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Structure of Protonated Ethanol; Thermal Energy Effects Studied by Mass Spectrometry

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$C_2H_5OH_2^+$, $C_2H_5OHD^+$, and $C_2D_5OHD^+$ have been studied using high-energy collision-induced decomposition (CID) mass spectrometry. The spectra, in particular the isotope distributions in the CID product ions, vary significantly depending on the reaction conditions of pressure and temperature under which the protonated ethanol or its deuterated equivalents are created. $C_2H_5OHD^+$ and $C_2D_5OHD^+$ were formed specifically by the deuteron or proton exchange reactions: $(C_6D_5F)H^+/C_2H_5OH$ and $(C_6H_5F)D^+/C_2D_5OD$, respectively. The reaction exothermicity is too small to allow the formation of the isomeric deuterated ethylene−water complex ($\equiv C_2H_4{\cdot}H_3O^+$) or isotope scrambling in the ion source. The variations in the CID spectra, dependent on the precursor ion temperature, are therefore highly unusual and unexpected. They indicate that high-energy CID in these molecules is sensitive to the degree of internal rotation of the −OHD around C−O and $-CH_3$ around the C−C bond. This explains variations observed previously for CID spectra of $(C_2H_5OH)H^+$ which have been attributed to the independent existence of two isomers formed by protonation of ethanol. The work supports the conclusion of Fairley et al. that the H_3O^+/C_2H_4 reaction leads to the formation of the lowest-energy isomer of protonated ethanol. It also gives a fresh insight into the mechanism for the collision-induced decomposition of $C_2H_5OH_2^+$.

Introduction

Protonated ethanol, $(C_2H_5OH)H^+$, has been the subject of many experimental and theoretical studies. Much of the interest has centered on the possibility of the formation of a stable $C_2H_4{\cdot}H_3O^+$ complex[1−7] (structure **2**), for example by the association reaction of H_3O^+ with C_2H_4 or by a sufficiently exothermic protonation of ethanol. Such complexes are of fundamental interest to mechanistic[6] and rate theories of ion−molecule reactions.[7] $(C_2H_5OH)H^+$ has also featured in studies concerning the mechanism of energy transfer in collision spectroscopy.[8] Recently it has been suggested[1,2] that the $C_2H_4{\cdot}H_3O^+$ complex may be an intermediate in the formation of ethanol in interstellar clouds. The only experimental evidence that it exists as a stable isomer comes from high-energy collision spectroscopy.[3,4]

Jarrold et al.[8] studied $(C_2H_5OH)H^+$ created in an ion source by proton transfer from H_3^+ to C_2H_5OH in H_2 gas. This is a highly exothermic reaction and using the technique of collision-induced decomposition (CID) mass spectrometry, they observed changes in the CID spectra, which were dependent on source pressure. Conversion to $(CH_3)_2OH^+$ was ruled out, and they concluded that $C_2H_5OH_2^+$ (structure **1**) was the only alternative. The result was therefore interpreted as showing a dependence on the degree of internal energy in the ion prior to CID, retained from the reaction exothermicity and moderated by the degree of collisional quenching in the source. This result is important, but also contentious, because a cornerstone of the use of CID mass spectrometry in analytical chemistry is that the technique is generally independent of the precursor-ion internal energy.[9]

However, it transpired that the $(C_2H_5OH)H^+$ potential energy surface had not been well mapped out at that time. Subsequently, Swanton et al.[5] carried out calculations which showed that the $C_2H_4{\cdot}H_3O^+$ complex is theoretically stable, with an energy of 53 kJ mol^{-1} and separated by a barrier of only 95 kJ mol^{-1} relative to $C_2H_5OH_2^+$ (see Figure 1). This is below the exothermicity of proton-transfer reactions used to create the $(C_2H_5OH)H^+$ in these studies or indeed the association reaction 1.

$$H_3O^+ + C_2H_4 \rightarrow C_2H_4{\cdot}H_3O^+ \tag{1}$$

Wesdemiotis et al.,[4] using the results of neutral reionization mass spectrometry (NRMS) in addition to high-energy CID mass spectrometry as evidence, therefore concluded that the $(C_2H_5OH)H^+$ population contains both isomers, the proportion of which depends on the source conditions. A subsequent study by Sirois et al.,[3] also using NRMS, concurred, particularly when the ion is formed as the product of the association reaction.

However, Fairley et al.[1] and Matthews et al.[2] have recently studied the kinetics of the ion created as the product of the association reaction in He at 0.35 Torr and 300 K. They conclude that it behaves as if it has the low-energy structure, **1**. Fairley et al.[1] have also recalculated the potential energy surface at the G2 level of ab initio molecular orbital theory. This gives a reverse activation energy of 28 kJ mol^{-1}, significantly lower than previously thought. If this is true, then it is likely to result in rapid rearrangement from **2** to **1**, even at modest temperatures.

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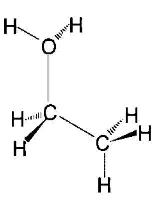
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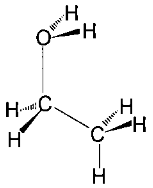
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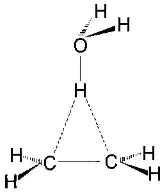
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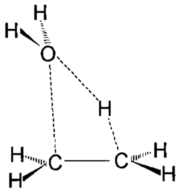
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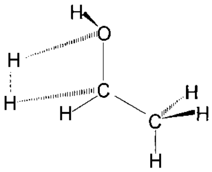
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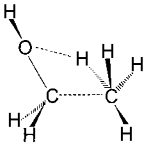
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In this work we have reexamined high-energy CID mass spectra of $(C_2H_5OH)H^+$ under carefully controlled protonating reaction conditions in the ion source, as a function of pressure and temperature, in an attempt to further clarify the apparently conflicting evidence. In particular we have investigated the CID of $(C_2H_5OH)D^+$ created by reaction 2:

$$(C_6D_5F)H^+ + C_2H_5OH \rightarrow C_2H_5OHD^+ + C_6D_5F \qquad (2)$$

This system has not been studied before, but it has the advantage over previous studies that the exothermicity of the reaction is <23 kJ mol^{-1}, which is far below the height of the barrier between the two isomers. The formation of ethanol deuterated on the O atom is therefore guaranteed at all temperatures and pressures. The mechanism found here for the collision-induced decomposition of the product contradicts some of the previous findings.[4] Furthermore, the low-energy isomer appears to be the product even of the high-exothermicity reactions.

In agreement with Jarrold et al.[8] we find the spectra exhibit a significant dependence on excess internal energy. Also studied is whether temperature itself could have an effect on the efficiency of CID processes. Although there is no precedent in the literature for such an effect,[10] we are able to show that the sensitivity to change extends down to thermal energies. It is deduced that the internal rotations in the ion during collisional excitation must have an effect on the direction of decomposition after it.

Experimental Section

A. Method. The experiments were carried out using a high-pressure ion−molecule reaction source attached to a mass spectrometer system of forward geometry, previously modified and described in detail elsewhere.[11] The gaseous reaction mixtures were premixed in a heated gas storage bulb by injection of pure liquid ethanol, or mixtures of ethanol in perdeuterated fluorobenzene in the molar mixing ratio of 1:10, directly into the reagent bath gas of CH_4. The mixing ratio of ethanol in the bath gas was <1:1000. The mixture was allowed to flow continuously into the reactor, maintained at a constant pressure by an automatic control valve and pressure transducer arrangement. The temperature could be varied between −100 and +400 °C, and the source pressure up to 4 Torr.

Reactant and product ions drifting through the ion exit aperture were accelerated to a beam energy of 6 keV. To generate a CID spectrum of the ion of interest, the beam was passed through N_2, as the collision gas in the first field-free region, at a pressure sufficient to attenuate the main beam down to between 60 and 70%. CID peak intensities were recorded, as before,[12] by linked scanning of the magnetic field (strength B) and electrostatic analyzer (field E), while maintaining a constant B/E ratio. The full mass spectrum was collected by continuous automated scanning in the usual way. However, quantitative peak height ratios were measured by manual tuning, individually onto the selected fragment ion peaks of interest, and recording the collector current of the beam at the top of the peak. This perhaps over-cautious method was to ensure accurate tuning to find the top of the peak, which was not necessarily in its exact theoretical position because of translational energy loss in the collision. The long-term reproducibility of this method for peak height ratios was found to fall well within the limits of ±15%.

B. Isobaric and Other Interferences. The ions selected for study were at $m/z = 47$ ($C_2H_7O^+$), 48 ($C_2H_6DO^+$), and 53 ($C_2D_6HO^+$). The contribution of $^{13}CCH_6O^+$ toward the signal corresponding to $C_2H_7O^+$ was <1%. The $^{13}CCH_7O^+$ contribution toward $C_2H_5OHD^+$ and that of $^{13}CCD_6O^+$ toward $C_2D_6HO^+$ were always <3%.

A major source of interference in the spectra of $C_2H_5OHD^+$ was caused by the collision-induced decomposition of reaction 3:

$$\textit{CID:} \qquad (C_2H_5OH)_2H^+ \rightarrow C_2H_5OH_2{}^+ + C_2H_5OH \qquad (3)$$

This very low energy process, studied previously,[13] occurred readily in the accelerating region close to the source ion exit, during our experiments. In the B,E plane,[14] the signal from fragment ions emanating from this region overlap the $48^+ \rightarrow 47^+ + 1$ CID signal occurring in the first field-free region. This was established by exploration of the B,E plane. It was also easily distinguished since the very high ion current at this point in the B,E plane was observed to decrease as the collision gas pressure was increased (because the fragment ions for this process are already present in the incident beam, which itself becomes attenuated by collision with the added collision gas). This was not true of any of the other ions. The effect was highly dependent on the source temperature and pressure because the relative abundances of the protonated ethanol clusters and their stabilities leaving the ion source are highly dependent on source pressure and temperature. The effect was negligible in the experiments at higher temperatures, but very large at low temperatures. It was concluded that the efficiency of collision-induced loss of H from $C_2H_5OHD^+$ could not be reliably assessed except at the higher source temperatures.

Because the first field-free region is relatively close to the ion source, gas leakage from the source caused the background spectral intensities to be relatively high at 10−15% of the value when the CID gas was added. The spectra recorded here are background-subtracted, to ensure that the peak intensities are pure CID signals. However, the relative intensities of peaks did not change significantly from the value without background subtraction, except for H loss from $C_2H_5OHD^+$.

C. Chemicals. The methane and argon (BOC, research grade, 99.995%), ethanol (Aldrich, 99+%), ethanol-*d6*, fluo-

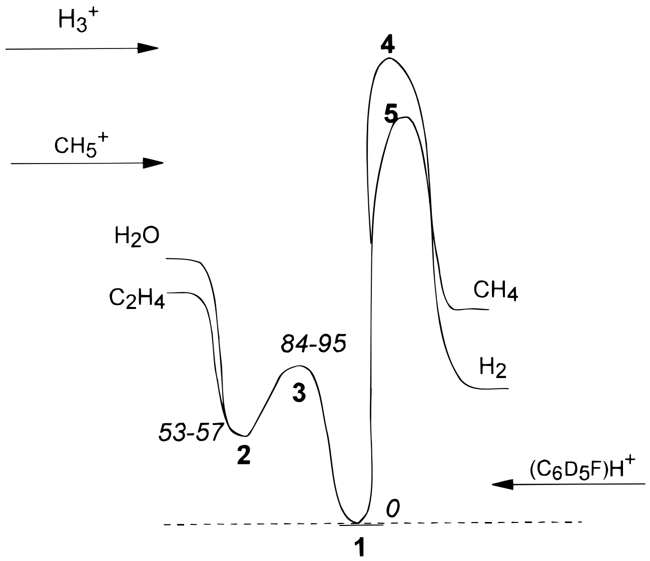


Figure 1. Schematic of a section of the potential energy surface of protonated ethanol; neutral losses are shown for the lower-energy decomposition channels; the arrows indicate the exothermicity for protonation by specific reagent ions; numbers in italics are energies in units of kJ mol^{-1}.

TABLE 1: Energies Pertinent to the Potential Energy Surface of $(C_2H_5OH)H^+$

Proton Transfer Reaction Exothermicity[25]

$AH^+ + C_2H_5OH \rightarrow C_2H_5OH_2^+ + A$

reagent	ΔH kJ/mol	reagent	ΔH kJ/mol
CH_5^+	236	$C_2H_5OH^+$	100
$C_2H_5^+$	108	$C_6H_5FH^+$	23

Isomer or Transition State Structure Energy[5] (see Fig. 1)

	energy barrier, kJ/mol	energy kJ mol^{-1}		energy barrier, kJ/mol	energy kJ mol^{-1}
1a		0	**3**	(84)[1]	95
1b		4.5	**4**		257
2	(57)[1]	53	**5**		223

Decomposition Products and Minimum Energies[5,25] (see Fig. 1)

m/*z*	ion fragment	neutral loss	energy barrier, kJ/mol	ΔH kJ/mol
19	H_3O^+	C_2H_4	136	136
29	$C_2H_5^+$	H_2O	153	153
31	CH_3O^+	CH_4	(223)	122
45	CH_3CHOH^+	H_2	(257)	76
46	$CH_2CH_2OH_2^+$	H	443	443
46	$CH_3CH_2OH^+$	H	486	486
27	$C_2H_3^+$	$H_2 + H_2O$	?	363
28	$C_2H_4^+$	$H + H_2O$	?	535
26	$C_2H_2^+$	$H + H_2 + H_2O$	?	797

robenzene-*d5*, and D_2O (Aldrich, all 98.5+ atom %D, respectively) were used as received. Any impurities present were not significant in the chemical ionization spectrum and therefore did not interfere with the reactions under study.

Results and Discussion

A. Energies. Energies pertinent to the processes occurring in these experiments are shown in Table 1. The calculated structures of isomers and transition states are given[5] as **1**−**5** and the potential energy surface of $C_2H_7O^+$, appropriate to this work is represented in Figure 1.

When $C_2H_7O^+$ is created either by self-protonation (reaction 4) or in standard reagent gases (reaction 5), it has been thought[3−5] that two isomers are formed:

$$C_2H_5OH^+ + C_2H_5OH \rightarrow (C_2H_5OH)H^+ + C_2H_5O \quad (4)$$

$$AH^+ + C_2H_5OH \rightarrow (C_2H_5OH)H^+ + A \quad (5)$$

The most stable form is that in which the proton is attached to the O atom, $C_2H_5OH_2^+$ (**1**). This is lower in energy[1,5,6] than the protonated ethylene−water complex, $C_2H_4{\cdot}H_3O^+$ (**2**). Two theoretical values are reported[1,5] for their difference in energy: 53 kJ mol^{-1} and 57 kJ mol^{-1}. They are separated by a theoretical barrier of 95 kJ mol^{-1} or 84 kJ mol^{-1}.

B. CID Spectra of $C_2H_7O^+$: Pressure and Temperature Dependence. It has been concluded previously, from both low-energy[15,16] and high-energy[3,4,8,16] CID experiments, that processes 6−9 are evidence of the presence of the two isomers.

$$\text{CID:} \quad C_2H_5OH_2^+ \rightarrow C_2H_4OH_2^+ + H \quad (6)$$

$$CH_2OH^+ + CH_4 \quad (7)$$

$$\text{CID:} \quad C_2H_4{\cdot}H_3O^+ \rightarrow C_2H_5^+ + OH_2 \quad (8)$$

$$H_3O^+ + C_2H_4 \quad (9)$$

Swanton et al.[5] have concluded that **1** is probably also the precursor to loss of H_2, as in reaction 10.

$$\text{CID:} \quad C_2H_5OH_2^+ \rightarrow CH_3CHOH^+ + H_2 \quad (10)$$

Both Swanton et al.[5] and Sirois et al.[3] have expressed the view that loss of water ought to be a channel also available to **1**. But, in view of the previously observed[4,16] isotope scrambling resulting from the CID of isotopomers of protonated ethanol, **2** is thought to be an intermediate in this process (reaction 11).

$$\text{CID:} \quad C_2H_5OH_2^+ \rightarrow (C_2H_4{\cdot}H_3O^+)^* \rightarrow C_2H_5^+ + OH_2 \quad (11)$$

As discussed in the Introduction it is thought[3−5] that both **1** and **2** can be formed because the energy of the transition state between them lies below the entry level of the incoming proton by either proton transfer from standard reagent ions (e.g., H_3^+ or CH_5^+ in Jarrold's experiments) or indeed from reaction 4, (Wesdemiotis' and Sirois' experiments). Once cooled by collisional quenching, it is suggested by Wesdemiotis[4] et al. that the stability of **2** relative to the transition state (i.e., the reverse activation energy) is sufficient that the higher-energy isomer becomes entrapped. While this is a reasonable argument, one would still expect the overwhelming majority of ions to be in the low-energy form for two reasons. First, during the proton-transfer encounter, the proton will be guided onto the molecule via the O atom because of ion−dipole effects. Second, the density of states above the well of the low-energy isomer will be very much greater than above that of **2**, at the same excitation energy; hence, the internal equilibrium at high energy will still favor **1**.

The preferred[1−3,7] method for the specific creation of $C_2H_4{\cdot}H_3O^+$ is by reaction 1. However, the exothermicity of this reaction is also much greater than that required to overcome the barrier to the formation of **1** and, according to the latest calculations,[1] the activation energy may be as little as 27 kJ mol^{-1}. In addition, the kinetic studies[1,2] support $C_2H_5OH_2^+$ as the favored product.

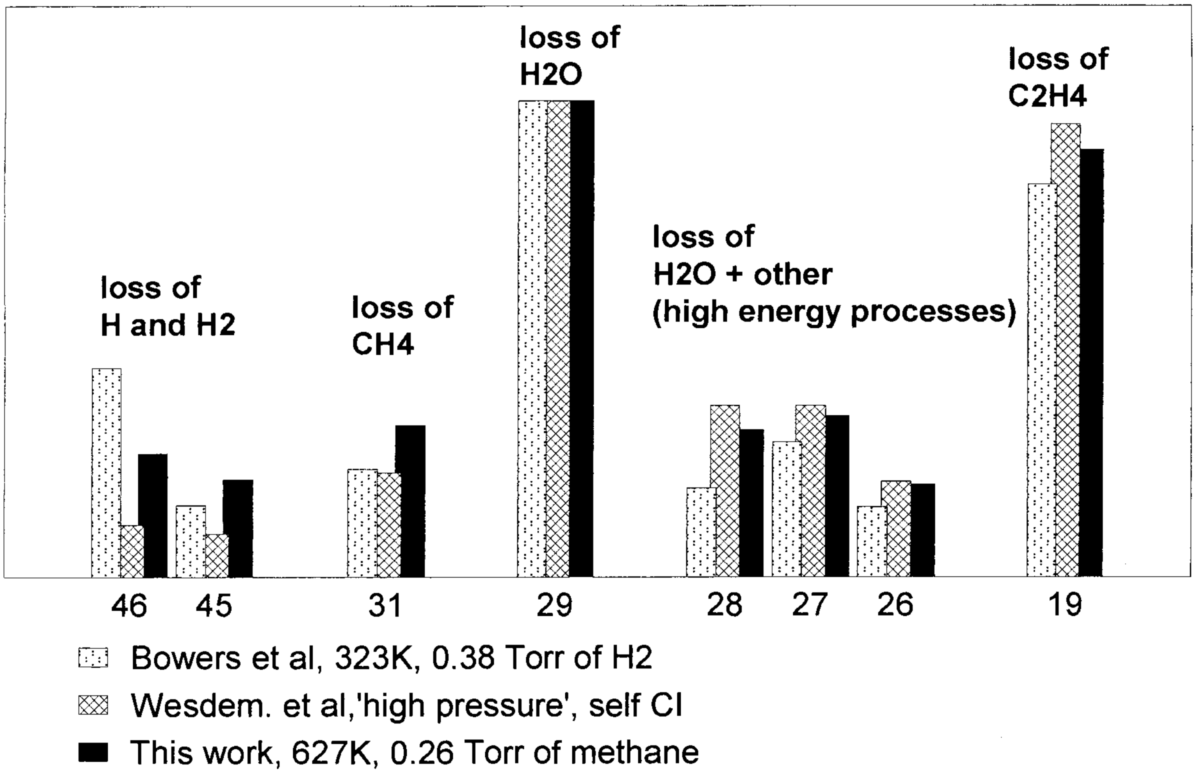


Figure 2. Bar chart comparison of selected peaks in the CID spectra of $(C_2H_5OH)H^+$ obtained in different laboratories as indicated by the legend; Bowers et al. alludes to ref 8, and Wesdem. et al. to ref 4.

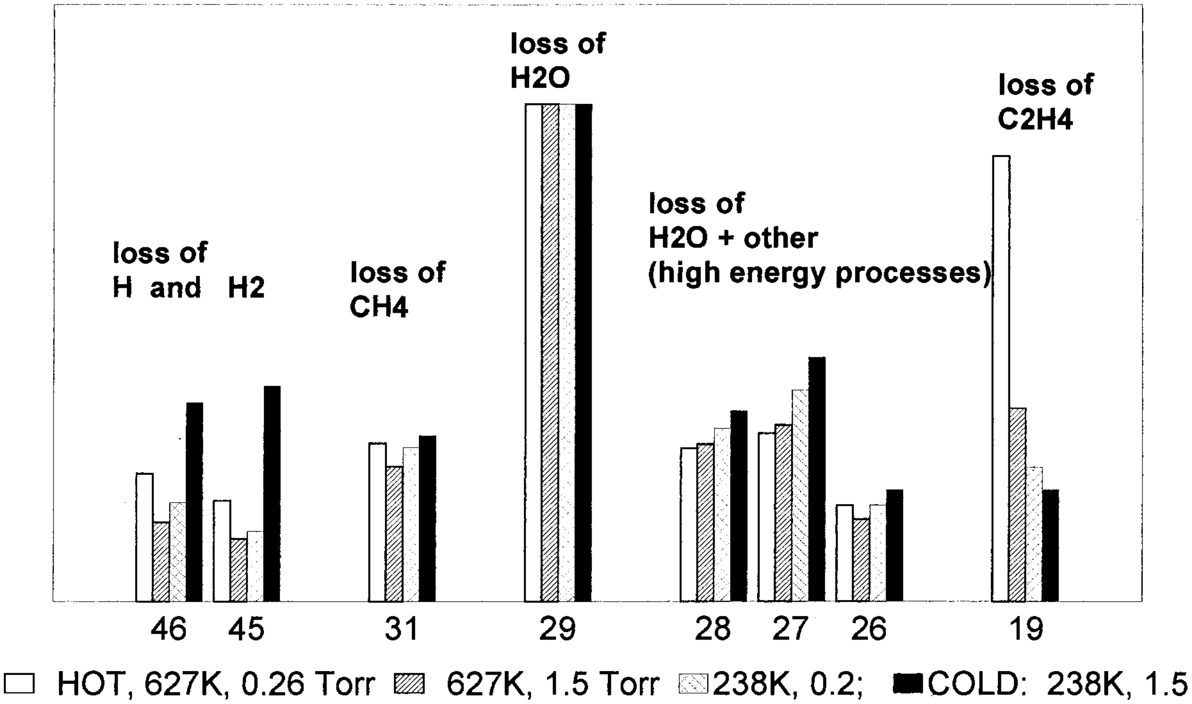


Figure 3. Bar chart comparison of selected peaks in the CID spectra of $(C_2H_5OH)H^+$, obtained in this work under varying conditions of the source temperature and pressure of methane gas, as indicated by the legend.

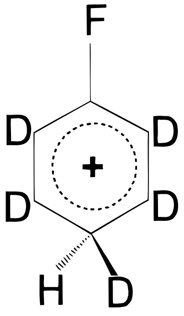
The evidence for the separate existence of **2** is based on CID and NRMS mass spectrometry. Figure 2 shows a comparison of high-energy CID spectra of $(C_2H_5OH)H^+$ obtained in the different laboratories. Despite the differences in instrumentation, the spectra are remarkably similar. However, this does depend on the source conditions, as exemplified in Figure 3 of data obtained in this work. The $C_2H_7O^+$ ions were created here in methane gas in which two acids are involved: CH_5^+ and $C_2H_5^+$. The exothermicity of their reactions relative to the formation of **1** is >226 and >100 kJ mol^{-1}, respectively. Self-protonation (reaction 4) is also possible with an exothermicity of 100 kJ mol^{-1}. All values are well above the barrier height, and yet the H_3O^+ peak (loss of C_2H_4) in spectra obtained here under conditions of strong collisional cooling, i.e., at high pressures and low temperatures, is generally very small in comparison to the previous work. This is opposite to expectation based on the arguments of Wesdemiotis et al.[4]

C. CID Spectra of $C_2H_5OHD^+$: Pressure and Temperature Dependence. Figure 3 clearly shows that there are substantial variations when the precursor ions are created under varying source conditions of both pressure and temperature. At low source pressure and high temperature the spectral peaks corresponding to the H_3O^+ and $C_2H_5^+$ are almost equal. It is possible that these variations are indicative of changing isomer populations. To overcome this source of ambiguity, the ion $C_2H_5OHD^+$ was prepared in the mixture of vapors ($C_2H_5OH + C_6D_5F$, in a 1:10 ratio) in a bath gas of methane. The sequence of reactions occurs:[17]

$$CH_5^+, C_2H_5^+ + C_6D_5F \rightarrow (C_6D_5F)H^+ \qquad (12)$$

$$H^+C_6D_5F + C_2H_5OH \rightarrow C_6D_4H\,F + C_2H_5OHD^+ \qquad (2)$$

The principle isomer of $(C_6D_5F)H^+$ has the σ complex structure[12] with the proton attached at the carbon atom para to the fluorine atom (**6**). Hence when it reacts with ethanol, either the proton or the deuteron can be transferred. In this system this is the only reaction by which the ethanol can be deuterated.[18]



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The reaction exothermicity is in the range 15−23 kJ mol^{-1}. Because this is more than 61 kJ mol^{-1} below the lowest transition state, there is very little chance of either isomerization or scrambling. The only likely exchange, (reaction 13), would pass through the transition state structure,[5] **3**:

$$CH_3CH_2OHD^+ \rightarrow \mathbf{3'} \rightarrow CH_2DCH_2OH_2^+ \qquad (13)$$

This is highly constrained compared with the ground state, hence the rate constant[19] for the reaction must be $\ll 2.5 \times 10^{-6}$ s^{-1} at 240 K. Even if the whole of the excess energy available to the proton-transfer products was transferred to the ion, this rate constant would still be $< 2.6 \times 10^{-1}$ s^{-1}. This is very slow compared to the average residence time of ions in the source, which is determined by the ambipolar diffusive loss rate. This has been studied separately[20] and found to be in the region of a few tenths of a millisecond, depending on pressure and temperature. The only other possible sink process in the source, reaction 14, does not affect these experiments.

$$C_2H_5OHD^+ + C_2H_5OH \rightarrow C_2H_5OD + C_2H_5OH_2^+ \qquad (14)$$

Figure 4 shows the variation, with source pressure, of the CID spectra of $C_2H_5OHD^+$ at a constant source temperature of 240 K. There are clearly very significant changes. Because of potential interference (see above) the loss of H is not included. Figure 5 shows the effect of temperature at the same gas density and hence the same number of quenching collisions prior to leaving the source.[21] The effect of increasing temperature from 240 to 628 K at a density equivalent to 1.5 Torr at 240 K has a very similar effect to decreasing pressure at 240 K from 1.5 down to between 1 and 0.5 Torr.

D. Mechanism of Decomposition and Internal Energy Effects. The above shows that the spectrum of the low-energy isomer $C_2H_5OHD^+$ is strongly sensitive to its internal energy prior to CID. It is most unlikely that the whole exothermicity, derived from reaction 2, is transferred as excess energy to $C_2H_5OHD^+$. Besides, much of the excess will already have become quenched, even at 0.5 Torr.[8] The only internal motions which could be strongly influenced by temperature must have a very low frequency. In the species studied this could only be provided by the internal rotations of (a) HDO around the C−O bond, and (b) CH_3 around the C−C bond. According to theory,[5] **1b** is an alternative conformation of $C_2H_5OH_2^+$, with a slightly higher energy than **1a**. The theoretical barrier[5] to rotation between **1a** and **1b** is only 4.5 kJ mol^{-1}. This is similar to the barriers to methyl group rotations around the C−C bond.[22] It is concluded therefore that it is these changing conformations of the precursor which are likely to be the cause of different decomposition channels becoming favored, when the ion is activated at high collision energies. There is some supporting evidence from the dispersal of D among the fragments, which is observed to change greatly as a function of the internal excitation.

When the parent has a relatively high internal energy before CID there is a significant degree of scrambling, but when it is cold the degree of scrambling is very much less. This is shown from the measured isotope ratios, which are compared with statistical values in Table 2. As shown above, scrambling must be caused by the collisional activation process because the activation energies are too high for it to occur in the source.

An important observation, therefore, is the result for the collision-induced loss of H_2O and HDO. It is thought[4,5,7] that loss of water occurs by the equivalent of reaction 11, involving the excited complex as intermediate (here, for example, it could be $C_2H_4{\cdot}H_2DO^+$) from which transfer of the D to either C atom could readily occur. Complete scrambling would then lead to a high ratio in favor of loss of H_2O. However, when the ion is cold, the spectra show a very high ratio in favor of loss of HDO. This is indicative of a more direct mechanism: i.e., rapid decomposition via direct C−O bond cleavage (reaction 15):

$$\textit{CID:} \qquad C_2H_5OHD^+ \rightarrow CH_3CH_2^+ + OHD \qquad (15)$$

With increased excess internal energy (low pressure) or when the ion is hot the H_2O/HDO ratio increases significantly. This implies that higher internal energies of the precursor help promote the ion into the rearrangement channel and hence the chance for scrambling. This can be rationalized without violating unimolecular reaction rate theory.

According to the statistical theories of reaction,[23] for a given excitation energy the distribution of products resulting from unimolecular decomposition are effectively reduced to a dependence on two parameters. These are (a) the excess energy above the transition states leading to each product, and (b) the degree of rearrangement required to reach the transition state (i.e., the starting geometry on the excited potential energy surface; this determines the density of states available to the reaction channel). Also the higher the excitation energy transferred the greater the promotion of direct bond cleavage reactions because of their higher frequency-factor over lower-

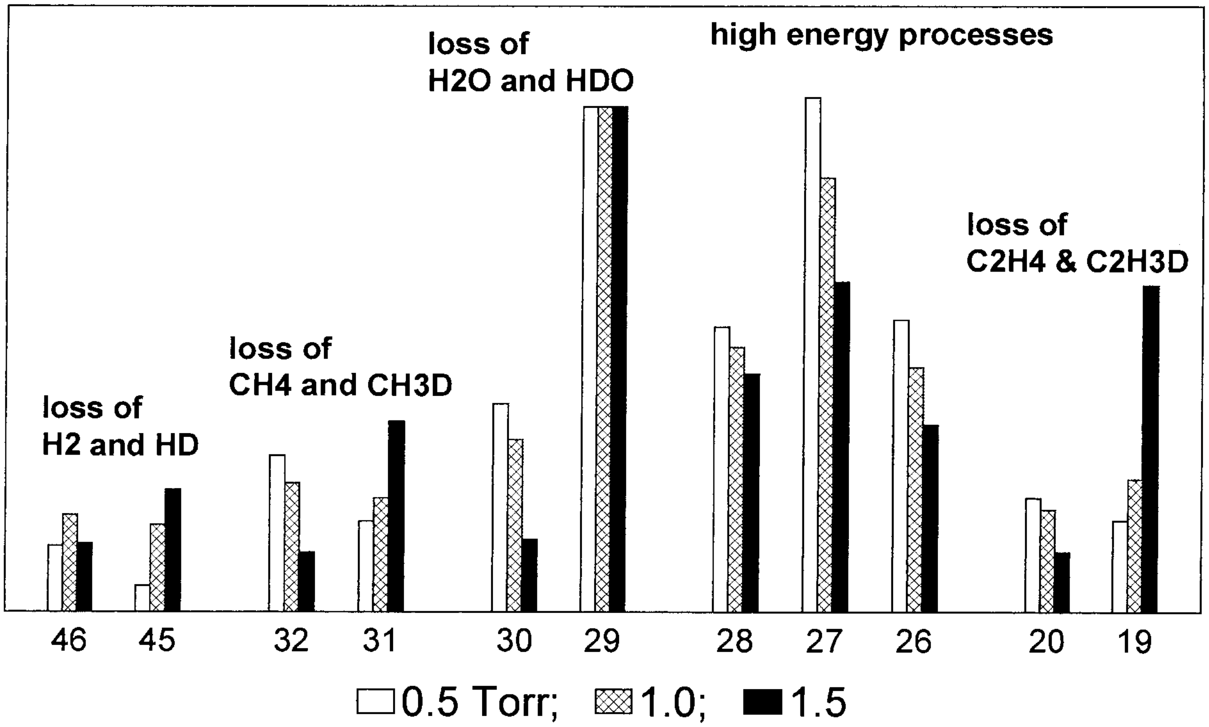

Figure 4. Bar chart comparison of selected peaks in the CID spectra of $C_2H_5OHD^+$ formed by reaction 2 in methane gas at varying pressures, but a fixed temperature of 240 K.

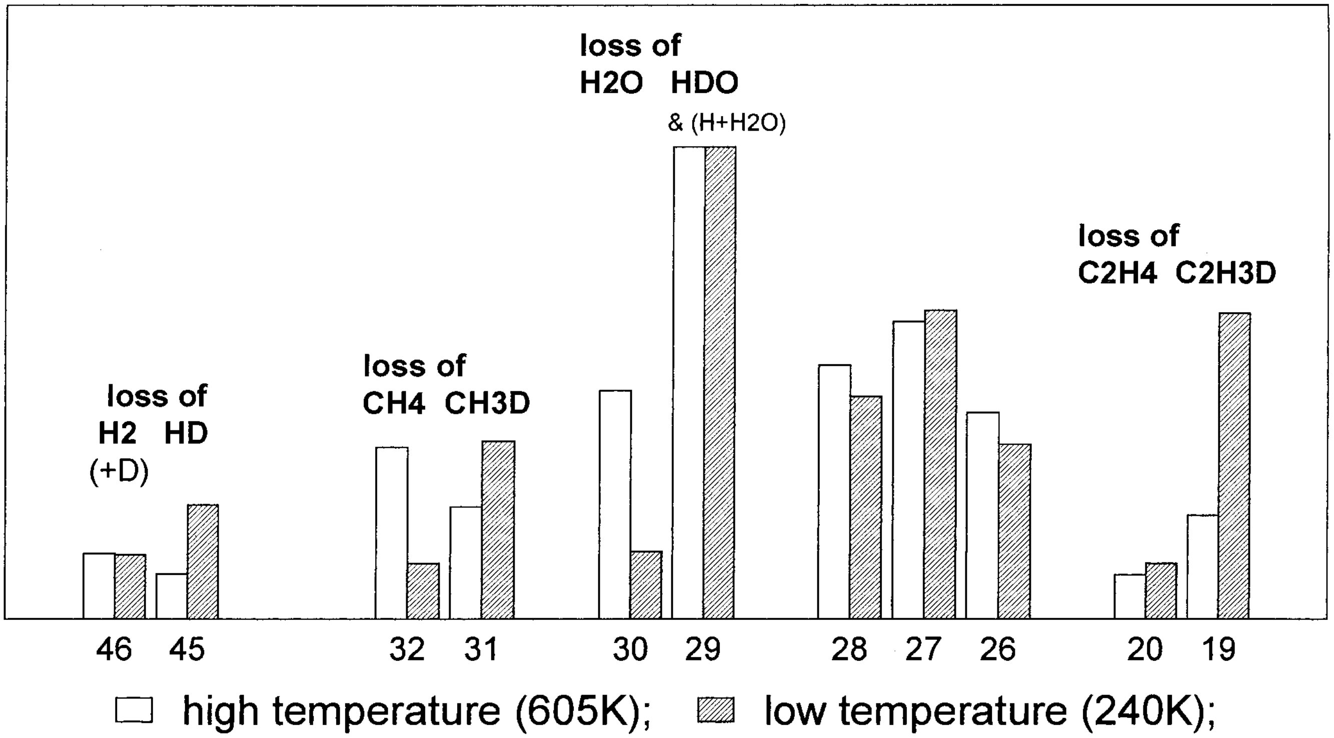

Figure 5. Bar chart comparison of selected peaks in the CID spectra of $C_2H_5OHD^+$ formed by reaction 2 in methane gas at widely different temperatures, as indicated by the legend, but a fixed gas density of 6 × 10^{16} cm^{-3} (≡1.5 Torr @ 240 K).

energy rearrangement reactions.[24] The mechanism of energy transfer in high-energy collisions is thought to be fast electronic excitation, which obeys the Franck−Condon principle.[24] It can therefore be envisaged that rapid access to different channels on the excited potential energy surface may also depend on favorable dynamics within the molecule at the point of excitation. If favorable motions of the parent ion are affected significantly by the temperature, this could be reflected in the pattern of the CID spectrum, as appears to be the case here.

The transition state for the formation of the complex $C_2H_4\cdot H_3O^+$ is shown as **4**. To acquire that structure from ground-state $C_2H_5OH_2^+$ requires stretching the CO bond, rotation of the methyl group to bring an H atom into the CCO plane, and rotation of the HOH group to twist the plane of HOH into a position almost perpendicular to that of CCO. The probability that this occurs must be increased if the $-CH_3$ and $-OH_2$ groups are already rotating toward these conformations at the moment of excitation. The torsion barriers to group rotations around

TABLE 2: Isotope Ratios

ion product ratio	neutral loss ratio	theory *random*	theory *restricted*	expt. 240 K	expt. 627 K
		$C_2H_5OHD^+$			
$\frac{C_2H_4OH^+}{C_2H_4OD^+ (+C_2H_5OH^+)}$	$\frac{HD}{H_2 (+D)}$	0.4	1.0[b]	1.8	0.68
$\frac{CH_2OH^+}{CH_2OD^+}$	$\frac{CH_3D}{CH_4}$	1.33	4.0[c]	3.2	0.66
$\frac{C_2H_5^+ (+C_2H_3D^+)^a}{C_2H_4D^+}$	$\frac{HDO+(H+H_2O)}{H_2O}$	0.4	∞[d]	6.9	2.1
$\frac{H_3O^+}{H_2DO^+}$	$\frac{C_2H_3D}{C_2H_4}$	1.33		5.4	2.3
		$C_2D_5ODH^+$			
$\frac{C_2D_5OD^+}{C_2D_5OH^+}$	$\frac{H}{D}$	0.17	1	6.6	1.5
$\frac{C_2D_4OD^+}{C_2D_4OH^+}$	$\frac{HD}{D_2}$	0.4	0.67	5.2	2.0
$\frac{C_2D_5^+ (+CD_2OD^+)}{C_2D_4H^+ (+CD_2OH^+)}$	$\frac{HDO (+CD_3H)}{D_2O (+CD_4)}$	0.4 (1.3)	∞ (4)	2.6	1.5
$\frac{D_3O^+}{HD_2O^+}$	$\frac{C_2D_3H}{C_2D_4}$	1.3		1.1	1.2

[a] Compare similar losses from $C_2H_5OH_2^+$ in Figure 3; the peak at $m/z = 28$, equivalent to loss of H + H_2O, to give $C_2H_4^+$, under the same conditions as here, has a height which is 39% of the $C_2H_5^+$ peak. The peak at $m/z = 28$ for $C_2H_5OHD^+$ is 41% of the sum of the peaks at $m/z = 29$ and 30. This is consistent therefore with the composition of the peak at $m/z = 29$ being predominantly due to loss of HDO. Indeed, *at low temperature* and *high source pressure*, the pattern of peaks over the range $m/z = 29-26$, comparing with Figure 3, is consistent with these high-energy processes being dominated by the channels: loss of (HDO), (HDO + H), (HDO + H_2) and (HDO + H_2 + H), accompanied by very little scrambling. [b] Atoms considered are highlighted in bold as follows: $CH_3C\mathbf{H_2}O\mathbf{HD}^+$. [c] Atoms considered are highlighted in bold as follows: $C\mathbf{H_3}CH_2O\mathbf{HD}^+$. [d] Atoms considered are highlighted in bold as follows: $CH_3CH_2O\mathbf{HD}^+$.

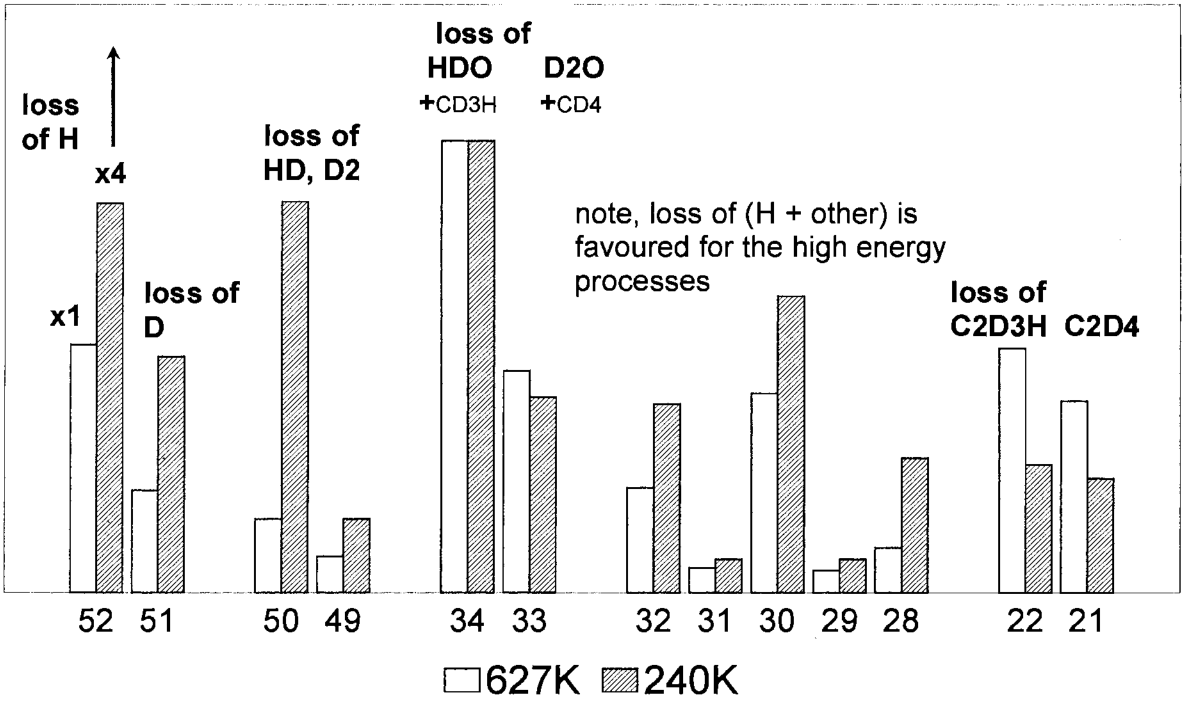

Figure 6. Bar chart comparison of selected peaks in the CID spectra of $C_2D_5ODH^+$ formed by reaction with $(C_6H_5F)D^+$ in Ar, at different pressures, but a fixed temperature of 240 K.

the C−C or the C−O bonds are low (see above). The density of states due to these internal rotations will obviously increase with temperature, and this will be carried over in the high-energy collision. In more prosaic terms, an increase in temperature will more often bring the atoms into a conformation more favorable to the desired transition state geometry, at the moment of collisional excitation, thus channeling the reaction toward the intermediate complex.

The changes in the isotope ratios of the other decompositions support this view. Swanton et al.[5] suggest that the transition states for elimination of H_2 and CH_4 are **4** and **5**, as shown in Figure 1. Loss of H_2 therefore involves atoms only of the $-CH_2-OH_2$ moiety, while CH_4 involves the atoms only of the methyl and $-OH_2$ groups. Hence if the water group has one D atom, the statistical distributions of D in the ejected neutrals are readily calculated. In Table 2**,** two values are given. *Random* values are the statistics for the involvement of all the H atoms in the molecule, while *restricted* values are those restricted to the moieties involved in the individual transition states. It is clear that when the ion is very cold the isotope distributions are indeed close to the restricted values. When it is hot the values get much closer to those expected for more complete scrambling, which would require access to the intermediate complex.

An interesting feature of the cold ion is that there is a significant isotope effect in favor of the CID channel giving H_3O^+ (and loss of C_2H_3D). This could arise from distortions due to zero point energies differences, otherwise this reproducible result is difficult to rationalize in a straightforward manner.

E. CID Spectra of $C_2D_5ODH^+$: Loss of H. The $CD_3CD_2ODH^+$ ion, formed in the mixture ($CD_3CD_2OD + C_6H_5F + D_2O$) in Ar was also studied. Although many peaks in the CID spectrum are isotopically ambiguous, the data (see Figure 6 and Table 2) were generally consistent with the above. A surprising result is that for the loss of H. At low internal energies of the precursor, it completely dominates the spectrum and there is a very large isotope effect. This strongly suggests that the loss occurs directly from the −OHD group as reaction 16:

$$\textit{CID:}\qquad C_2D_5ODH^+ \rightarrow C_2D_5OD^+ + H \qquad (16)$$

This has a threshold energy which is 40 kJ mol^{-1} higher than loss of D from $-CD_3$, the channel which is the equivalent to reaction 6 and is the expected route.[4,5] At high temperature the ratio is much closer to the value expected if scrambling had occurred prior to decomposition. When the precursor is cold, there is also a very clear increase in favor of the elimination of HD relative to the other channels and relative to loss of D_2. The D_3O^+/HD_2O^+ peak ratio was close to the expected statistical value.

$(CH_3CD_2OD)D^+$ and $(CH_3CD_2OD)H^+$, which have been studied before,[4,16] were reexamined during this work. They gave supportive results, although the products of the designated low-exothermicity reaction with C_6D_5F in CH_4 could not be distinguished from possible high-energy self-protonation or deuteration reactions. In addition the CID fragment ions are mostly isotopically ambiguous.

Conclusions

The high-energy CID spectra of deuterated ethanol produced in its lowest-energy isomeric form, $C_2H_5OHD^+$, are highly sensitive to internal energy of the precursor ion, even down to thermal levels. Most of the changes observed can be rationalized if the collisional activation process is by vertical electronic excitation and the fragmentation to different products is affected by the starting configuration of the ion. When it is very cold the main loss process is by a high-energy direct bond cleavage of HDO from the rest of the molecule, with very little scrambling. This is at odds with the current consensus regarding the decomposition of this species. Scrambling does occur as the internal energy is increased. Within the time scale of the reactions studied, this cannot occur by any thermal mechanism within the source and must be induced within the collisionally activated molecule prior to decomposition. This is consistent with the participation of the excited complex $C_2H_4{\cdot}H_2DO^+$, but only when the precursor ion is hot.

It is argued here that increased internal rotations are the only significant motions which would be affected by thermal energies. Dynamically, this increase favors the channeling of the ion into the low-energy (but otherwise low-entropy) configuration upon high-energy collisional excitation. Jarrold et al.[8] considered external rotation and its effect on H loss. Because of an interfering overlap in our experiments we were not able to reliably investigate this aspect using $C_2H_5OHD^+$. However, when the precursor ion has a low temperature there is a very strong isotope effect in favor of H loss from $C_2D_5ODH^+$. This indicates that the H is lost directly from the −OHD group, whereas the lowest-energy and statistically more probable channel would be loss of D from the $-CD_3$ group. In agreement with Jarrold et al.,[8] we find H loss from $C_2H_5OH_2^+$ to increase significantly when the internal energy of the precursor is decreased. This has been rationalized in terms of external angular momentum effects. In our case the changes are even dependent on the temperature and are similar to the effect on the loss of H_2. This suggests the explanation may be more closely allied to changes in the internal rather than external rotation.

In CH_4 as the reagent gas, when the pressure is low or the temperature high, the spectrum of $(C_2H_5OH)H^+$ is very similar to spectra obtained elsewhere. The exothermicity of the reaction is well above the transition state to the $C_2H_4{\cdot}H_3O^+$ isomer. Yet under cold, high-pressure conditions it changes to resemble the spectrum obtained for $C_2H_5OHD^+$. This suggests that the ion does cool to the low energy structure without significantly becoming entrapped as the complex. This supports the conclusion of Fairley et al.[1] and of Matthews et al.[2] that this is also the likely structure of this species in outer space.

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the pressures used in these experiments and they act as chemical ionization reagent ions. Any ions created by direct electron impact with ethanol or perdeuterated fluorobenzene are in very low abundance by comparison, as shown by the conventional mass spectrum of ions emanating from the source. The reagent ions react to protonate any species present in the mixture with a higher proton affinity than the conjugate bases of the reagent ions (i.e., CH_4 and C_2H_4). Again, the conventional mass spectrum shows this up very well since the main peaks in the spectrum are the reagent ions and the protonated ethanol and perdeuterated fluorobenzene. It would be difficult to construct any other mechanism from ions present in the source and there is ample precedent since this is a very well-established and much used technique in analytical mass spectrometry (Harrison, A. G. *Chemical Ionization Mass Spectrometry*, CRC Press: Florida, 1983) and pulsed-high-pressure source experiments to determine proton affinities (Kebarle, P. *Techniques for the Study of Ion−Molecule Reactions*; Farrar, J. M., and Saunders, W. H. Jr., Eds.; J. Wiley & Sons: New York, 1988.).

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(19) Conventional transition state theory gives the upper limit for the rate constant of a thermal unimolecular reaction as: $k = ekT/h \exp(\Delta S^{\#}/R) \exp(-E^{\#}/R)$, where $\bar{k}$ = Boltzmann's constant, h = Planck's constant, $\Delta S^{\#}$ is the entropy of activation and $E^{\#}$ the energy of activation, R is the gas constant, and T is temperature. For a reaction involving a relatively constrained transition state, $\Delta S^{\#}$ will be small or negative.

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