CD work[19] indicates that some bis(nucleotide) complexes of Pt(II) exhibit enhanced Cotton effects, similar in nature to the enhancement of the CD spectra of polynucleotides induced by low levels of *cis*Pt.[20-22] If the intracomplex base-base interactions found in this and previous studies reflect binding in the *cis*Pt-DNA complex, then large local distortions in the DNA structure would occur since the base-base overlap found here is dramatically different from that postulated for the various forms of DNA.[18,23]

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters and structure factor amplitudes of [(tn)-Pt(Me-5′-GMP)$_2$] (20 pages). Ordering information is given on any current masthead.

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Gas-Phase Heats of Formation of $C_2H_5^+$ and $C_3H_7^+$

Sir:

The $C_2H_5^+$ and $C_3H_7^+$ radical cations are among the most ubiquitous and important alkyl ions encountered in mass spectrometry. It is therefore surprising that there should still be a question concerning their gas-phase heats of formation. Yet this appears to be the case. Recently, Houle and Beauchamp[1] investigated the photoelectron spectra (PES) of a series of alkyl radicals. From these data, they derived heats of formation of the corresponding ions. These values are based on the heats of formation of the neutral radicals and on the assumption that the ion and neutral structures are sufficiently similar so that an adiabatic ionization energy can be obtained from the PES. Of course, the shape of the PES gives some indication as to whether this latter assumption is justified.

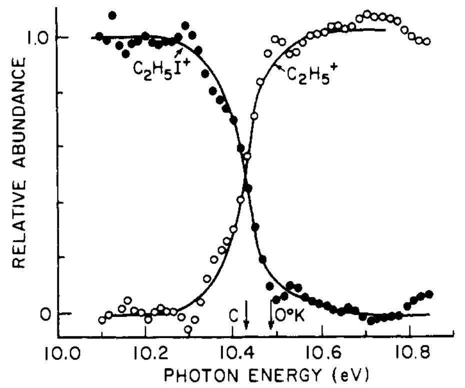

Figure 1. The breakdown diagram in the vicinity of the $C_2H_5^+$ onset. The arrow labeled C points to the crossover point, while the arrow labeled 0 K points to the calculated 0 K onset.

Ionic heats of formation can also be determined by dissociative photoionization of molecule whose neutral heat of formation is well established. The pitfalls in this approach are ion-pair formation, kinetic shift, and the presence of a reverse activation energy.

This communication reports on a photoionization and photoion-photoelectron coincidence (PIPECO)[2] study of $C_2H_5^+$ and $C_3H_7^+$ formation from C_2H_5I and C_3H_7I, respectively. The onset for $C_2H_5^+$ from ethyl iodide was investigated with particular care. The kinetic energy release was measured[3] and found to approach 0 at the dissociation onset, thereby making a significant reverse activation energy very unlikely. The I atom loss is the first dissociation event and it was found to be fast, thereby eliminating a kinetic shift in the onset. Finally, the onset was determined by both photoionization and PIPECO. In the latter experiment, the ion is measured in delayed coincidence with zero energy electrons. Therefore ion-pair formation ($C_2H_5^+ + I^-$) is not observed because the time correlation between $C_2H_5^+$ and I^- is different from that in $C_2H_5^+$ and its electron. Figure 1 shows the breakdown diagram in the vicinity of the $C_2H_5^+$ onset obtained by collecting $C_2H_5I^+$ and $C_2H_5^+$ ions in coincidence with threshold electrons. Our onset in a mass analyzed photoionization scan of $C_2H_5^+$ was 10.42 eV which agrees with the 10.42 ± 0.05 eV onset quoted by Akopyan et al.[4] These onsets are in agreement with the breakdown curve results suggesting that ion-pair processes are not very important.

The crossover point at 10.43 eV in Figure 1 is by definition the energy at which half of the $C_2H_5I^+$ ions have sufficient energy to dissociate. A 0 K onset can be calculated taking into account the internal thermal energy in ethyl iodide at 200 K. It has been amply demonstrated[5] that thermal vibrational and rotational energy in the precursor molecule is available for dissociation. With these assumptions, a 0 K onset of 10.49 eV is calculated. Using the 0 K heats of formation for C_2H_5I and I given in Table I, the 0 K heat of formation of $C_2H_5^+$ is calculated to be 218.2 ± 1.0 kcal/mol.

To convert this value to a 298 K heat of formation, we consider the fundamental equation:

$$2C(s) + {}^5\!/\!_2H_2 \rightarrow C_2H_5^+ + e^- \qquad (1)$$

The heat reaction is by definition the heat of formation of

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Table I. Standard Heats of Formation

	kcal/mol	
	$\Delta H_f°(0\ K)$	$\Delta H_f°(298\ K)$
I	25.631[a]	25.535[a]
C_2H_5I	1.95[a]	−1.84[a]
i-C_3H_7I	−4.5	−9.8[b]
$C_2H_6^+$	218.2 ± 1.0	215.3 ± 1.0, 219,[a] 219.2 ± 1.0[c]
$C_3H_7^+$	195.4 ± 1.0, 196.5[d]	190.8 ± 1.0; 191,[a] 187.3 ± 1.0[c]

[a] Reference 6. [b] Reference 7. [c] Reference 1. [d] Calculated using 11.59-eV 0 K onset for H loss from C_3H_8 from ref 8.

$C_2H_5^+$. This equation is the definition at 0 K as well as at 298 K. The difference in the heats of reaction at 298 and 0 K is the difference in the enthalpy changes (vibrational, rotational, and translational) at 298 and 0 K. At 0 K; the internal energy is 0 on both sides of eq 1. Therefore, the difference in $\Delta H_f°$(298 K) and $\Delta H_f°$(0 K) is just the 298 K enthaloy difference between right- and left-hand sides of eq 1. We ignore the energy of the electron by assuming that it is 0 at all temperatures in accordance with the suggestion of Rosenstock et al.[6] This calculation leads to a 298 K heat of formation of 215.3 kcal/mol for $C_2H_5^+$. A similar analysis was carried out for the $C_3H_7^+$ ion, although only the photoionization results were used for determining the onset. The results are listed in Table I along with values reported by other workers.

No other reliable values obtained by dissociative photoionization exist for $C_2H_5^+$. Chupka and Berkowitz[8] obtained an onset for $C_2H_5^+$ from C_2H_6, but, because this onset is over 0.5 eV above the onset for C_2H_4, the former onset is subject to a considerable kinetic shift arising from the competition between the two dissociation paths. On the other hand, their $C_3H_7^+$ onset[8] from C_3H_8 is the lowest energy fragmentation channel and is therefore not affected by a kinetic shift. It agrees reasonably well with our value.

Of particular interest is the large discrepancy between the values for the heat of formation of $C_2H_5^+$. The two values of 219 kcal/mol are both based on the ionization energy of the C_2H_5 radical which has been measured to be 8.39 ± 0.01 by numerous techniques.[9] However, the photoelectron band is broad and there may be some question as to whether this value is in fact the adiabatic ionization energy. The 4-kcal/mol discrepancy corresponds to 0.17 eV which would place the adiabatic ionization energy at 8.21 eV, just at the beginning of the PES band.

The other uncertainty in the heat of formation of $C_2H_5^+$ as determined by the PES of C_2H_5 is the heat of formation of C_2H_5. Houle and Beauchamp[1] have reviewed these values and it appears that the heat of formation of C_2H_5 is, if anything, >25.7 kcal/mol and not 4 kcal/mol less as would be required by our results.

These discrepancies in the heats of formation, particularly in the case of $C_2H_5^+$, which are far beyond the experimental uncertainties of the studies mentioned here, seem to suggest that the structures of C_2H_5 and $C_2H_5^+$ are different. This is contrary to what is known about the very similar system CH_3 and CH_3^+. Further work, particularly ab initio calculations, may shed some light on this problem.

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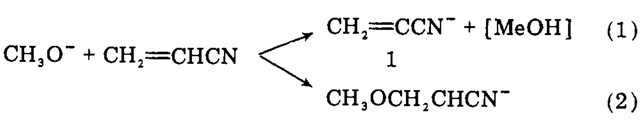
Solvent Effects on Ion-Molecule Reactions. Vinyl Anions vs. Conjugate Addition

Sir:

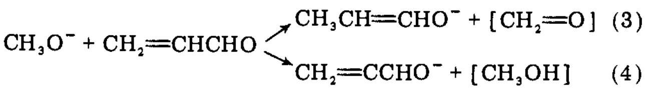
The removal of all solvation from chemical species can drastically alter both their orders of reactivity[1] and the mechanisms by which they react.[2] We report here that the products of the reaction in the gas phase of methoxide with such α,β-unsaturated species as acrylonitrile depend on whether the methoxide is bare or monosolvated.

In a trapped ICR spectrometer,[3] acrylonitrile reacts with methoxide, formed by thermal electron impact on methyl nitrite,[4] to give only the M − 1 anion of the nitrile. No M + 31 ion from the conjugate addition reaction 2 is observed, even though addition is the principle mode of reaction in the condensed phase.[5] We assume the α proton is the acidic one, based on solution phase analogues[6] and the favorable resonance structures which may be drawn. Vinylic anions have been made previously in the gas phase by deprotonation of methyl vinyl ether,[7] although a much stronger base was required in that case. Ethylene is at least 24 kcal/mol less acidic than methoxide, however.[8] The remaining two protons in the M − 1 anion **1** exchange in the presence of CH_3OD.[9] The acidity of acrylonitrile may be determined by reversible equilibration of **1** with compounds of known acidity[10] such as acetonitrile. We find acrylonitrile to be 2.0 kcal/mol more acidic than its saturated analogue, propionitrile, consistent with sp[2] carbon being more electronegative than sp[3] carbon[11] both as the carbanionic site and as the substituent.



$$CH_3O^- + CH_2{=}CHCN \begin{array}{l} \nearrow CH_2{=}\underset{1}{C}CN^- + [MeOH] \quad (1) \\ \searrow CH_3OCH_2CHCN^- \quad (2) \end{array}$$

Similar reactivities are seen for acrolein and nitroethylene: deprotonation by methoxide to give an M − 1 anion, but no addition to yield an M + 31 ion. Competing side reactions have prevented determination of the acidities of these two compounds. The hydride transfer reaction 3 is a factor of 2 slower than proton transfer 4, and has precedence in the literature.[12] Corresponding M + 1 ions are not seen for nitroethylene or acrylonitrile. Using literature $\Delta H_f°$(298) values,[10,13] we obtain −19.0 kcal/mol for $\Delta H°$ (eq 3), −15 kcal/mol for the corresponding hydride transfer to acrylonitrile, and −36 kcal/mol for nitroethylene. Further investigation is in progress to determine why the other hydride transfers do not occur. A large amount of the radical anion of nitroethylene was also observed in all experiments with that compound. Double resonance indicates this arises both from electron transfer from methoxide[14] and from direct attachment of thermal electrons.[15]



$$CH_3O^- + CH_2{=}CHCHO \begin{array}{l} \nearrow CH_3CH{=}CHO^- + [CH_2{=}O] \quad (3) \\ \searrow CH_2{=}CCHO^- + [CH_3OH] \quad (4) \end{array}$$

The preference for substitution rather than addition reactions in the gas phase can be ascribed to the instability of addition products when they are formed with excess energy. In the condensed phase, this energy of reaction is removed by the

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