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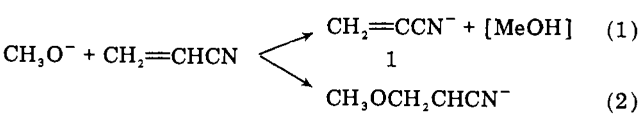
Solvent Effects on Ion-Molecule Reactions. Vinyl Anions vs. Conjugate Addition

Sir:

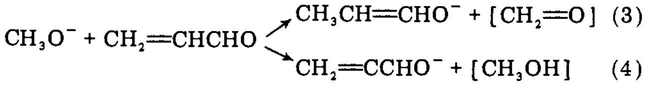
The removal of all solvation from chemical species can drastically alter both their orders of reactivity[1] and the mechanisms by which they react.[2] We report here that the products of the reaction in the gas phase of methoxide with such α,β-unsaturated species as acrylonitrile depend on whether the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



$$CH_3O^- + CH_2{=}CHCN \rightarrow \underset{\mathbf{1}}{CH_2{=}CCN^-} + [MeOH] \quad (1)$$
$$CH_3O^- + CH_2{=}CHCN \rightarrow CH_3OCH_2CHCN^- \quad (2)$$

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]



$$CH_3O^- + CH_2{=}CHCHO \rightarrow CH_3CH{=}CHO^- + [CH_2{=}O] \quad (3)$$
$$CH_3O^- + CH_2{=}CHCHO \rightarrow CH_2{=}CCHO^- + [CH_3OH] \quad (4)$$

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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solvent, thus stabilizing addition intermediates, while, in the gas phase, the excess energy causes such an intermediate either to revert to reactants or to fragment in a different manner to products. There are several ways in the gas phase to remove this excess energy and obtain addition products: by collision with a third body,[16] by radiative emission,[14,17] and by using a single molecule of solvent.[18] The first two methods do not occur for the reactants and pressures used in this work; we have utilized monosolvation of the anion as a means of stabilizing the M + 31 ions.

Using the Riveros reaction

$$CH_3O^- + HCO_2CH_3 \rightarrow CO + \underset{\mathbf{2}}{CH_3O^-\cdot\cdot HOCH_3} \qquad (5)$$

to generate a monosolvated methoxide,[19] we have reacted **2** with $CH_2{=}CHCN$, $CH_2{=}CHCHO$, and $CH_2{=}CHNO_2$. In all three cases, an M + 31 anion is the major product. Double resonance ejection indicates that it arises exclusively from **2**. Some M − 1 ion is also seen in these experiments, but it comes from reaction with bare methoxide, since reactions 1 and 5 proceed at comparable rates ($\sim 3 \times 10^{-10}$ cm molecule^{-1} s^{-1}). The basicity and $\Delta G_f°$ (298) of **2** may be estimated from literature values for the bonding energy of such cluster ions;[20] we obtain $\Delta G_f°$ (298) (**2**) = -135 ± 5 kcal/mol. This inplies that deprotonation of acrylonitrile by **2** is endergonic by 9 kcal/mol (the monosolvation reduces methoxide basicity by ~18 kcal/mol), but the observed addition of methoxide is near ergoneutral.

A true Michael addition involves a carbanionic nucleophile. Adding acetaldehyde to **2** results in an interchange of anions and production of monosolvated enolate **3**:

$$CH_3O^-\cdot\cdot HOCH_3 + CH_3CHO \rightarrow \underset{\mathbf{3}}{CH_2{=}CHO^-\cdot\cdot HOCH_3} + CH_3OH$$

Reaction of **3** with acrylonitrile gives only a trace of M + 43 anion at long times. This small yield is not necessarily due to the Michael addition being slow, but rather to it being the fourth reaction in the sequence, and simply commencing too late in the sequence to be observed, relative to collisional ion loss from the ICR cell.

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Clusters and Catalysis: On the Requirement for Multinuclear Centers to Catalyze the Hydrogenation of Carbon Monoxide

Sir:

Efficient homogeneous catalysis by mononuclear complexes of certain "difficult" reactions, such as methanation and Fischer–Tropsch synthesis, has not been achieved. It has been suggested that the lack of activity may be due to a requirement for multinuclear metal centers to activate the substrate sufficiently.[1] Early impetus in this direction was provided by experiments which showed that in toluene solution mononuclear carbonyl complexes were inactive for methanation, whereas some cluster complexes were active.[2] However, coordinatively unsaturated species in solution can readily oligimerize,[3] most carbonyls (including all of the mononuclear complexes) undergo decomposition[4] at temperatures below that expected for efficient catalysis of methanation,[5] and the activities of even the cluster complexes are extremely low;[6] so the results are not definitive. Further, in experiments similar to those used to test for methanation activity,[2] the mononuclear group 6b hexacarbonyls were found to be inactive for the hydrogenation of ethylene at 140 °C[7] and it has been previously reported that after photolysis these materials are inactive for the hydrogenation of monoolefins at 25 °C.[8,9] Since this reaction is facilely catalyzed by a number of homogeneous *mononuclear* complexes, the inability to catalyze the much more difficult reduction of CO may reflect the inactive form of the catalysts and not their mononuclear nature.

It has recently been demonstrated that temperature programmed decomposition (TPDE) of carbonyls *adsorbed on silica or alumina* leads to the formation of novel subcarbonyl species which are highly dispersed and which can be stable to >250 °C,[10-13] a temperature sufficient for catalysis of methanation over supported metals.[5] It was also shown that small amounts of CH_4 were formed during the TPDE in flowing He of some *mononuclear* carbonyls.[10-13] Further, both thermal activation (near 150 °C) as well as photolytic activation (near ambient) of the group 6b hexacarbonyls supported on alumina yields catalysts which are extremely active for olefin hydrogenation,[12,14] being far more active than "traditional"[15] heterogeneous catalysts of these metals. Hence, these catalysts should be especially well suited for the investigation of the reduction of CO. Since the above proscription on methanation

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