

JMS Letters

Dear Sir,

Acetonitrile in Chemical Ionization of Monounsaturated Hydrocarbons: a ^{13}C and ^2H Labeling Study

Acetonitrile is an interesting reactant for the chemical ionization (CI) of long-chain hydrocarbons,^{1,2} leading to abundant $[\text{M} + \text{CH}_2\text{CN}]^+$ cations. In contrast to what is usually observed with the electron ionization (EI)³ and $\text{CI}(\text{CH}_4)$ ⁴ mass spectra of this class of compounds (e.g. the dependence of the mass spectra on the ion source temperature), the production of the $[\text{M} + \text{CH}_2\text{CN}]^+$ adduct was proved¹ to be independent of the ambient temperature in the range 30–200 °C. Previous studies^{1,2} on acetonitrile as a CI reactant gas were carried out using an ion trap mass spectrometer, which is able to separate in time the generation of reactant ions from the CI of analytes, thus being particularly effective.

By introduction of acetonitrile into a Saturn 2000 (Varian, Walnut Creek, CA, USA) ion trap with an ionization time of 100 μs and a sample vapor pressure (as read directly on the ion gauge) of 3×10^{-5} Torr (1 Torr = 133.3 Pa), the mass spectrum shown in Fig. 1(a) was obtained. It consists of three main ionic species at m/z 40 $[\text{M} - \text{H}]^+$, 42 $[\text{M} + \text{H}]^+$ and 54. The last ionic species can be attributed in principle to two different elemental compositions, $\text{C}_3\text{H}_4\text{N}$ or $\text{C}_2\text{H}_2\text{N}_2$. Since the ions at m/z 54 and the $[\text{M} - \text{H}]^+$ ions were found to appear simultaneously in the spectrum, it seemed reasonable

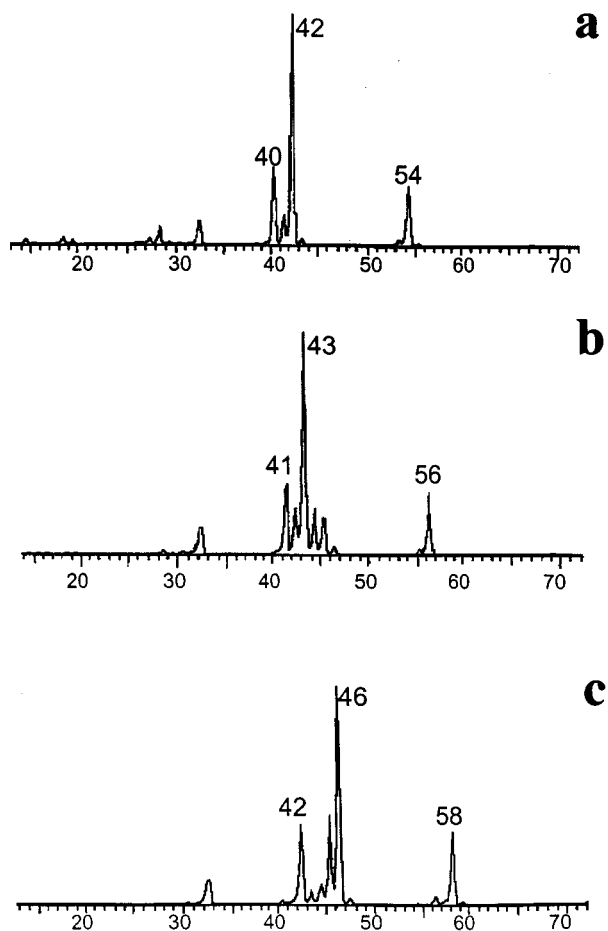
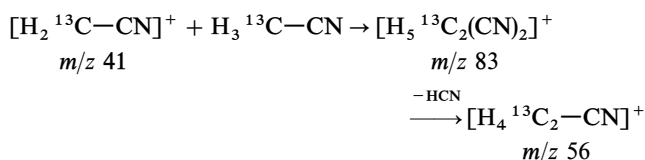


Figure 1. Ion trap EI mass spectra of (a) CH_3CN , (b) $^{13}\text{CH}_3\text{CN}$ and (c) CD_3CN .

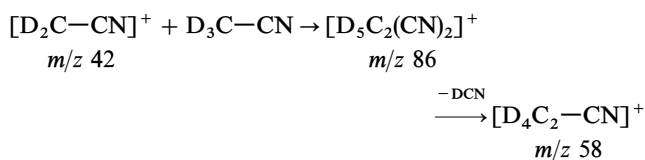
to assume that the species at m/z 54 corresponding to $\text{C}_3\text{H}_4\text{N}^+$ originate from reaction of $[\text{M} - \text{H}]^+$ ions with neutral CH_3CN . This hypothesis was supported by accurate mass measurements performed on this ionic species produced by EI of acetonitrile in the conventional ion source of a VG ZAB 2F mass spectrometer, operating in the CI mode with a sample vapor pressure of 1×10^{-5} Torr (calculated for $\text{C}_3\text{H}_4\text{N}$, 54.0343; found, 54.0322 ± 0.003).

In order to gain insight into the formation and reactivity of the ionic species at m/z 54 formed in the ion trap, studies were carried out on both ^{13}C - and ^2H -labeled acetonitrile. The mass spectrum obtained on introducing $^{13}\text{CH}_3\text{CN}$ (molecular mass 42) into the ion trap is shown in Fig. 1(b). As can be seen, three main ionic species are detected at m/z 41 $[\text{M} - \text{H}]^+$, 43 $[\text{M} + \text{H}]^+$ and 56. The shift of two mass units for the last ionic species clearly indicates the presence of two ^{13}C in its structure, formally corresponding to $[\text{M} - \text{H}] + ^{13}\text{CH}_2]^+$. For its formation, the following reaction pathway can be proposed:



The activation complex $[\text{H}_5 \text{ } ^{13}\text{C}_2(\text{CN})_2]^+$, not detectable in the spectrum, gives rise, through the neutral loss of HCN, to the ion $[\text{H}_4 \text{ } ^{13}\text{C}_2\text{H}_4\text{N}]^+$ at m/z 56.

This hypothesis was confirmed by examining the behavior of the deuterated derivative CD_3CN (molecular mass 44); its mass spectrum shows [see Fig. 1(c)] the presence of abundant ions at m/z 42 $[\text{M} - \text{D}]^+$, 46 $[\text{M} + \text{D}]^+$ and 58. The last species can be attributed to $[(\text{M} - \text{D}) + \text{CD}_2]^+$, invoking for its formation a reaction pathway perfectly superimposable on that reported above:

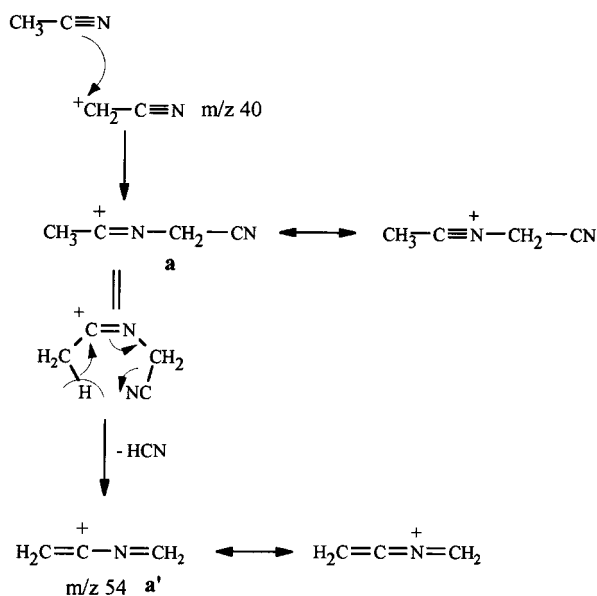


Again, the activation complex is not detected in the spectrum.

The mechanism proposed for the formation of the ionic species at m/z 54 from CH_3CN is outlined in Scheme 1. An addition reaction between the $^+\text{CH}_2-\text{CN}$ species and the polar $\text{C}\equiv\text{N}$ bond of acetonitrile yields an intermediate species **a** which is resonance stabilized. From this intermediate species **a**, species **a'** at m/z 54 can then be formed by loss of HCN via a favorable concerted rearrangement reaction.

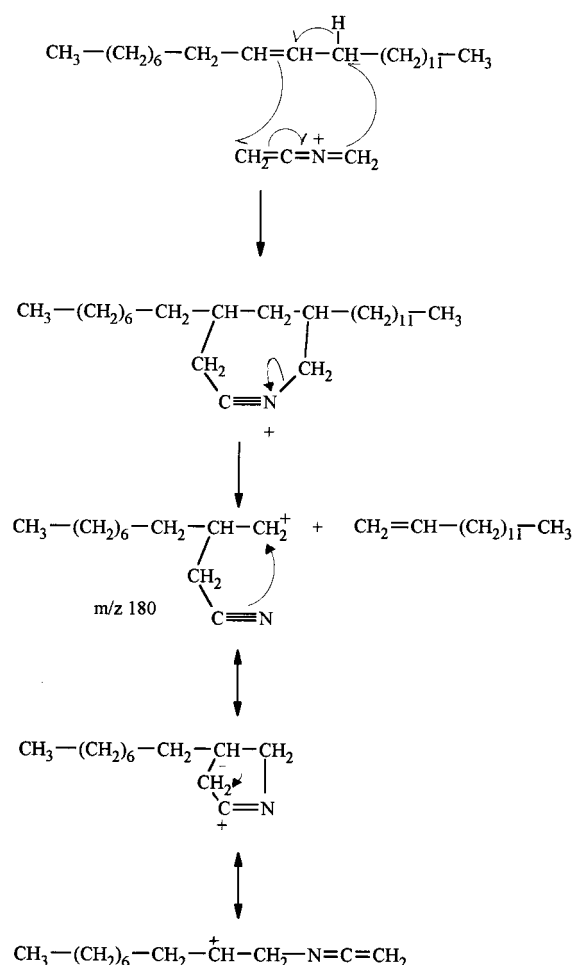
In a previous investigation,² it was observed that the $[\text{M} - \text{H}]^+$ species of CH_3CN shows high reactivity towards long-chain saturated hydrocarbons, whereas the species at m/z 54 appears to be selective for unsaturated hydrocarbons. In that study, it was emphasized that in the $\text{CI}(\text{CH}_3\text{CN})$ mass spectrum of monounsaturated hydrocarbons of molecular mass M , together with $[\text{M} + 40]^+$ and $[\text{M} + 54]^+$ ions, two diagnostic fragment ions were always observed. Their formation could be rationalized by addition of species **a'** at m/z 54 on each of the two C atoms of the double bond [Fig. 2(a)].

Performing the same CI experiments on monounsaturated hydrocarbons using $^{13}\text{CH}_3\text{CN}$ or CD_3CN as reactant gas, a different view of the reaction with ionic species **a'** was obtained. As expected, using $^{13}\text{CH}_3\text{CN}$, the two adduct ions



$[M + 41]^+$ and $[M + 56]^+$ are observed, but the two 'diagnostic' fragment ions show a formal addition on the double-bonded C atoms of a species of mass 55 [see Fig. 2(b)]. This implies that only one of the two ^{13}C atoms of the reactant species at m/z 56 is retained in the fragment ions.

The results obtained by use of CD_3CN as reactant are presented in [Fig. 2(c)]: together with $[M + 44]^+$ and $[M + 58]^+$ adducts, the two fragment ions of interest show a formal addition of a species of 57 mass units consistent with the incorporation of one CD_3 group. A mechanism for the formation of the fragment ion at m/z 180 which is in agreement with the observed mass shift of 1 and 2 units when using $^{13}\text{CH}_3\text{CN}$ and CD_3CN , respectively, is formulated in Scheme 2. Briefly, we propose that the addition of $\text{C}_3\text{H}_4\text{N}^+$ species to



the double bond occurs with a concomitant H rearrangement yielding a cyclic $[M + 54]^+$ ion. From the latter ion a terminally unsaturated alkene could be eliminated by a charge-driven process resulting in the ion at m/z 180 which is resonance stabilized. The same mechanism but involving attack of the $\text{C}_3\text{H}_4\text{N}^+$ species at the C-8 position can be formulated to rationalize the formation of the fragment ion at m/z 250.

Yours,

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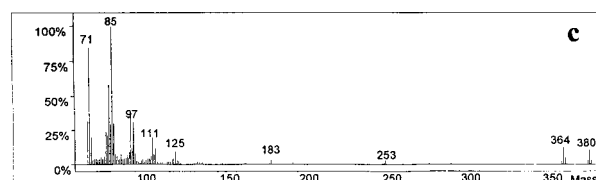
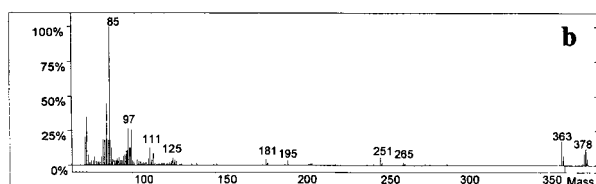
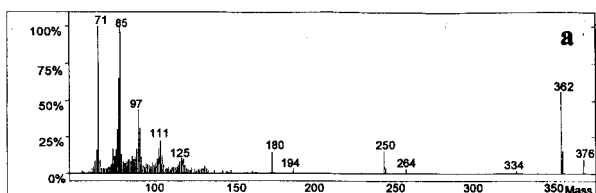


Figure 2. (a) $\text{PICl}(\text{CH}_3\text{CN})$ mass spectrum of monounsaturated hydrocarbon (9)C23:1; (b) $\text{PICl}(^{13}\text{CH}_3\text{CN})$ mass spectrum of monounsaturated hydrocarbon (9)C23:3; (c) $\text{PICl}(\text{CD}_3\text{CN})$ mass spectrum of monounsaturated hydrocarbon (9)C23:1.

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