Application of Reactive Collisions for Differentiation of Isomeric Organic Ions in the Gas Phase

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The structures of $C_2H_3O^+$ and $C_2H_5O^+$ isomers produced from various precursor molecules were identified using unsaturated hydrocarbons (buta-1,3-diene and benzene) as reactive collision gases in a triple quadrupole mass spectrometer.

Structure elucidation of isomeric organic ions in the gas phase was first based on unimolecular ('metastable') decompositions in double focusing mass spectrometers.[1] The introduction of a collision cell through which the ions are transmitted increased significantly the variety and intensity of fragment ions. These dissociation products are formed either by unimolecular or by collisionally activated dissociations (CAD).[2] Application of these high energy (keV) CAD reactions of organic ions to structural analysis has received wide attention during recent years.[3] However, it is found that differences in CAD mass spectra of isomeric ions are not large. Moreover, the overall secondary ion yield is also quite low (0.1—1%).

Larger reaction cross sections and higher secondary ion yields are obtained by low energy (10—100 eV) CAD processes in triple quadrupole mass spectrometers (TQMS) which accordingly, provide an interesting alternative for CAD based mass spectroscopic analysis.[4] These instruments are also able to accommodate primary ions of a very low (*ca.* 1 eV) kinetic energy, leading to greatly diminished CAD processes but at the same time new reactive collisions, *e.g.* protonation and adduct ion formation may occur depending on the collision gas. This provides new exciting prospects to probe ion structures.

There are a few preliminary studies[5] where reactive collisions have been noted using TQMS. However, any systematic research as to the general applicability of this method has not yet been undertaken. Therefore, we selected two very thoroughly examined simple systems, $C_2H_3O^+$ and $C_2H_5O^+$ isomers, for study in order to compare the results obtained in the reactive collision conditions with corresponding high energy CAD studies.

Of the potential $C_2H_3O^+$ isomers, the acetyl cation [$CH_3C^+{=}O$] and 1-hydroxyvinyl cation [$CH_2{=}C^+{-}OH$] are characterised by CAD studies[6,7] and theoretical[8] studies as being the most stable species. It was first believed[6] that acetone would produce the former ion and ethanol the latter in electron impact ionisation but later more detailed studies indicated that the $C_2H_3O^+$ ions from these precursors are, in fact, different mixtures of structures.[7]

By employing a home-made TQMS (Chemistry Dept., University of St. Andrews)[9] $C_2H_3O^+$ ions were made on electron impact from acetone and ethanol and directed at 1 eV kinetic energy to a collision cell (second quadrupole) where buta-1,3-diene, benzene, or toluene acted as reactive gases. The results are shown in Table 1 together with high energy CAD data from the literature. It is clear that in both cases a more reliable distinction between different isomers (or mixtures of isomers) is obtained using reactive collisions. Evidently, in the future this method will also give further information on ion structures.

The most important feature is that in reactive collisions not only relative intensities of the peaks can differ but also totally *new specific peaks* may appear depending on various ion/molecule reaction channels available for the isomer. This observation can create an extra dimension for the ion structure evaluation in quadrupole systems: specific collision gases. In high energy CAD the small variations in the relative intensity of the *same peaks* are usually employed to characterise isomeric ions as seen in Table 1.

$C_2H_5O^+$ isomers serve as another example to distinguish

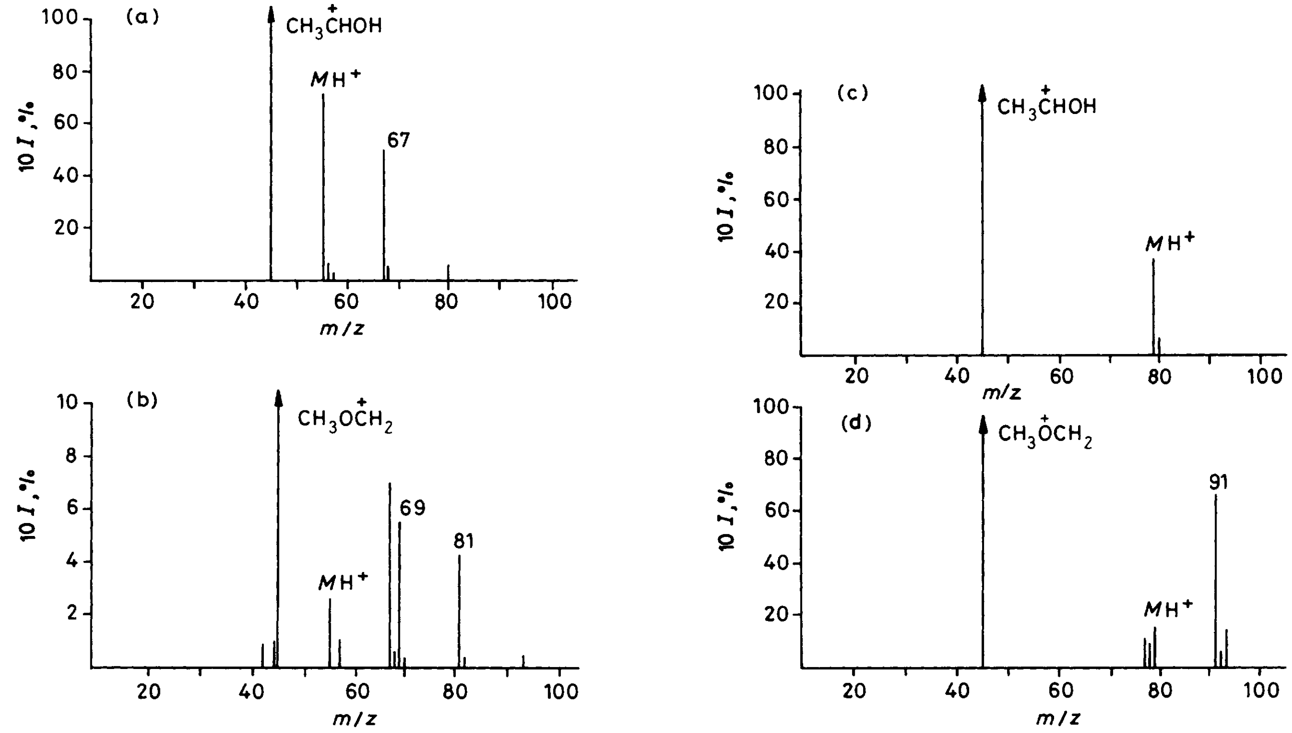

Figure 1. Reactive collisions of $C_2H_5O^+$ isomers with buta-1,3-diene (a,b) and benzene (c,d).

Table 1. Comparison of mass spectra of isomeric $C_2H_3O^+$ and $C_2H_5O^+$ ions produced by CAD and reactive collisions.

Precursor	Ion	Gas	Intensity[b] (*m/z*)										Ref.
CH_3COCH_3	$C_2H_3O^+$	Buta-1,3-diene	26(15)	11(41)	5(54)	26(55)			14(67)				This work[a]
CH_3CH_2OH	$C_2H_3O^+$	Buta-1,3-diene			5(54)	39(55)	7(56)	30(66)		7(76)	5(78)	9(80)	This work
CH_3COCH_3	$C_2H_3O^+$	Benzene	18(77)	25(78)	37(79)	3(80)	11(91)						This work
CH_3CH_2OH	$C_2H_3O^+$	Benzene	9(77)	13(78)	67(79)	5(80)		6(100)					This work
CH_3COCH_3	$C_2H_3O^+$	CAD[c]	6(13)	11(14)	57(15)	4(26)	8(28)	5(29)	13(41)	44(42)			7a
CH_3CH_2OH	$C_2H_3O^+$	CAD	4(13)	8(14)	40(15)	4(26)	5(28)	7(29)	10(41)	60(42)			7a
$(CH_3OCH_2)_2$	$C_2H_5O^+$	CAD	8(14)	49(15)	2(19)	2(26)	4(27)	190(29)[d]	12(42)	31(43)			2
CH_3CH_2OH	$C_2H_5O^+$	CAD	2(14)	4(15)	4(19)	7(26)	13(27)	16(29)	16(42)	33(43)			11

[a] Experiments were performed on a TQMS[9] consisting of three VG-QXK-300 quadrupoles in series, the second quadrupole providing an RF-only collision region. Reagent gas pressures were in the range 10^{-4} to 10^{-3} mbar. [b] Abundances relative to total ion abundance (100%). Small ion abundances excluded. [c] High energy CAD, He as collision gas. [d] Excluded because of strong unimolecular component.

isomeric ions in the gas phase using reactive collisions. Two of the most stable isomers[10] of $C_2H_5O^+$ ions are the 1-hydroxyethyl cation [CH_3C^+HOH] and methoxymethyl cation [$C^+H_2OCH_3$]. Figure 1 shows how these ions can be differentiated using buta-1,3-diene (1a,1b) and benzene (1c,1d) as collision gases. In Figure 1a and 1c [CH_3C^+HOH] was produced from ethanol and in Figure 1b and 1d, [$C^+H_2OCH_3$] from 1,2-dimethoxyethane. These ions are also distinguishable in their CAD spectra (Table 1). It is not possible without more detailed investigations to comment on the structures of secondary ions formed. However, it is very probable that *e.g.* the $C_7H_7^+$ ion at *m/z* 91 in Figure 1d is produced *via* the same process as is observed in ion cyclotron resonance conditions.[12]

In conclusion, reactive collision in a commercial triple quadrupole mass spectrometer has allowed a new exciting method to be developed for the structure elucidation of organic isomeric and possibly stereoisomeric ions in the gas phase. Comparison with the collisionally activated dissociation method used in sector mass spectrometers shows the advantages of this new approach.

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