Investigations of Oxonium Ions

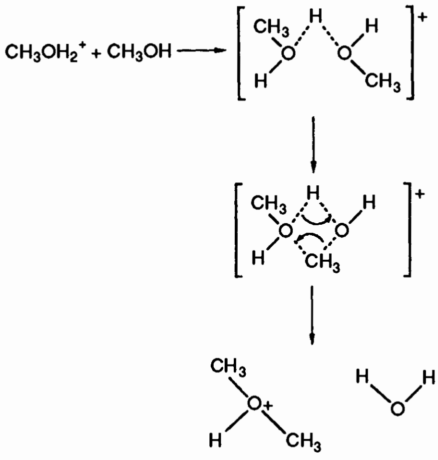
John M. Tedder and G. Stewart Walker*,†
Department of Chemistry, St. Andrews University, St. Andrews, Fife, KY16 9ST, Scotland, UK

Isotopically labelled methanol was used in an investigation of the ion–molecule reactions of methanol in the gas phase using a triple quadrupole mass spectrometer. A quinqua quadrupole mass spectrometer was used to investigate the formation of trimethyl oxonium ions. The results were used to examine the validity of the alternative mechanisms for the reaction (1) that have been

$$CH_3OH_2^+ + CH_3OH \longrightarrow (CH_3)_2OH^+ + H_2O \quad (1)$$

proposed in the literature. The results provide unequivocal support for the S_N2 mechanism.

The formation of ions from methanol in the gas phase has been studied for many years.[1–8] From the results of double resonance ion–cyclotron experiments Henis[9] concluded that protonated dimethyl ether was formed by fragmentation of the addition complex of two methanol molecules and a proton. The mechanism that he proposed involved a methyl group and a proton shifting from one oxygen to the other (Scheme 1).



Scheme 1

Recent interest in the reactions of methanol has been heightened by its use in studies of clusters and by the development of the Mobil methanol-to-gasoline (M.T.G.) process. Reaction (1) is thought to be the fundamental first step in the conversion of methanol to hydrocarbons.[10–12] The present work was initiated by a desire to investigate the reaction mechanisms associated with the M.T.G. process.

The rate constants for the competing reactions (1) and

$$CH_3OH_2^+ + CH_3OH \longrightarrow (CH_3)_2OH^+ + H_2O \quad (1)$$

$$CH_3OH_2^+ + CH_3OH \longrightarrow (CH_3OH)_2H^+ \quad (2)$$

(2) have been determined as a function of temperature and pressure with the use of ion–cyclotron resonance spectroscopy.[13]

A metastable reaction (3) involving the elimination of water

$$(CH_3OH)_2H^+ \longrightarrow (CH_3)_2OH^+ + H_2O \quad (3)$$

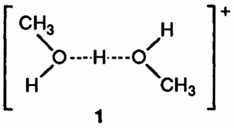
from the proton bound dimer of methanol to form protonated dimethyl ether was observed in the field free region of the mass spectrometer. This would support the mechanism proposed by Henis.[9]

MIKES (Mass Analysed Ion Kinetic Energy Spectroscopy) and CAD (Collisionally Activated Dissociation) spectra have yielded the ratios of water loss to methanol loss from the proton bound dimer of methanol.[14] The $C_2H_9O_2^+$ ion formed in a MIKES high-pressure ion source preferentially lost water [reaction (4)] rather than methanol [reaction (5)] in the ratio 5.5:1.

$$(CH_3OH)_2H^+ \longrightarrow (CH_3)_2OH^+ + H_2O \quad (4)$$

$$(CH_3OH)_2H^+ \longrightarrow CH_3OH_2^+ + CH_3OH \quad (5)$$

The CAD spectrum showed a reversal in this ratio. Reaction (4) was less favoured than reaction (5) in the ratio of 1:3. Iraqi and Lifshitz[14] took these results to indicate that the ion $C_2H_9O_2^+$ had the structure **1**.



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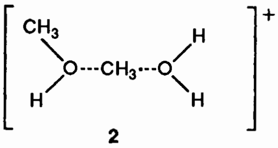
Kleingeld and Nibbering have reported experimental results using ^{16}O and natural abundance ^{18}O methanol in which the oxygen from the neutral methanol was preferentially retained in the protonated dimethyl ether by a factor of 3:1 [see reactions (6) and (7)]. Their experiments cast doubt on the intermediacy of an ion structure such as **1** with symmetrical hydrogen bonds and supported the suggestion of an S_N2 attack through an intermediate of structure **2**.



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† *Present address:* Department of Chemistry, La Trobe University, Bundoora, Victoria, 3083, Australia.

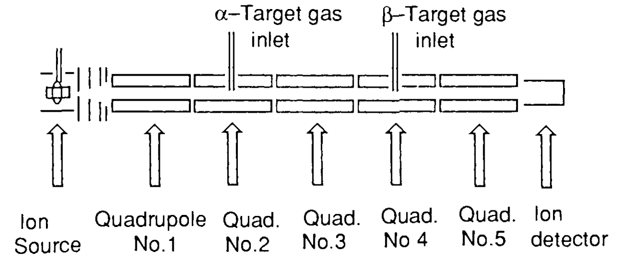


Fig. 1 Schematic diagram of quinqua quadrupole mass spectrometer

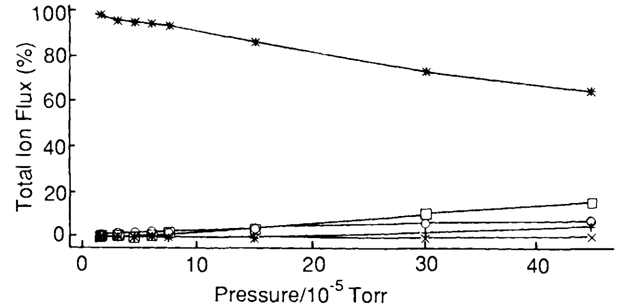


Fig. 2 Ion flux *vs.* pressure for the reaction of $CD_3OD_2^+$ and CH_3OH. □ = *m*/*z*, 33 ($CH_3OH_2^+$); ○ = *m*/*z*, 34 (CH_3OHD^+ and CD_3O^+); * = *m*/*z*, 38 ($CD_3OD_2^+$, primary ion); + = *m*/*z*, 47 (CH_3-OH-CH_3^+); × = *m*/*z*, 50 (CD_3-OH-CH_3^+).

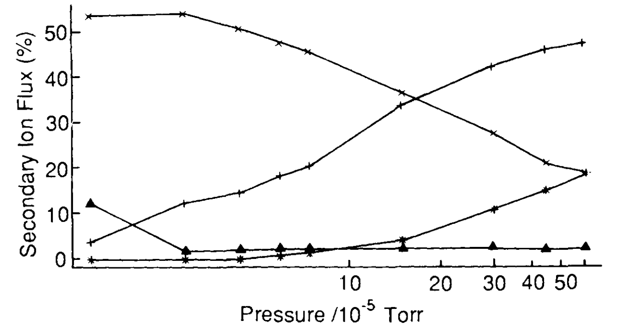
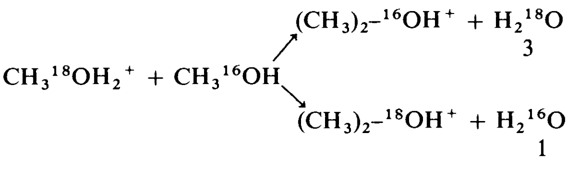
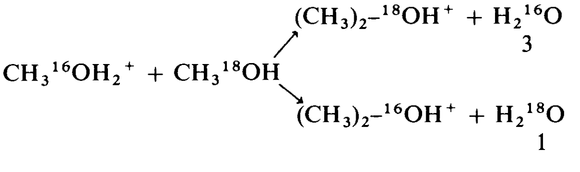


Fig. 3 Secondary ion flux *vs.* pressure. + = *m*/*z*, 33 ($CH_3OH_2^+$); × = *m*/*z*, 34 (CH_3OHD^+ and CD_3O^+); * = *m*/*z*, 47 (CH_3-OH-CH_3^+); ▲ = *m*/*z*, 50 (CH_3-OH-CD_3^+).



$$CH_3{}^{18}OH_2^+ + CH_3{}^{16}OH \begin{array}{l} \nearrow (CH_3)_2\text{-}{}^{16}OH^+ + H_2{}^{18}O \quad 3 \\ \searrow (CH_3)_2\text{-}{}^{18}OH^+ + H_2{}^{16}O \quad 1 \end{array} \quad (6)$$



$$CH_3{}^{16}OH_2^+ + CH_3{}^{18}OH \begin{array}{l} \nearrow (CH_3)_2\text{-}{}^{18}OH^+ + H_2{}^{16}O \quad 3 \\ \searrow (CH_3)_2\text{-}{}^{16}OH^+ + H_2{}^{18}O \quad 1 \end{array} \quad (7)$$

A recent investigation compared the relative kinetics of the S_N2 and proton transfer reactions between protonated methanol and ammonia.[16] Although the S_N2 reaction was favoured over the proton transfer reaction by the reaction enthalpy, the experimentally derived rate constants show the opposite preference. It was concluded that the reaction was controlled by the entropy factor as well as the enthalpy factor and in the case of protonated methanol and ammonia the proton transfer reaction was favoured over the S_N2 reaction. In these experiments the proton affinities of the neutral and protonated species were identical or similar, so the basicity of the neutral species was no longer a factor in determining the relative favourability of the proton transfer and S_N2 reactions. Other reports in the literature have failed to clarify unequivocally the mechanism involved.[17,18]

The present work was undertaken using a triple quadrupole mass spectrometer in which a specific primary ion could be selected and separated in the first quadrupole mass spectrometer and reacted in isolation from other ions with neutral methanol in the second quadrupole. The ions produced in these reactions could be analysed in the third quadrupole mass spectrometer. Utilizing this technique with labelled methanol enabled the mechanisms of the reactions to be determined. A quinqua quadrupole mass spectrometer was also used to investigate these reactions.

Experimental

The triple quadrupole mass spectrometer used has been described in the literature.[19] The quinqua quadrupole mass spectrometer used was of a similar design (Fig. 1).

Ions formed in the ionization chamber were analysed by using the first quadrupole as a mass analyser. Ions of one mass were separated and allowed into the second quadrupole by operating the first quadrupole as a mass filter. An α-target gas was allowed into the second quadrupole by means of the α-gas inlet. The ions produced in the reaction of the α-primary ion with the α-target gas were called α-secondary ions and were analysed in the third quadrupole. An α-secondary ion was separated from the other ions, by operating the third quadrupole as a mass filter, and passed into the fourth quadrupole in which a β-target gas had been admitted through the β-gas inlet. The products from this reaction, β-secondary ions, were analysed by operating the fifth quadrupole as a mass analyser. In this way sequential ion-molecule reactions were investigated in the pressure range 10^{-6} to 10^{-3} Torr.*

All gases and liquids used were commercially available at >99% purity and were used without further purification.

Discussion

Reaction of $CD_3OD_2^+$ *with* CH_3OH.—The reaction of CD_3–OD_2^+ with CH_3OH produced both $CD_3OHCH_3^+$ and $CH_3OCH_3^+$ ions. At low pressures only $CD_3OHCH_3^+$ ions were formed. As the pressure was increased $CH_3OHCH_3^+$ ions grew in intensity to become the larger peak of the two protonated dimethyl ethers (Figs. 2 and 3). This indicated that the non-deuteriated ion was formed by a competing reaction—deuteration of methanol [reaction (8)] and subsequent addition with elimination [reaction (9)]. The presence of an ion of *m*/*z* 48 indicated that H/D exchange was occurring [reaction (10)].

$$CD_3OD_2^+ + CH_3OH \longrightarrow CD_3OD + CH_3OHD^+ \quad (8)$$

$$CH_3OHD^+ + CH_3OH \longrightarrow CH_3\text{-}OH\text{-}CH_3^+ + DHO \quad (9)$$

$$CD_3OD_2^+ + CH_3OH \longrightarrow \xrightarrow{CH_3OH} \longrightarrow \begin{array}{c} CH_3\text{-}OD\text{-}CH_3^+ \\ \text{or} \\ CH_3\text{-}OH\text{-}CH_2D^+ \end{array} \quad (10)$$

The formation of these three ions $[C_2H_nD_mO]^+$ (where n = 4, 7 and 3, and m = 3, 0 and 4, respectively) would be consistent with the S_N2 mechanism but does not establish it conclusively.

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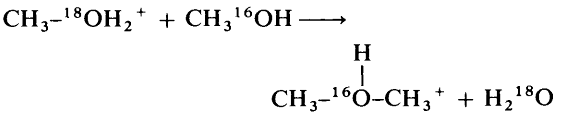
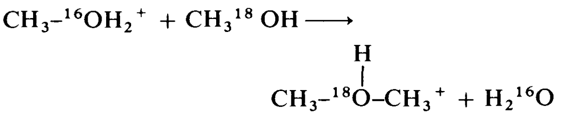
* 1 Torr *ca.* 1 mmHg.

The following experiments were done qualitatively to access the relative ratios of isotopes in the product ions. In all cases the reactions proceeded to form only one arrangement of isotopes in the product ions.

Identification of the Source of the Oxygen Atom in Protonated Dimethyl Ether.—The reaction of ^{18}O labelled methanol allowed the source of the oxygen atom in the protonated dimethyl ether to be traced. The reaction of ^{18}O labelled protonated methanol with ^{16}O methanol produced only ^{16}O in the protonated dimethyl ether [reaction (11)]. In the reverse reaction in which ^{16}O protonated methanol was reacted with ^{18}O methanol the protonated dimethyl ether contained only ^{18}O [reaction (12)]. This showed that the oxygen in the protonated dimethyl ether comes exclusively from the neutral methanol. This is consistent with the S_N2 mechanism but does not prove it.

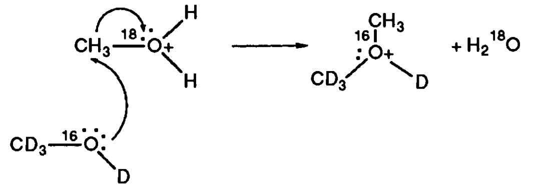


$$CH_3\text{-}^{18}OH_2^+ + CH_3{}^{16}OH \longrightarrow CH_3\text{-}^{16}\overset{\overset{\textstyle H}{|}}{O}\text{-}CH_3^+ + H_2{}^{18}O \quad (11)$$



$$CH_3\text{-}^{16}OH_2^+ + CH_3{}^{18}OH \longrightarrow CH_3\text{-}^{18}\overset{\overset{\textstyle H}{|}}{O}\text{-}CH_3^+ + H_2{}^{16}O \quad (12)$$

Reaction of $CH_3{}^{18}OH_2^+$ *with* $CD_3{}^{16}OD$.—In the definitive experiment, $CH_3{}^{18}OH_2^+$ ions were treated with $CD_3{}^{16}OD$. Each methyl group, each oxygen and the protons on each oxygen could be traced in the reaction. At low pressures the only protonated dimethyl ether observed had a *m/z* of 51 which must be formed by the addition-with-elimination reaction (Scheme 2). At higher pressures a very small peak of *m/z* 50 was observed.

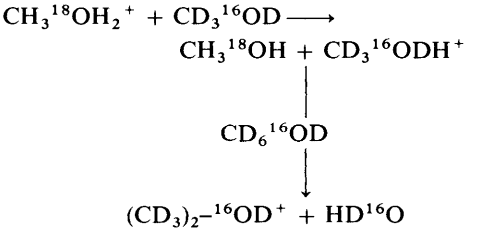


Scheme 2

This tertiary ion was the result of H/D exchange which produced $CD_3{}^{16}OH$ [reaction (13)].

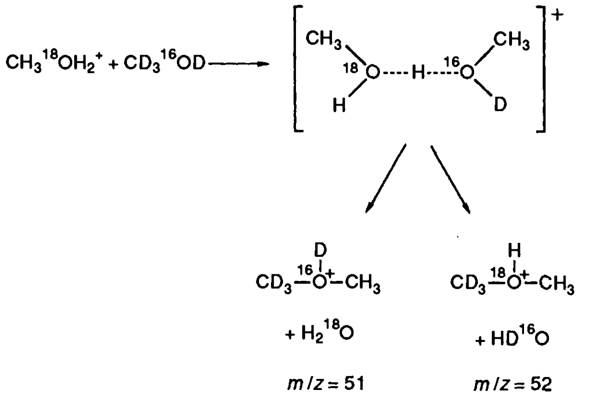
$$CH_3{}^{18}OH_2^+ + CD_3{}^{16}OH \longrightarrow C_2H_4D_3{}^{16}O^+ + H_2{}^{18}O \quad (13)$$

At the highest pressure used an ion of *m/z* 54 was observed. This was due to the further reaction of $CD_3{}^{16}ODH^+$ which had been formed by protonation of $CD_3{}^{16}OD$ by $CH_3{}^{18}OH_2^+$ [reaction (14)].



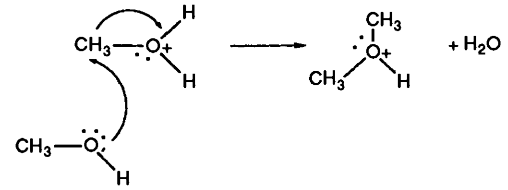
$$\begin{array}{l} CH_3{}^{18}OH_2^+ + CD_3{}^{16}OD \longrightarrow \\ \quad CH_3{}^{18}OH + CD_3{}^{16}ODH^+ \\ \qquad\qquad | \\ \qquad CD_6{}^{16}OD \\ \qquad\qquad \downarrow \\ (CD_3)_2\text{-}^{16}OD^+ + HD^{16}O \end{array} \quad (14)$$

All three protonated dimethyl ethers could only be formed *via* the S_N2 mechanism. The production of protonated dimethyl ether by loss of water from an addition complex with symmetrical hydrogen bonds would result in a mixture of isotopes from the protonated methanol and the neutral methanol. In each of the labelled reactions carried out in this investigation there was absolutely no mixing of isotope (Scheme 3).

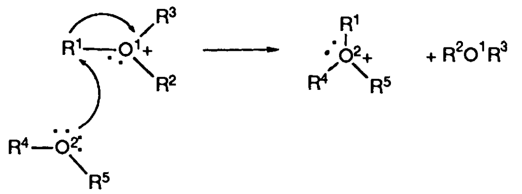


Scheme 3

The mechanism of Henis would predict that both of the ions of *m/z* 51 and 52 would be formed. In the present experiments reported here only the ion of *m/z* 51 was obtained. Only the S_N2 mechanism can account for the results of all the experiments (Scheme 4). This reaction scheme was generalized, as shown in Scheme 5 to account for the formation of trimethyl oxonium ions and the ethyl analogues of the methyl oxonium ions.



Scheme 4



R^1	R^2	R^3	R^4	R^5	O^1	O^2
CH_3	H	H	CH_3	H	^{16}O	^{16}O
CD_3	D	D	CH_3	H	^{16}O	^{16}O
CH_3	H	H	CD_3	D	^{16}O	^{16}O
CH_3	H	H	CH_3	H	^{18}O	^{16}O
CH_3	H	H	CH_3	H	^{16}O	^{18}O
CH_3	H	H	CD_3	D	^{18}O	^{16}O
CD_3	D	D	CH_3	H	^{16}O	^{18}O
CH_3	CH_3	H	CH_3	H	^{16}O	^{16}O
CH_3	H	H	CH_3	CH_3	^{16}O	^{16}O
C_2H_5	H	H	C_2H_5	H	^{16}O	^{16}O
C_2H_5	H	H	C_2H_5	C_2H_5	^{16}O	^{16}O

Scheme 5 Generalized reaction scheme

The formation of trimethyl oxonium ions from the reaction of protonated dimethyl ether with dimethyl ether was shown to occur in an experiment using the quinqua quadrupole mass spectrometer (Fig. 4). CH_2N^+ ions were isolated from the other ions formed by electron bombardment of methylamine and put

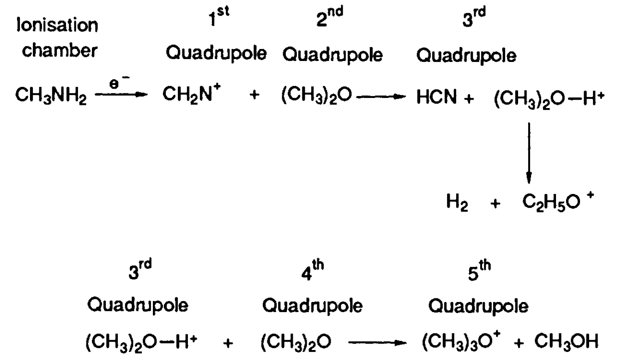


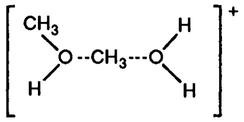
Fig. 4 Detection of trimethyl oxonium ions formed during reaction using quinqua quadrupole mass spectrometer

into dimethyl ether in the second quadrupole. The protonated dimethyl ether thus formed was selected from the third quadrupole and put into dimethyl ether in the fourth quadrupole. The ions observed in the fifth quadrupole were: unreacted protonated dimethyl ether, $m/z = 47$, $C_2H_5O^+$, $m/z = 45$—a fragment of protonated dimethyl ether—and the trimethyl oxonium ion, $m/z = 65$.

Conclusions

The triple quadrupole mass spectrometer and the quinqua quadrupole mass spectrometer were used to form, isolate, react and analyse ions involved in the ion-molecule reactions of methanol and its derivatives.

By using isotopically labelled ions and molecules the formation of dimethyl and trimethyl oxonium ions from protonated methanol and methanol or dimethyl ether were shown to be formed through an S_N2 mechanism. This would suggest an intermediate with asymmetrical hydrogen bonds, such as **2**, rather than an intermediate with symmetrical hydrogen bonds such as **1**.



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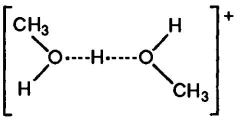

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The results reported in the literature that supported either the symmetrical hydrogen bonded intermediate,[9,13,14,16] or the asymmetrical hydrogen bonded intermediate,[15,17] did so on the basis of comparing the ratio of products from two reaction routes or the ratio of isotopic retention in the products. In the present experiments there was 100% retention of isotopes and all experimental results could be explained by one reaction route. It can be concluded from these results that, under the conditions of these experiments, the formation of oxonium ions occurs exclusively through an S_N2 mechanism. This is an indication of the power of the triple and the quinqua quadrupole mass spectrometers in studying ion-molecule reactions in the gas phase.

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