Competing mechanisms for methyl cation formation upon collision-induced dissociation of protonated acetaldehyde

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Abstract

Isotopic labeling and energy-resolved collision-induced dissociation (CID) experiments show that methyl cation loss from protonated acetaldehyde occurs by at least two different mechanisms, one involving direct cleavage and the second involving rearrangement. A statistical scrambling mechanism is ruled out from the CID appearance curves for the CH_3^+ and CH_2D^+ products from $CH_3C(OD)H^+$, whereas a possible kinetic isotope effect is ruled out by using the alternately labeled $CD_3C(OH)H^+$ acetaldehyde ion. The results show that dissociation of protonated aldehydes is even more complex than is suggested by standard CID spectra. (Int J Mass Spectrom 207 (2001) 69–72) © 2001 Elsevier Science B.V.

Keywords: CID; Protonated aldehydes; Kinetic isotope effects; Energy-resolved mass spectrometry; Dissociation mechanisms

1. Introduction

In a recent study [1], energy-resolved collision-induced dissociation (CID) of protonated nitriles (RCN, $R = CH_3$, C_2H_5, C_2H_3, $t\text{-}C_4H_9$, and C_6H_5) was used to determine the enthalpy of formation of hydrogen isocyanide, HNC (eq. 1). The enthalpy of formation of HNC determined by using

$$RCNH^+ \rightarrow R^+ + HNC \qquad (1)$$

this approach, 49.7 ± 2.9 kcal/mol, is in good agreement with previous experimental and theoretical studies. In an attempt to extend this method to the determination of the enthalpy of formation of hydroxycarbene (HCOH) [2–5], we sought to carry out energy-resolved CID of protonated acetaldehyde (eq. 2).

$$\text{(2)}$$
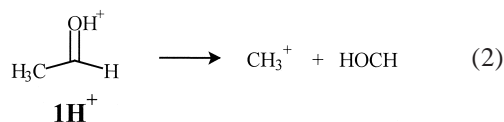
Although ion $1H^+$ dissociates to give methyl cation, as well as other products, we show by using isotopic labeling and CID appearance curve measurements that formation of methyl cation is a complex process, and occurs by at least two different mechanisms.

Protonated acetaldehyde, $1H^+$, was generated by the reaction of acetaldehyde with H_3O^+ in the source region of a flowing afterglow—triple quadrupole instrument, and low energy CID was carried out in the second quadrupole of the EXTREL triple quadrupole analyzer [6]. The CID mass spectrum of $1H^+$ obtained at a collision energy (center-of-mass) of 18.6 eV with xenon target [$P(Xe) = 0.200$ mTorr] is shown in Fig. 1. The products observed in the spectrum are
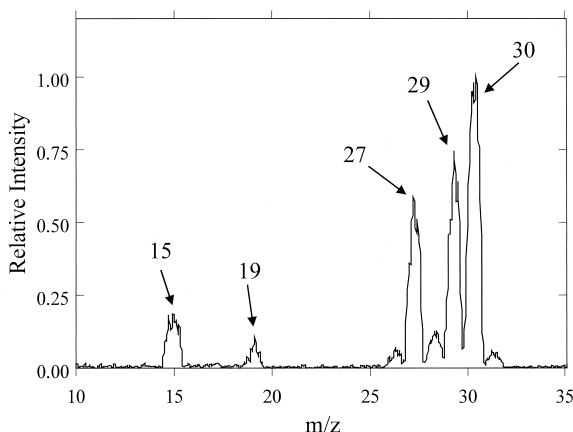
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Fig. 1. CID mass spectrum of protonated acetaldehyde, $1H^+$, at 18.6 eV (center-of-mass) collision energy with Xe target.

Scheme 2.

at m/z 15, 19, 27, 28, 29, 30, and 31, which are tentatively assigned to CH_3^+, H_3O^+, $C_2H_3^+$ (vinyl cation), CO^+, HCO^+, H_2CO^+, and H_2COH^+ (protonated formaldehyde), respectively. In order to identify the origins of the products, we repeated the experiments using the deuterated ion, $1D^+$, prepared from the reaction of acetaldehyde with D_3O^+. Deuterium incorporation into the ions at m/z 19, 30, and 31 is observed, indicating that they include the oxygen proton. Surprisingly, although undeuterated methyl cation, CH_3^+, is formed, we also observed an ion at m/z 16, corresponding to CH_2D^+, indicating that the proton initially on the oxygen is incorporated into the methyl cation fragment. The CH_3^+/CH_2D^+ ratio is about 1:3 at 18.6 eV. Control experiments show that neither $C_2H_3^+$ nor H_2COH^+ produce CH_3^+ upon CID, indicating that the methyl cation is a primary fragmentation product from $1D^+$.

Whereas the formation of CH_3^+ can be attributed to simple bond cleavage, at least three possible mechanisms for the formation of the CH_2D^+ upon dissociation of $1D^+$ can be envisioned. A first possibility is a concerted H/D exchange, as indicated in Scheme 1.
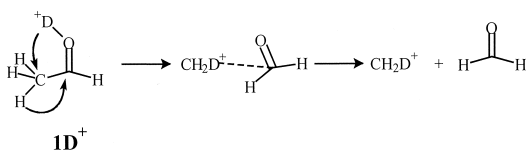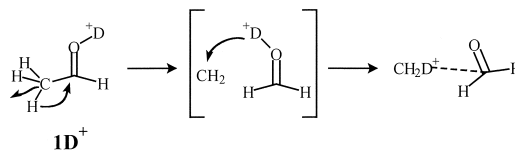
Transfer of the D from the carbonyl oxygen accompanied by transfer of H to the carbonyl carbon results in the formation of CH_2D^+ and formaldehyde. Theoretical calculations predict that the energy difference between formaldehyde and hydroxycarbene is about 50 kcal/mol [3–5] such that the formation of methyl accompanied by rearrangement is thermodynamically favored over direct dissociation.

A second possibility, shown in Scheme 2, involves proton exchange. If hydroxycarbene is 50 kcal/mol higher in energy than formaldehyde (proton affinity = 170.4 kcal/mol) [7], then it will have a proton affinity of ~220 kcal/mol. Because the proton affinity of singlet methylene is only 206 kcal/mol [7], exothermic proton transfer can occur during dissociation to form singlet CH_2 and protonated formaldehyde (triplet CH_2 formation is thermodynamically more favorable but requires an intersystem crossing). Subsequent D^+ transfer to form CH_2D^+ and formaldehyde is exothermic by 35 kcal/mol. However, neither the mechanism in Scheme 2 nor that in Scheme 1 account for the formation of CH_3^+. Therefore, if the CH_2D^+ ion is formed by the mechanisms shown in Scheme 1 or 2, then the presence of the CH_3^+ indicates a second available pathway.

In order to establish that multiple pathways are involved, it is necessary to rule out mechanisms that account for both products. A single mechanism that would result in the formation of both CH_3^+ and CH_2D^+, shown in Scheme 3, involves transfer of a deuteride from the carbonyl oxygen to form HCO^+
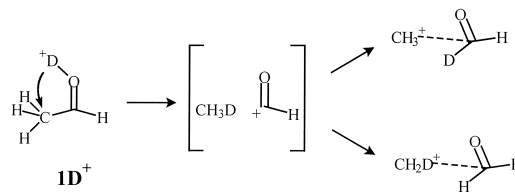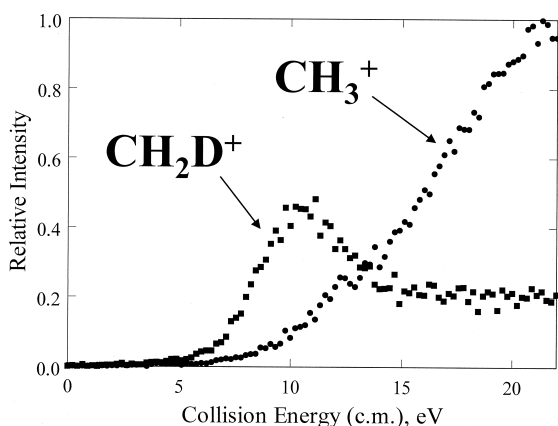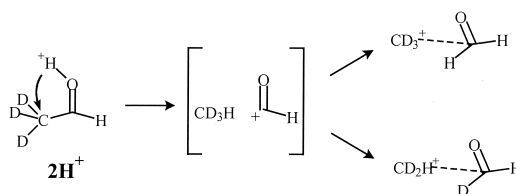

Scheme 1.

Scheme 3.

Fig. 2. Relative CID yields for the formation of CH_3^+ and CH_2D^+ from $1D^+$ as a function of collision energy with xenon target.

Scheme 4.

and CH_3D. From estimates of the enthalpy of formation of HOCH, this step is calculated to be ~100 kcal/mol exothermic. Subsequent H^- or D^- transfer back to the HCO^+ to generate formaldehyde is ~50 kcal/mol endothermic, but could be driven by the exothermicity of the first step. Moreover, a scrambling mechanism would be expected to give a CH_3^+/CH_2D^+ ratio of 1:3, in agreement with what is observed.

The mechanism in Scheme 3 can be ruled out by using energy-resolved mass spectrometry. Because formation of either CH_3^+ or CH_2D^+ occurs through the same intermediate, it would be expected that the energetic and dynamic requirements for the two channels should be the same. However, when carrying out energy-resolved CID, the apparent onset for formation of CH_2D^+, ~6 eV, is lower than that for CH_3^+ formation, ~8 eV, (Fig. 2) suggesting that the CH_3^+ and CH_2D^+ ions are being formed by different mechanisms. Moreover, the shapes of the curves are significantly different, as the yield of CH_2D^+ reaches a maximum near 10 eV, whereas the yield of CH_3^+ steadily increases out to 22 eV.

A possible explanation for the results observed in Fig. 2 is that the dissociation occurs by the reaction shown in Scheme 3, but that the endothermic transfer of hydride to the HCO^+ is subject to a kinetic isotope effect (KIE). In order to test for a KIE, the energy-resolved CID experiments were repeated using proto-

nated d_3-acetaldehyde, $2H^+$ [8]. As shown in Scheme 4, if the differences between the appearance curves in Fig. 2 are due to kinetic isotope effects, then formation of CD_2H^+ should be slower than formation of CD_3^+ and will have a higher onset. However, if CD_3^+ is formed by direct dissociation and CD_2H^+ is formed by the mechanism such as that shown in Scheme 1 or 2, then CD_2H^+ formation will have a lower energy onset than that for CD_3^+. As expected, both CD_3^+ and CD_2H^+ are observed in the CID spectrum of $2H^+$, with a ratio of ~2:1 at 22 eV. The CID appearance curves for formation of CD_2H^+ and CD_3^+, shown in Fig. 3, are very similar to those in Fig. 2. Most importantly, the appearance curve for formation of CD_2H^+ from $2H^+$ closely resembles that for CH_2D^+ from $1D^+$, with an apparent onset near 6 eV and a maximum at about 10 eV, whereas the curve for formation of CD_3^+ from $2H^+$ resembles that for CH_3^+ from $1D^+$, with an apparent onset of ~8 eV. The corresponding energy dependences for the direct dissociation and rearrangement products from the two
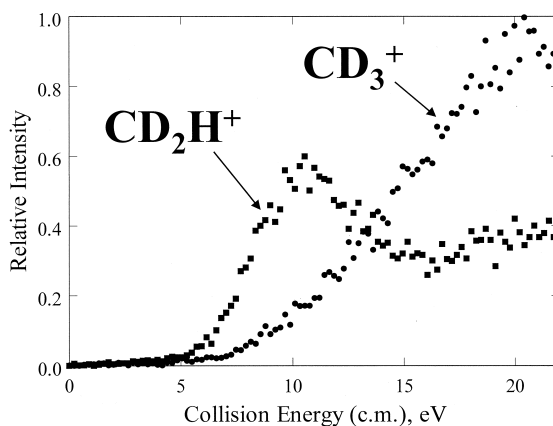

Fig. 3. Relative CID yields for the formation of CD_3^+ and CD_2H^+ from $2H^+$ as a function of collision energy with xenon target.

ions rules out a KIE as the origin of the difference between the appearance curves in Fig. 2. Therefore, the differences between the two appearance curves are attributed to the presence of competing pathways for the dissociations.

The results presented here indicate that, although protonated aldehydes dissociate by apparent α cleavage, the reaction occurs by at least two mechanisms. Whereas one mechanism appears to be direct dissociation, the isotope scrambling and low onset for the second pathway suggest a more complicated process involving rearrangement to a more stable neutral. The presence of competing mechanisms is apparently common for protonated aldehydes, as results similar to those described above have been found for all the aldehydes we have examined, including propionaldehyde, trimethylacetaldehyde, phenylacetaldehyde, and benzaldehyde. Therefore, before it will be possible to use CID of the ions to determine the thermochemical properties of hydroxycarbenes, it will be necessary to fully characterize all the products and the mechanisms by which they are formed.

Acknowledgements

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