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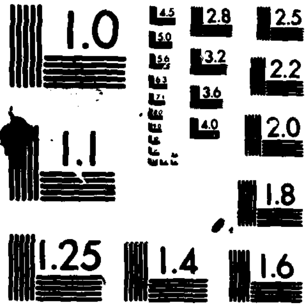

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Structures and Fragmentation Mechanisms of the Ions of Ethanol By Triple Quadrupole Mass Spectrometry

by

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The low energy (10-25 eV) collisionally activated decomposition of the molecular ion and of some important fragment ions of ethanol, ethanol-OD, and 2,2,2-d_3 ethanol has been studied by triple quadrupole mass spectrometry to obtain information regarding the ions' structures and fragmentation pathways. In this technique, ions generated by electron impact in the mass spectrometer ion source are mass selected in the first quadrupole, undergo collisionally activated decomposition (CAD) in the second, RF-only, quadrupole collision cell, and the resulting daughter ions are mass analyzed by the third quadrupole.

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The unit resolving power of the final quadrupole analyzer is a distinct advantage over other implementations of MS/MS in that structural information contained in deuterated species is readily obtainable. Ethanol ions thus studied include $[CH_3CH_2OH]^{(+)}$, $[CH_3CHOH]^{(+)}$, $[CH_2COH]^{(+)}$, $[CH_2CO]^{(+)}$, $[CH_3OH]^{(+)}$ and $[CH_2OH]^{(+)}$. Fragmentation mechanisms based on CAD spectra are consistent with the fragmentation of a particular ion's deuterated analogs. The elucidation of the decomposition mechanism leads to an unambiguous assignment of parent ion structure in many cases. The observed dissociations parallel closely those observed in both electron impact and high energy CID in sector instruments. The data suggest that fragmentation reactions which follow electron impact and collisional activation at both high and low energies are at least qualitatively independent of the method of excitation. Thus isotopic labeling in conjunction with low-energy collisionally activated decomposition in the triple quadrupole mass spectrometer is a convenient and useful tool for the determination of ion structure and fragmentation mechanisms, and is complementary to high energy collisional techniques.

Structures and Fragmentation Mechanisms of the Ions of Ethanol By Triple Quadrupole Mass Spectrometry

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ABSTRACT

The low energy (10-25 eV) collisionally activated decomposition of the molecular ion and of some important fragment ions of ethanol, ethanol-OD, and 2,2,2-d_3 ethanol has been studied by triple quadrupole mass spectrometry to obtain information regarding the ions' structures and fragmentation pathways. In this technique, ions generated by electron impact in the mass spectrometer ion source are mass selected in the first quadrupole, undergo collisionally activated decomposition (CAD) in the second, RF-only, quadrupole collision cell, and the resulting daughter ions are mass analyzed by the third quadrupole. The unit resolving power of the final quadrupole analyzer is a distinct advantage over other implementations of MS/MS in that structural information contained in deuterated species is readily obtainable. Ethanol ions thus studied include $[CH_3CH_2OH]^{+\cdot}$, $[CH_3CHOH]^+$, $[CH_2COH]^+$, $[CH_2CO]^{+\cdot}$, $[CH_3OH]^{+\cdot}$ and $[CH_2OH]^+$.

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Fragmentation mechanisms based on CAD spectra are consistent with the fragmentation of a particular ion's deuterated analogs. The elucidation of the decomposition mechanism leads to an unambiguous assignment of parent ion structure in many cases. The observed dissociations parallel closely those observed in both electron impact and high energy CID in sector instruments. The data suggest that fragmentation reactions which follow electron impact and collisional activation at both high and low energies are at least qualitatively independent of the method of excitation. Thus isotopic labeling in conjunction with low-energy collisionally activated decomposition in the triple quadrupole mass spectrometer is a convenient and useful tool for the determination of ion structure and fragmentation mechanisms, and is complementary to high energy collisional techniques.

INTRODUCTION

Low energy collisionally activated decomposition of gaseous ions provides a direct yet simple method for the elucidation of ionic structure. Triple quadrupole mass spectrometry[1] is a technique which embodies the low energy collision process; when coupled with isotopic labeling, it can yield unambiguous structural and mechanistic information[2]. A major advantage of triple quadrupole mass spectrometry (TQMS) for the study of ionic structure and fragmentation is the unit mass resolving power of both analyzer sections which allows fragments which differ by only one amu to be independently observed. In the present paper, the structure of some important ions of ethanol are determined by low energy collisionally activated decomposition

(CAD) and the mechanisms involved in their dissociation are explored with the aid of deuterium labeled isotopes.

Ethanol has been a popular molecule for the test of new techniques or theories in ionic structures [3-8]. Friedman et al.[3] in 1957, predicted a fragmentation scheme for ethanol based on appearance potentials and thermochemical calculations. However, more recent proposals for ethanol fragmentation have been made by Danchevskaya and Torbin[4]. Their work, based on electron impact studies of ethanol and several deuterated analogs, predicts both ion structure and fragmentation mechanisms.

Selected ion fragmentation in reversed geometry sector instruments has been well demonstrated for organic structure determination[9,10] Cooks [7] and coworkers in 1975 have performed high energy (∿8 keV) collision-induced dissociation of the ions of ethanol in a thermochemical study, which allowed the description of the reactions of highly excited ions.

In the present work, the ethanol fragments at m/z 46, 45, 43, 42, 32, and 31 are studied by low energy (10-25 eV) CAD. In addition, a comparison of the methods and results from electron impact, CID and CAD is offered.

EXPERIMENTAL

The triple quadrupole mass spectrometer used in this study has been described in detail in earlier work[11]. Briefly, the instrument consists of, in series, an electron impact ion source of special design, a quadrupole mass filter (Q1), an RF-only quadrupole collision cell (Q2), and a second quadrupole mass filter (Q3). The ion source, not previously described, is a cross axial type with a magnetically confined electron beam. An elongated, wire mesh enclosed ionization region provides electron energy homogeneity and minimizes interactions with unionized molecules. The ion volume exit aperture leads to three focusing lenses and an Extranuclear Labs 'ELFS' leaky dielectric quadrupole entrance aperture to avoid effects of fringing fields. Detection is via a Galileo 4800 channel electron multiplier. The output current is amplified by a Kiethly 18000-20 picoammeter, and data recorded by an H-P 7044A X-Y recorder.

The ethanol used for analysis was reagent grade and used without further purification. Ethanol-OD (min 99 atom %D) and 2,2,2-d_3 ethanol (98 atom %D) were purchased from Merck and Co. (St. Louis, MO 63116).

The sample was degassed by standard freeze-pump-thaw cycle and was then bled into the source through a Granville-Phillips variable leak, to a pressure of 5 millitorr (1 torr = 133 Pa). The electron energy was 70 eV with an emission current of 0.25 mA. The argon target gas was from Airco Industrial Gases (Southfield, MI 48075), 99.998% pure. Target gas pressure was measured by a calibrated Bayard-Alpert type ionization gauge and regulated by a Granville-Phillips model 216 flow controller.

An ion of particular m/z produced in the source and chosen for study was selected by quad 1; argon target gas was then bled into the collision cell and automatically regulated to 4×10^{-4} torr. The resulting fragmentations were determined by scanning the second analyzer (Q3). Spectra were recorded with 10 V and 25 V axial energy. The axial energy, E_{AX}, is approximately equal to the offset voltage between source ion volume and the quadrupole rods of the collision region. Axial energy profiles (I vs. E_{AX}) give characteristic information regarding CAD product ions' nature and origin[12]. Profiles were obtained for all ions suspected of arising from charge exchange or proton transfer to determine the nature of the transition. CAD spectrum were obtained for every ion in the EI spectra of ethanol ethanol-OD, and 2,2,2-d_3 ethanol, having an intensity greater than 5% of the base peak. Data given in Tables 1-4 are accurate to within 10%.

RESULTS AND DISCUSSION

Tables 1 — 4 show low energy (E_{AX} = 25V) CAD spectra of the major ions formed by electron impact from ethanol, ethanol-OD, 2,2,2-d_3 ethanol, and methanol/methanol-OD. The intensities given for the parent ion relative to the base daughter ion peak are indicative of the collision cross-sections for the parent ion. A higher parent peak implies a lower cross-section. The structures and fragmentation mechanisms reported for the ions of ethanol are consistent with those of their isotopically labeled analogs.

m/z 46: $[CH_3CH_2OH]^{+\cdot}$

The structure of the molecular ion is unambiguous in this case since it arises from a saturated molecule, and has only one site of nonbonding electrons available for ionization. Upon collision (E_{AX}

= 25V into argon) the molecular ion produces $[45]^+$, and $[31]^+$ directly, both by α-cleavage, as seen in Schemes 1 and 2. This is consistent with the labeled analogs' behavior: ethanol-OD shows $[M]^{+\cdot} \rightarrow [CH_3CHOD]^+ + H$, and $[M]^{+\cdot} \rightarrow [CH_2OD]^+ + \cdot CH_3$, while d_3 ethanol yields the analogous $[M]^{+\cdot} \rightarrow [CD_3CHOH]^+ + H$ and $[M]^{+\cdot} \rightarrow [CH_2OH] + \cdot CD_3$. Loss of methyl provides the base peak, and loss of H forms an ion of approximately 50% base peak in all cases. Other peaks seen in CAD spectrum of ethanol molecular ion, viz. m/z 30, 27, and 15, may arise from $[M-H]^+$ at m/z 45, since these transitions are strong in the $[45]^+$ CAD spectrum itself, and appear there in the same ordering as observed in the $[46]^{+\cdot}$ CAD spectrum.

The target pressure response for this fragmentation is shown in Figure 1. The parent ion at m/z 46 is attenuated at increasing pressure due to fragmentation; at higher pressures some scattering loss is observed. The $[M-H]^+$ fragment at m/z $45^{\ddagger}$ is composed of both a metastable and a collisional contribution. If the metastable contributor (∿8%) is removed, the contribution from collisionally activated decomposition can be determined, and is shown by the dashed line at m/z 45 in the figure. Other daughter ions at m/z 31, 30, 27, and 15 show their pressure dependence as indicated. If the fragment ion response is normalized to the scattering-corrected parent ion intensity, the log-log slope of the fragments indicates the order of the reaction:

m/z	$45^{\ddagger}$	45	31	30	27	15
Slope	0	1.0	1.1	1.0	1.9	1.9

These reaction orders demonstrate that the parent ion produces m/z 45, 31 and possibly 30 by a first order (single collision) process. Analogous to the $[46]^{+\cdot} \rightarrow [31]^{+}$ transition may be the loss of methyl from $[45]^{+} \rightarrow [30]^{+\cdot}$ The cross-sections for these reactions at 10^{-5} torr target pressure are well within a factor of 3: 13 and 5.9 Å^2, respectively. The second order processes (two collisions) may follow $[46]^{+\cdot} \rightarrow [45]^{+} \rightarrow [27]^{+}$ and $[46]^{+\cdot} \rightarrow [45]^{+} \rightarrow [15]^{+}$ pathways; it is possible, however, for the second order processes to follow a first order collisional excitation of the parent ion $[46]^{+\cdot} \rightarrow [46^{*}]^{+\cdot} \rightarrow [27]^{+}$ and $[46]^{+\cdot} \rightarrow [46^{*}]^{+\cdot} \rightarrow [15]^{+}$.

The ion at m/z 29 is a mixture of $[C_2H_5]^+$ and $[CHO]^+$. The library reference spectra of $[C_2H_5]^+$ show a $15^+:14^+:13^+:12^+$ ratio of 100:55:2:0 while $[CHO]^+$ reference spectra give a $13^+:12^+$ ratio of about 10:4. Ethanol $[29]^+$ provides a 10:7:8:3 ratio of the 15^+-to-12^+ series which, assuming the molecular ion fragments similarly to $[29]^+$ by EI and CAD, indicates the presence of a mixture which is approximately 80 ± 10% $[CHO]^+$. Friedman and coworkers[3] have determined this value by high resolution MS to be 77%. The $[C_2H_5]^+$ arises from a charge site-initiated loss of OH from the molecular ion, while the $[CHO]^+$ is probably formed through the $[45]^+$ intermediate.

Protonated or deuterated water ions are formed at m/z 19 from ethanol molecular ion, at m/z 19 and 20 from ethanol-OD and at m/z 22^+, 21^+, and 20^+ from d_3 ethanol from both $[46]^+$ and $[45]^+$ parent ions by rearrangement, the exact mechanisms of which are highly complex[7].

m/z 45: $[CH_3CHOH]^+$

The $[45]^+$ ion was seen to have arisen from α cleavage of the molecular ion at $[46]^{+\cdot}$. As such, its CAD spectrum should be analogous to the $[46]^+$ from ethanol-OD and the $[48]^+$ from d_3 ethanol. Scheme 3 shows a four centered loss of H_2 from the carbonyl and α carbon. Ethanol-OD and d_3 ethanol show an analogous reaction, loss of H_2 and HD, respectively.

Scheme 4 shows odd electron ion formation from an even electron species. Although decompositions of even electron species have been poorly understood[13], a recent review article by McLafferty [14] describes their utility in characterizing structure. This particular even electron mechanism is seen often in CAD of even electron ions[15,16]. The driving force of the fragmentation is necessarily inductive in nature, but instead of attracting an electron pair, only one of the electrons of the bond is attracted to the charge site. The other electron leaves with the neutral radical, molecule or atom. Since this mechanism does not involve a true electron pair induction, for purposes of this discussion we will refer to it as electron unpairing, after Sigsby, Day and Cooks[15,16] and give it the notation i*. A loss of methyl radical from $[45]^+$ by electron unpairing forms $[HCOH]^{+\cdot}$ at m/z 30. Ethanol-OD $[46]^+$ and 2,2,2-d_3 ethanol $[48]^+$ similarly lose $\cdot CH_3$ and $\cdot CD_3$ to form $[31]^{+\cdot}$ and $[30]^{+\cdot}$, respectively.

The formation of $[27]^+$ and H_2O from $[45]^+$ involves the loss of hydroxyl and the competing loss of hydrogen from both the number one and two positions. While the ethanol-OD analog at m/z 46 shows predominantly a loss of 19 (OD plus unspecified H), the 2,2,2-d_3 ethanol demonstrates loss of 18 (H from no. 1 carbon) and the loss of 19 (D from no. 2 carbon) in a 3:2 ratio respectively (Scheme 5).

The $[CHO]^+$ daughter ion at m/z 29 is formed by the loss of the terminal methyl and the hydroxyl proton. This is indicated by the observation that $[29]^+$ is similarly intense in the spectra of all three analogs, although the exact mechanism of formation remains unclear.

The m/z 45 parent can also form $[CH_3]^+$ by induction from the carbonium ion as shown in Scheme 6. The d_3 analog similarly forms $[CD_3]^+$ at m/z 18, as well as $[CD_2H]^+$ and $[CDH_2]^+$ from rearrangement prior to fragmentation.

m/z 43: $[CH_2COH]^+$

This ion at m/z 43 arises from loss of vicinal H_2 from $[45]^+$. The important resonance contributors of this ion can be seen in Table 5. The charge site can exist on the oxygen or carbonyl carbon (Schemes 7 and 8). From the former, electron unpairing results in the loss of H, (or D from the -OD analog) while the similar mechanism induced by the charge on carbon results in the formation of the acetylene ion in both cases, and loss of neutral OH (or OD). The migration of the hydroxyl proton to the terminal carbon is very important in this ion due to the high stability of the carbon monoxide leaving group. This results in the inductive formation of $[15]^+$ as the base peak for the ethanol sample (Scheme 9), and $[16]^+$ for the ethanol-OD analog whose parent appears at m/z 44. The corresponding d_3 ethanol ion at m/z 45 contains rearrangement ions, e.g. CDH_2COH^+, which can cause ambiguity in interpretation.

m/z 42: $[CH_2CO]^{+\cdot}$

The structure of the ion at m/z 42 is seen to arise from a loss of four protons, one of which is the hydroxyl proton (cf. Scheme 7). The fragmentation of m/z 42 is shown in Scheme 10 and is equivalent to the ethanol-OD spectrum at the same m/z; both show loss of CO to form the $[CH_2]^{+\cdot}$ species as the base peak. The d_3 ethanol spectrum which corresponds to this structure occurs at m/z 44. Although this ion fragments to the analogous $[CD_2]^{+\cdot}$ at m/z 16, this $[44]^{+\cdot}$ may contain rearranged $[CDHCOH]^+$ as well, which would also produce a peak at m/z 16, i.e. $[CDH_2]^+$ by Scheme 9.

m/z 32: $[CH_3OH]^{+\cdot}$

For completeness, the ions of methanol and methanol-OD are included. For the molecular ions, two important reactions are observed: the radical site initiated α cleavage to form $[M\text{-}H]^+$ as the base peak, and the charged induced formation of methyl ion (Schemes 11 and 12).

m/z 31: $[CH_2OH]^+$

The species at m/z 31 has two important resonance contributors shown in Table 5. Four centered loss of hydrogen is shown in Scheme 13; electron unpairing forms $[CH_2]^{+\cdot}$ at m/z 14, leaving behind the neutral hydroxyl molecule (Scheme 14). Analogous behavior is again observed in both ethanol-OD and methanol-OD ions at $[32]^+$. In addition, the ethanol spectrum is identical to the d_3 ethanol spectrum at m/z 31, which is consistent with the mechanism for formation of this ion.

Agreement with Other Work

The fragmentation of ethanol has been the subject of a number of studies. Friedman et al.[3] employed a semiempirical application of the statistical theory of mass spectra to assign structures and fragmentation pathways to the mass spectrum of ethanol. Although important differences exist in the nature of electron impact and low energy CAD which preclude direct correlations of fragmentation pathways, a general comparison an be made. For example, Friedman predicts two products from direct decomposition of the molecular ion which are unobserved in the CAD study, viz. $[46]^{+\cdot} \rightarrow [44]^{+\cdot}$ and $[46]^{+\cdot} \rightarrow [30]^{+\cdot}$. In addition, CAD shows six processes in the fragmentation of $[45]^{+}$ which are not predicted in the theoretical model.

A direct comparison of the assignment of ion structures can be made, however, since the parent ion in the CAD study arises from electron impact. The earlier work and the present work concur on the assignment of ionic structures at m/z 46, 45, 44, 31, and 30. However, the structure at m/z 43 is postulated by Friedman to be $[CH_3CO]^{+}$; the present work proposes the structure to be $[CH_2COH]^{+}$. The evidence which suggests that $[CH_3CO]^{+}$ may not be the structure of $[43]^{+}$ is that its precursor loses H_2 from vicinal hydrogens to form $[CH_2COH]^{+}$ (Scheme 3) and also that the terminal methyl structure is unlikely to lose OH, required for the formation of $[C_2H_2]^{+\cdot}$. As mentioned earlier in the discussion regarding $[CH_2COH]^{+}$, migration of the hydroxyl proton is important for the elimination of CO, and therefore, $[CH_3CO]^{+}$ must exist for at least some time prior to CO loss.

Danchevskaya and Torbin[4] propose the structure of this ion to be $[CH_2CHO]^+$. Their work does imply a migration of the acidic proton to the carbonyl site, however. In all other cases their hypotheses of ion structures agree with ours.

Cooks and coworkers[7] have studied the fragmentation of ethanol in a work on the thermochemistry of reactions of highly excited ions. Of the 16 high energy (8 kV) collision-induced dissociations reported by Cooks, all but one are observed in the present low energy (25 eV) study, although in some cases, relative intensities do not correspond (Table 6).

Jennings [17] has pointed out that distribution within groups of CID peaks was very similar to that observed within the same groups in a 70 eV mass spectrum. This suggests that despite the different methods of excitation, the distribution of excitation energies is not very different in the two cases. He therefore concludes that relative abundance of fragments depends only on the initial energy transferred to the molecules and not upon the method by which the energy is transferred.

By comparing the present study with the results of Cooks [7] we have shown that low energy CAD fragmentation spectra are quite similar to those resulting from both high energy CID and electron impact. Although collisional activation in high and low energy systems involves electronic [18] and vibrational [19] excitation respectively, the amount of energy thus deposited must be approximately the same in both cases.

CONCLUSIONS

Ions of ethanol, ethanol-OD, and 2,2,2-d_3 ethanol were directly characterized by low energy CAD in the triple quadrupole mass spectrometer. The structure of ethanol ions at m/z 46, 45, 43, 42, 32, and 31 are postulated to have the following structures: $[CH_3CH_2OH]^{+\cdot}$, $[CH_3CHOH]^+$, $[CH_2COH]^+$, $[CH_2CO]^{+\cdot}$, $[CH_3OH]^{+\cdot}$, and $[CH_2OH]^+$. In addition, the mechanisms for the formation and fragmentation of these ions are demonstrated. Fragmentations can be the result of multiple collisions in the "RF only" quadrupole.

A mechanism is described which rationalizes the appearance of odd-electron collision products from even-electron parent ions. This mechanism, termed electron unpairing [14,15], is initiated by the charge site and involves the breaking of an adjacent bond, only one of whose electrons is captured by the charge site. The other electron leaves with the neutral species as a radical or H.

In addition, the similarities in the nature of low-energy CAD, high-energy CID and electron impact spectra suggest that the resulting spectra depend only on the initial energy transferred to the molecule or ion, and not upon the method by which this energy is transferred. These similarities appear to provide complementary information which may prove useful in areas of structure elucidation and ion physics.

Triple quadrupole mass spectrometry, when applied to studies of isotopically labeled analogs can yield unambiguous information regarding the structure of the selected ion, and the mechanisms of its collisionally activated decomposition.

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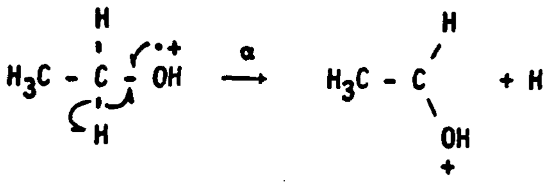
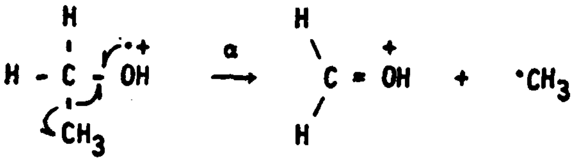
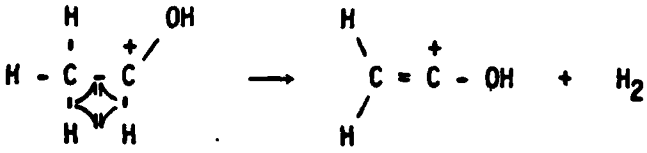


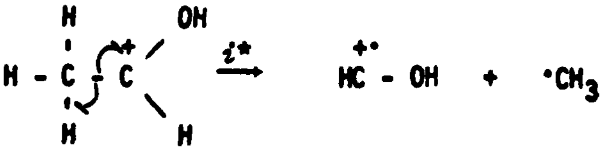
SCHEME 1: $[46]^{+\cdot} \rightarrow [45]^{+}$



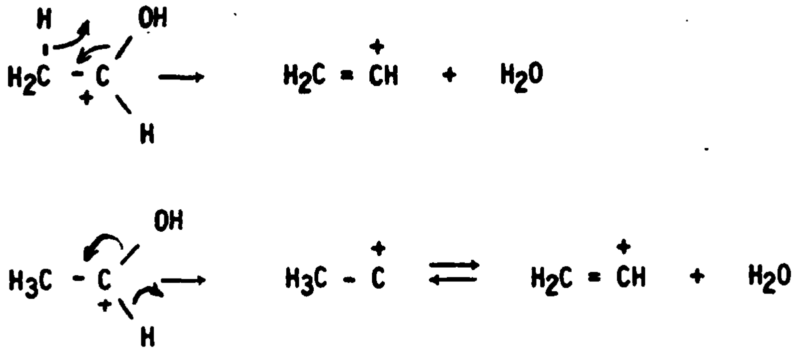
SCHEME 2: $[46]^{+\cdot} \rightarrow [31]^{+}$



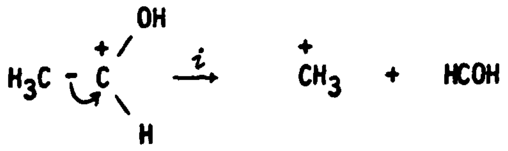
SCHEME 3: $[45]^{+} \rightarrow [43]^{+}$



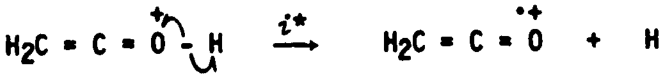
SCHEME 4: $[45]^{+} \rightarrow [30]^{+\cdot}$



SCHEME 5: $[45]^+ \rightarrow [27]^+$

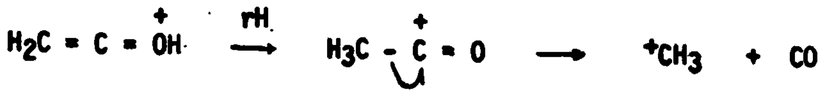


SCHEME 6: $[45]^+ \rightarrow [15]^+$

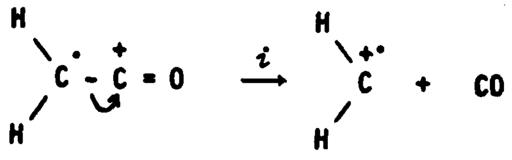


SCHEME 7: $[43]^+ \rightarrow [42]^{+\cdot}$

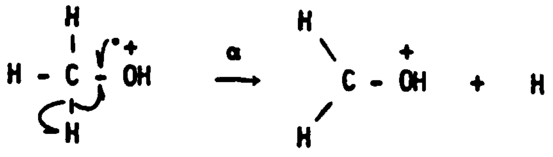
SCHEME 8: $[43]^+ \rightarrow [26]^{+\cdot}$



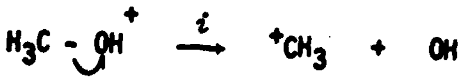
SCHEME 9: $[43]^{+} \rightarrow [15]^{+}$



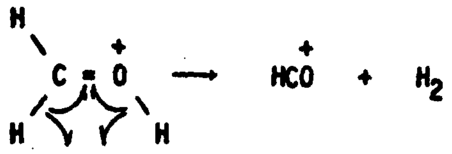
SCHEME 10: $[42]^{+\cdot} \rightarrow [14]^{+\cdot}$



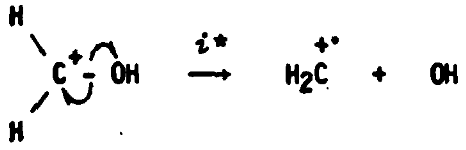
SCHEME 11: $[32]^{+\cdot} \rightarrow [31]^{+}$



SCHEME 12: $[32]^{+\cdot} \rightarrow [15]^{+}$



SCHEME 13: $[31]^+ \rightarrow [29]^+$



SCHEME 14: $[31]^+ \rightarrow [14]^{+\cdot}$

Table 1. Low Energy (E_{AX} = 25 eV) CAD Spectra of Ethanol Ions. Intensities are given as % of most abundant daughter ion.

CAD Ions	Parent Ions, m/z					
m/z	46	45	43	42	31	30
46	300					
45	45	3600				
43		12	450			
42			15	420		
31	100				5900	
30	3.0	64				920
29	10.6	100	2.4		99	100
28		7.1				
27	4.8	98				
26		7.1	1.2			
25						
19	1.2	66				
15	1.9	21	100			
14			4.3	100	100	2.9
13				2.3	7.7	4.6

Table 2. Low Energy (E_{AX} = 25 eV) CAD Spectra of Ethanol-OD Ions.

CAD Ions	Parent Ions, m/z					
m/z	47	46	44	42	32	31
47	265					
46	54	3000				
44		9.4	1100			
42			12	750		
32	100				7000	
31	2.9	100				3000
30		6.2	8.3		30	
29	7.0	53	13		100	100
28		6.2				
27	2.9	75				
26			5.6			
20	.58	53				
19	.35	7.8				
16	.19	7.8	100			
15	.69	3.7	10			
14			10	100	48	10
13				2.7	5.0	3.1

Table 3. Low Energy (E_{AX} = 25 eV) CAD Spectra of 2,2,2-d_3 Ethanol Ions.

CAD Ions	Parent Ions, m/z				
m/z	49	48	45	44	31
49	450				
48	55	2600			
45		4.0	830		
44		3.1	2.0	560	
32	6.2	2.1			
31	100	21			6250
30	7.1	100	1.5	.6	
29	6.1	66	3.7	1.3	100
28	.76	4.0	.67	.4	
27		1.6	2.1	.8	
22	1.0	1.5			
21	1.9	17			
20	.33	21			
19					
18	.71	2.6			
17	.52	8.4	100		
16		5.3	2.2	100	
15			1.2	1.2	
14				1.0	62
13					6.2

Table 4. Low Energy (E_{AX} = 25 eV) CAD Spectra of Methanol[a] and Methanol-OD[b] Ions.

CAD Ions m/z	Parent Ions, m/z $^{a}32$	$^{a}31$	$^{b}33$	$^{b}32$	$^{b}31$
33			1700		
32	1400		100	1800	
31	100	3400			7000
29		100		100	100
28					
16					
15	18		32	12	
14	4.8	25	5.8	11	41
13		3.6			6

Table 5. Structure of the major ions of ethanol[a] and methanol[b].

$^{a}[46]^{+\bullet}$	$H_3C - CH_2 - \overset{\bullet +}{O}H$
$^{a}[45]^{+}$	$H_3C - \overset{+}{C}H - OH$
$^{a}[43]^{+}$	$H_2C = \overset{+}{C} - OH \leftrightarrow H_2C = C = \overset{+}{O}H$
$^{a}[42]^{+\bullet}$	$H_2\overset{\bullet}{C} - \overset{+}{C} = O \leftrightarrow H_2C = C = \overset{\bullet +}{O}$
$^{b}[32]^{+\bullet}$	$H_3C - \overset{\bullet +}{O}H$
$^{a,b}[31]^{+}$	$H_2\overset{+}{C} - OH \leftrightarrow H_2C = \overset{+}{O}H$

Table 6. Comparison of High Energy CID in MIKES with Low-energy CAD in TQMS for the Fragmentation of Ions of Ethanol. Key: s: Strong, > 10%; m: medium, 1-10%; w: weak, <1%.

DECOMPOSITION	INTENSITIES	
	MIKES	TQMS
$[46]^{+\cdot} \rightarrow [45]^{+}$	s	s
$[46]^{+\cdot} \rightarrow [43]^{+}$	m	not observed
$[46]^{+\cdot} \rightarrow [31]^{+}$	m	s
$[46]^{+\cdot} \rightarrow [30]^{+\cdot}$	not reported	m
$[46]^{+\cdot} \rightarrow [29]^{+}$	w	m
$[46]^{+\cdot} \rightarrow [28]^{+\cdot}$	m	w
$[46]^{+\cdot} \rightarrow [27]^{+}$	w	m
$[46]^{+\cdot} \rightarrow [19]^{+}$	w	w
$[46]^{+\cdot} \rightarrow [15]^{+}$	not reported	m
$[45]^{+} \rightarrow [43]^{+}$	m	w
$[45]^{+} \rightarrow [31]^{+}$	w	w
$[45]^{+} \rightarrow [30]^{+\cdot}$	not reported	m
$[45]^{+} \rightarrow [29]^{+}$	m	m
$[45]^{+} \rightarrow [28]^{+\cdot}$	w	w
$[45]^{+} \rightarrow [27]^{+}$	m	m
$[45]^{+} \rightarrow [19]^{+}$	s	m
$[45]^{+} \rightarrow [15]^{+}$	w	w
$[43]^{+} \rightarrow [29]^{+}$	w	w
$[31]^{+} \rightarrow [29]^{+}$	s	m

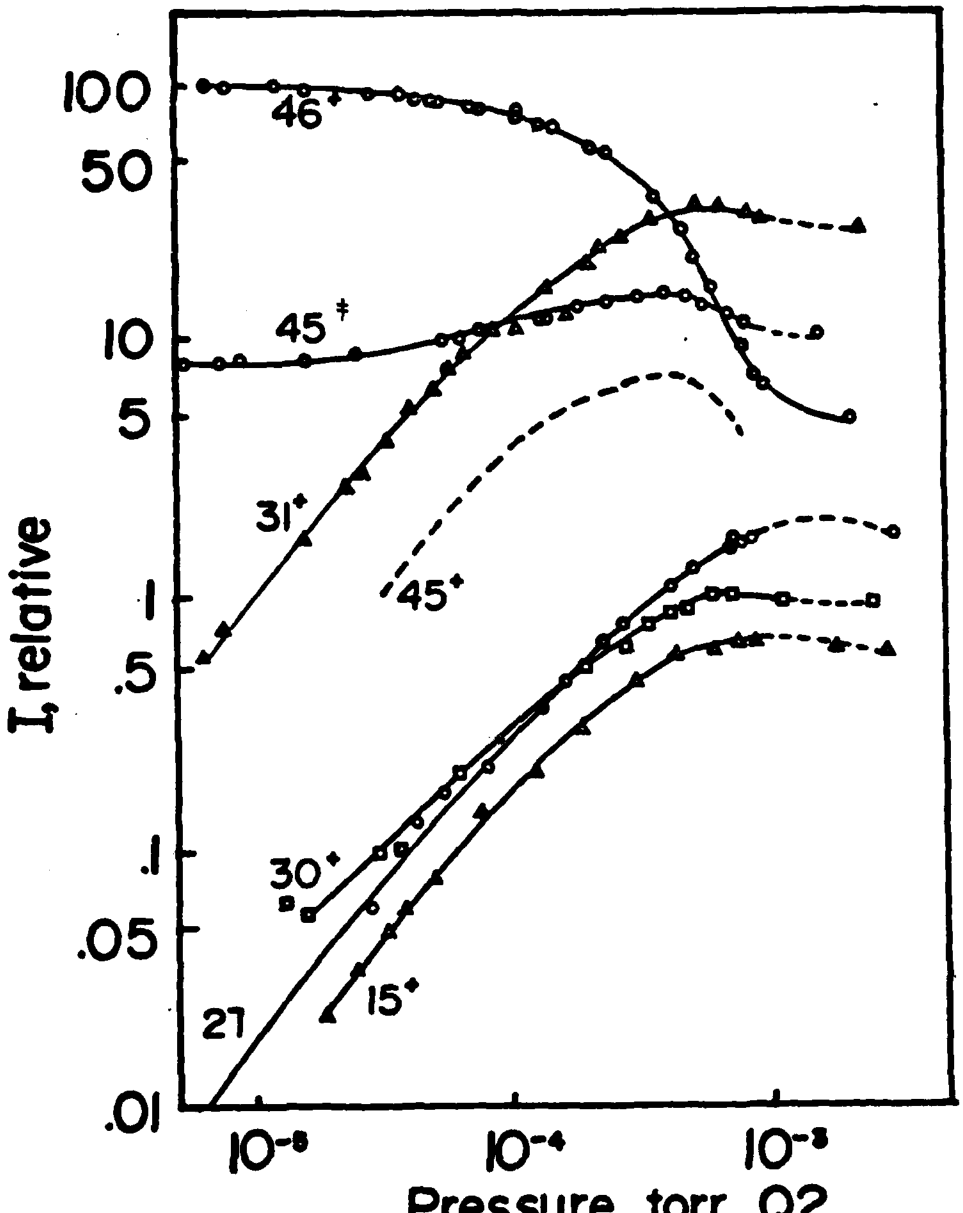


Figure 1: CAD product ion intensity vs. pressure for the fragmentation of 46^+ from ethanol.

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