nitropyridine of 208.5 kcal/mol, when inserted into the correlation, leads to a predicted $\Delta H_{f,298}[^+CH_2{-}NO_2] \sim 272$ kcal/mol. The G-2 computed $\Delta H_{f,298}[^\bullet CH_2NO_2]$ agrees well with experiment, but the computed $\Delta H_{f,298}[^+CH_2{-}NO_2]$ of 238.5 kcal/mol lies substantially lower than the estimate from the correlation. One can draw one of two possible conclusions. Either the bridged cation found by ab initio calculations is sufficiently different in character from the others that it should not fall on the line, or the experimentally determined proton affinity for 4-nitropyridine refers to O-protonation on the nitro group rather than protonation on the pyridine ring. There is insufficient evidence to make a definitive choice; however, the point is made that even deviations from the correlation yield information of chemical relevance.

Conclusion

We have reported a photoelectron spectrum for a simple radical that carries a strongly electron-withdrawing substituent. Combining the derived ion thermochemistry with proton affinities for 4-substituted pyridines produces a linear free energy relationship that spans a range of 28 kcal/mol in proton affinities and 120 kcal/mol in hydride affinities. The plot allows a classification of cations into those that are resonance-stabilized and those that are not and, furthermore, leads to predictions for ion thermochemistry that would be otherwise difficult or impossible to measure.

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Supporting Information Available: Franck−Condon factors for the cyanomethyl radical photoelectron spectrum, as well as Cartesian coordinates, absolute energies, and the frequencies for the nitromethyl and cyanomethyl radicals and cations from the ab initio calculations (10 pages). Ordering information is given on any current masthead page.

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