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What Ion Is Generated When Ionizing Acetonitrile?

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It has long been assumed that ionizing neutral acetonitrile produces ions with the same atomic connectivity, $CH_3CN^{+\bullet}$. Recent calculations on the $C_2H_3N^{+\bullet}$ potential energy surface have suggested that it may be difficult to generate pure $CH_3CN^{+\bullet}$ when ionizing acetonitrile. We have probed the interconversion of $CH_3CN^{+\bullet}$ and its lower energy isomer $CH_2CNH^{+\bullet}$ by calculation, collision-induced dissociation mass spectrometry and ion−molecule reaction. The latter ion, ionized ketenimine, is co-generated upon electron or chemical ionization of neutral acetonitrile in the ion source of a mass spectrometer. An estimate of the ratio of the two isomers can be obtained from their respective ion−molecule reactions with CO_2 or COS. $CH_3CN^{+\bullet}$ reacts by proton-transfer with CO_2 and charge transfer with COS, whereas $CH_2CNH^{+\bullet}$ is unreactive.

It has long been assumed that ionizing neutral acetonitrile produces ions with the same atomic connectivity, $CH_3CN^{+\bullet}$ (**1**).[1−3] Other $C_2H_3N^{+\bullet}$ include $CH_3NC^{+\bullet}$ (assumed to be formed by ionizing isocyanomethane), whereas dissociative ionization of larger nitriles has been shown to yield a different structure that has been assigned to ionized ketenimine $CH_2CNH^{+\bullet}$ (**2**).[1−3] Dissociative ionization of imidazole and pyrazole was postulated to produce the linear $CHCHNH^{+\bullet}$ structure.[1] These assignments are based on the relative peak heights in CID mass spectra. The key distinguishing factor that has been used in the literature is the CH_2^+/CH_3^+ (*m*/*z* 14:15) ratio.[1−3] In all cases, structure **1** (assumed to be generated by ionizing acetonitrile) was characterized by a peak at *m*/*z* 15 that has roughly twice the relative abundance as that for **2** (generated by dissociative ionization of butyronitrile).[1−3] This holds true for our CID experiments done on the Rome VG Micromass ZABSpec oa-TOF under conditions of high mass resolution.[4] In the present experiments, the CID of ionized acetonitrile yielded a mass spectrum with a ratio of *m*/*z* 14:15 of 10, whereas the $C_2H_3N^{+\bullet}$ ion generated from dissociative ionization of butyronitrile gave a ratio of 24. A ratio of 22 was obtained for the $C_2H_3N^{+\bullet}$ ion formed upon dissociation of protonated chloroacetonitrile. The absolute value of the *m*/*z* 14:15 ratio varies with instrument,[1−3] the reason for which will become apparent below.

The formation of pure ions **1** upon ionization of acetonitrile has recently been called into question by Choe[5] and Mair et al.[6] Choe reported kinetic energy distribution analysis of the H loss channel in **1** and mapped the interconversion of several of the isomers at the B3-LYP/6-311++G(3df,3pd) level of theory. We have examined the interconversion of **1** and **2** at the G3[7] level of theory (employing optimized MP2/6-31+G(d) geometries), and our results are in excellent agreement with Choe's work. Calculations at the G3 level of theory place **2** 232 kJ mol^{-1} lower in energy that **1**. The conversion of **1** to **2** requires a 1,3-hydrogen shift that lies 70 kJ mol^{-1} above **1** (Figure 1). The lowest energy dissociation channel for **1** is H loss to form the cyclic *c*-$CHCHN^+$ ion,[8] a process that lies 100 kJ mol^{-1} above the G3 1,3-H shift barrier.[9] Dissociation to $^+CH_2CN$ is 50 kJ mol^{-1} higher in energy.[11] RRKM calculations predict that the rate constant for the forward isomerization of **1** to **2** is 4−5 orders of magnitude greater than the reverse reaction and is greater than 10^9 s^{-1} just 2 kJ mol^{-1} above the threshold. The dissociation rate constant for metastable ions (ions with energies

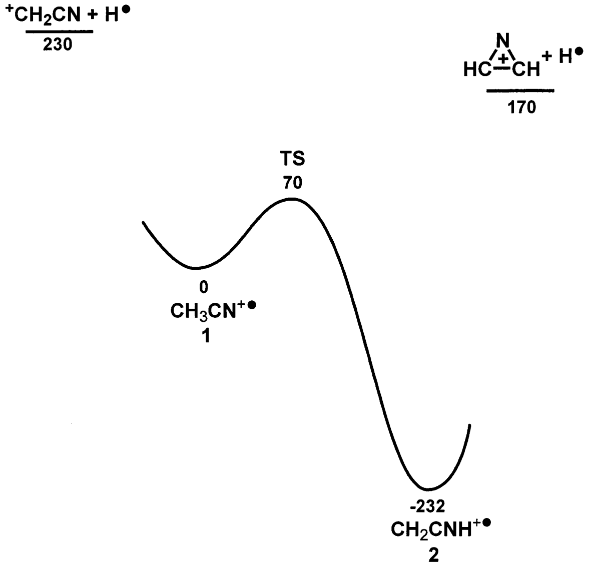

Figure 1. Potential energy diagram for the interconversion of $CH_3CN^{+\bullet}$ and $CH_2CNH^{+\bullet}$ (calculated at the G3 level of theory) and their lowest energy dissociation products (see text).

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TABLE 1: Gas-Phase Reactivity of $C_2X_3N^{+\bullet}$ (X = H, D) from Acetonitrile Toward Selected Neutrals N

source	X	N(IE)[a]	PA[b]	k_{exp}[c]	ϕ[d]
EI	D	CO_2(13.78)	541	2.2 (10%)	0.27
EI	D	CH_3F(12.50)	599	6.2 (25%)	0.36
EI	D	COS(11.18)	629	7.1 (70%)	0.60[e]
EI	D	CH_3CN(12.20)	779	7.8 (100%)	0.25[f]
CI	H	CO_2(13.78)	541	3.2 (50%)	0.38
CI	H	N_2O(12.89)	550	2.0 (25%)	0.23

[a] Ionization energies (IE) in eV are given in parentheses and are from ref 13. [b] Proton affinity (PA) values in kJ mol^{-1} are from ref 13. [c] Phenomenological rate constants in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, at the temperature of the FT-ICR cell of 300 K. The percentage of the ion population that is reactive is given in parentheses. The complement to 100% is unreactive. [d] $\phi = k_{exp}/k_{coll}$. k_{coll} was calculated using the ADO version of collision theory.[19] [e] Charge-transfer reaction [f] This reaction also proceeds by charge transfer, as side process (10%) with respect to X^+ transfer.

TABLE 2: Gas-Phase Reactivity of $CH_2CNH^{+\bullet}$ (from $CH_3CH_2CH_2CN$) toward Selected Neutrals N[a]

N (IE)[b]	PA[c]	k_{exp}[d]	ϕ[e]
CO_2 (12.50)	540.5		
COS (11.18)	628.5		
CH_3NO_2 (11.08)	754.6	0.13	0.004
CH_3CN (12.2)	779	5.9	0.18

[a] Reagent ion obtained upon EI of n-C_3H_7CN at 27 eV electron energy. [b] Ionization energies (IE) in eV are given in parentheses and are from ref 13. [c] Proton affinity (PA) values in kJ mol^{-1} are from ref 13. [d] Phenomenological rate constants in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, at the temperature of the FT-ICR cell of 300 K. [e] $\phi = k_{exp}/k_{coll}$. k_{coll} was calculated using the ADO version of collision theory.[19]

above threshold for dissociation) is small enough that equilibration of the two structures precedes decomposition, which obviously heavily favors structure **2**. Note that this does not affect ions **1** that are formed with internal energies below the isomerization barrier. At an internal energy of 4 eV, isomerization of **1** to **2** is 10−100 times faster than dissociation to $^+CH_2CN$ + H and remains marginally faster at internal energies up to 20 eV. So any **1** with internal energies above the barrier but less than 20 eV will spontaneously isomerize to **2** (in Choe's work, due to differences in calculated dissociation and isomerization thresholds, this upper limit to complete isomerization is ∼ 4 eV; with a molecular system this small, $k(E)$ is very sensitive to small changes in activation energy and entropy).[5] Therefore, the CID mass spectra mentioned earlier are necessarily characterizing mixtures of structures **1** and **2**, with slightly more **1** being present when acetonitrile is ionized as compared to when butyronitrile or chloroacetonitrile are dissociatively ionized. This conclusion was also drawn by Choe[5] and is consistent with a recent surface-induced reaction study by Mair et al.[6] It also accounts for some of the observed variation in the CID mass spectra between instruments (in which source conditions and experimental time scales will all be slightly different).[1−3]

Since it appears to be impossible to generate pure **1** under these experimental conditions, something other than CID mass spectra must be used to characterize **1** and **2**. The PA of the two ends of $^\bullet CH_2CN$ are very different (PA(C) = 524 kJ mol^{-1} and PA(N) = 763 kJ mol^{-1})[12] suggesting that the composition of the two isomers in a population of $C_2H_3N^{+\bullet}$ ions can be probed by examining ion−molecule reactions involving proton transfer. However, neutral substrates that have a PA between these two values may assist the proton transfer (proton transport catalysis)[15−17] thereby altering the ratio of **1** to **2** in the population. Charge transfer is another possiblity due to the different IE values of acetonitrile (12.2 eV) and ketenimine (8.7 eV, G3 value). To probe these reactions, CX_3CN (X = H, D) was ionized in the external ion source of a 4.7 T Bruker Apex TM 47e FT-ICR mass spectrometer[18] using 23 eV electrons. The resulting mixture of $C_2X_3N^{+\bullet}$ ions was led into the ICR cell and isolated from any other undesired species using low energy "single shots". The selected ions were then allowed to react with various substrates (Table 1) that were admitted at a constant pressure of 1×10^{-8}−4×10^{-8} mbar by a needle valve from an inlet system. The pressure readings obtained by an ion gauge were calibrated according to standard procedures.[18] Because ions that are transferred from the external source into the cell have excess kinetic energy, a routine practice consists of pulsing an unreactive gas into the cell to bring the ions to thermal equilibrium. However, this procedure was not adopted in the present experiments because in the time required for this sequence a significant portion of the original $C_2X_3N^{+\bullet}$ ion population would have already reacted with the neutral, depleting the relative amount of the most reactive isomer. As a consequence, kinetic measurements yield phenomenological rate constants and may not be representative of thermally equilibrated species. It is well documented in gas phase ion chemistry that translational excitation of the reagent ion typically results in a decreased efficiency for an exothermic reaction. Operating in this way, in all cases (except for N = CH_3CN), two populations of ions were observed, a reactive fraction (either due to proton or charge transfer) and an unreactive one. The reactions with CO_2, CH_3F, and CH_3CN occur by proton-transfer, whereas the reaction with COS was by charge-transfer alone. We are grateful to Philippe Mourgues for suggesting this reagent, also cited in a communication by Vinogradov in ref 6.

When $C_2H_3N^{+\bullet}$ ions were generated from the dissociative ionization of butyronitrile, they showed no reactivity with CO_2 or COS, indicating that butyronitrile is a source of pure ions (Table 2). Due to the fact that both molecules have PAs below 763 kJ mol^{-1} and IEs greater than that of neutral CH_2CNH, it seems most likely that this unreactive population of ions has structure **2**. This in turn means that the reactive fraction of ions in Table 1 must be due to those having structure **1**. The only other thermodynamically stable isomer on the calculated potential energy surface that could be accessed from **1** is $CH_2NCH^{+\bullet}$ (the barrier leading to this isomer from **2** is comparable to that leading from **2** to **1**).[5] However, the PA of the isonitrile carbon in $^\bullet CH_2NC$ is 790 kJ mol^{-1} and the IE of CH_2NCH is 7.9 eV (G3 value), so none of the reactions in Table 1 would proceed if this were the structure formed.[20]

To produce ionized acetonitrile (**1**) near threshold (and thus produce more ions below the isomerization barrier), charge exchange from ionized xenon was employed in the external ion source. The IE of Xe (12.13 eV) is slighly lower than that of acetonitrile (12.2 eV), and so charge transfer to acetonitrile will be slightly endothermic, resulting in lower internal energy ions **1**. The bulk Xe pressure was 6.6×10^{-5} mbar and only a trace of CH_3CN was introduced to avoid direct ionization. The results for the ensuing ion molecule reactions with CO_2 and N_2O are shown in Table 1. For CO_2, it is clear that a larger population of reactive ions is present, consistent with a greater population of **1** formed in the ion source.

So it is evident that it is very difficult to generate ionized acetonitrile ions in their unrearranged form. The thermal rotational and vibrational internal energy distribution of neutral acetonitrile extends beyond the 70 kJ mol^{-1} 1,3-H shift barrier. So, even threshold ionization with photons results in enough **1** made above the barrier that the observed rate constant for conversion to **2** is greater than zero (25 s^{-1}).[22] Any photon or electron energy above the threshold will therefore result in a greater observed rate constant and hence even less **1**. So, any ionization method other than perhaps threshold coincidence spectroscopy of cold neutral acetonitrile molecules will inevitably generate ionized ketenimine as a coproduct. Because of this, and the sensitivity of the ratio of the two structures to internal energy and the time scale of observation, CID mass spectrometry is not the best tool to quantify the amount of **1** in a given population. Ion−molecule reactions remain the most reliable way of estimating the fraction of **1** in any environment.

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(12) PA(C) was obtained from the known $\Delta_f H$ values[13] for CH_2CN, H^+ and CH_3CN^+ and PA(N) was from ref 14.

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(22) Let us assume thresold ionization of CH_3CN with 12.2 eV photons. The internal energy distribution of the resulting ions will be the same as that of the 298 K neutral. The observed rate constant for the reaction **1** → **2** is given by $k_{obs} = \int P(E,T)k(E)\,dE$, where $P(E,T)$ is the ro-vib internal energy distribution at 298 K and $k(E)$ is the 0 K microcanonical rate constant. Calculated over the ion internal energy range 1 to 100 kJ mol^{-1} (k_{obs} comes from the part of the population above 70 kJ mol^{-1}), k_{obs} comes out to ∼ 25 s^{-1}. Since this is too slow to be significant on the time scale of the ion source residence time on most mass spectrometers, it should be possible to make NEARLY pure **1** (but never absolutely pure **1**). The energy distribution of the ionizing species will make it even harder to make pure **1**.