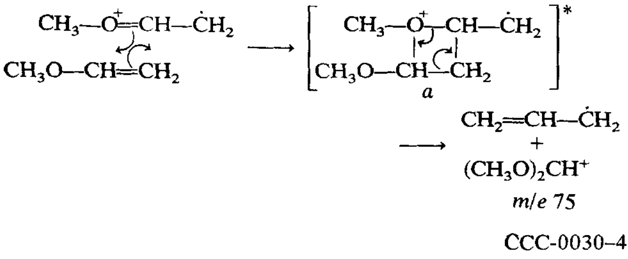
Ion–molecule Reactions of Methoxymethyl Cations With Some Organic Substrates Studied by Ion Cyclotron Resonance Spectrometry

R. van Doorn and N. M. M. Nibbering
Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

The reactions of methoxymethyl cations generated from dimethyl ether with propene, butene-2, vinyl methyl ether, acetaldehyde and acetone have been studied. The collision complexes, generated with the olefines, may eliminate an olefine, a methanol and a formaldehyde molecule as shown by double resonance experiments. From deuterium labelling it is found, that in the cases of propene and butene-2 the elimination of an olefine is accompanied by an extensive H/D interchange in the collision complexes, which has been shown not to occur in the long-lived reactant methoxymethyl cations if the internal energy of the methoxymethyl cations is less than 2.3 eV. The H/D interchange in these collision complexes is reduced in the elimination of methanol and is almost completely suppressed in the elimination of formaldehyde. In reactions with vinyl methyl ether, however, the eliminations of methanol and formaldehyde from the corresponding collision complexes appear to proceed with extensive H/D interchange. These observations point to acyclic collision complexes rather than 4-membered ring complexes. The collision complexes generated with acetaldehyde and acetone decompose by elimination of formaldehyde only. Deuterium labelling has shown that the formaldehyde molecule contains the original methylene group of the reactant methoxymethyl cations. In addition, ^{18}O labelling in acetone has shown that the original oxygen atom of the methoxymethyl cations is retained completely in the eliminated formaldehyde. These observations exclude any formation of 4-membered ring collision complexes and can only be explained by acyclic complexes. Possible mechanisms of all reactions mentioned are discussed in the light of these results.

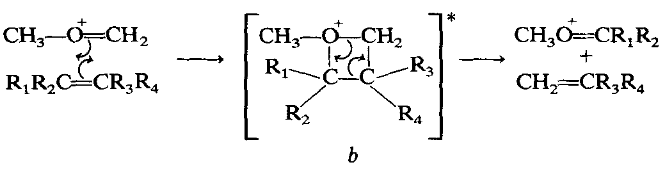
INTRODUCTION

The thermal suprafacial [2+2] cycloaddition of two double bonds is a symmetry forbidden reaction according to the Woodward–Hoffman rules.[1] Nevertheless, many reactions between olefinic molecules are known, which result in [2+2] cycloaddition products. On the basis of theoretical arguments and experimental evidence, the intervention of 1,4 biradical[2] to 1,4 zwitterionic[3] intermediates has been put forward for these reactions to circumvent the Woodward–Hoffmann rules. Examples of formal [2+2] cycloaddition reactions have been found also in gas phase reactions between ions and molecules, as studied by ion cyclotron resonance (ICR) mass spectrometry. For example, it has been shown that the molecular ions of fluoroethylene and fluoropropenes react with their corresponding neutral molecules through 4-membered ring collision complexes,[4] although it is not clear whether these are formed in a concerted or stepwise manner. Such a type of collision complex has also been suggested in reaction (1), where the molecular ion of vinyl methyl ether (VME) reacts with neutral VME[5] to form ion *m/e* 75:



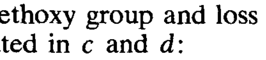
(1)

In principle, a similar collision complex could be formed also in reactions of the methoxymethyl cation with olefines, as illustrated by complex *b* [reaction (2)]:

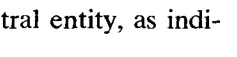


(2)

On the basis of deuterium labelling experiments it has been postulated that ions with a 4-membered ring structure like *b* are generated from reactions of *t*-butyl cations with methoxymethyl formate and methoxymethyl acetate under CI conditions.[6] It is also possible, however, that reactions (1 and 2) proceed through open chain collision complexes like *c* and *d*, which then decompose by a simultaneous shift of the methoxy group and loss of the neutral entity, as indicated in *c* and *d*:



c



d

Related to the question of whether reactions (1 and 2) proceed through complexes *a* and *b* or *c* and *d*, is the EI induced loss of a formaldehyde molecule from the $[M-CH_3]^+$ ion of methoxymethyl isopropyl ether. It has been shown that this formaldehyde loss occurs by

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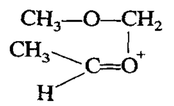
methyl as well as methoxyl migration in the $[M-CH_3]^+$ ion.[7] Both migrations involve 4-membered transition state rearrangements, but the methoxyl migration has the higher activation energy and the higher frequency factor. This result could best be interpreted with the open chain ion *e*, which is similar to *c* and *d*:


e

A collision complex with structure *e* might, in principle, be formed in reactions of the methoxymethyl cation with carbonyl compounds.

All these questions prompted us to study the ion–molecule reactions of methoxymethyl cations with some olefines and carbonyl compounds to obtain some insight into whether 4-membered ring or open chain collision complexes are involved. For this purpose isotopic labelling has been used, which proved to be very helpful, as shown below.

RESULTS AND DISCUSSION

Dimethyl ether was selected as a source for the generation by EI of methoxymethyl cations. These ions have been studied previously with D-labelling; they can decompose by elimination of methane, a reaction which requires an activation energy of 83 kcal mol^{-1} and which is accompanied by a complete randomization of all hydrogen atoms.[8] In the present work, however, we are dealing with *non-decomposing* methoxymethyl cations. Therefore, it was essential from the outset to know whether or not the hydrogen atoms in these ions randomize.

Ion-molecule reactions of $[CD_3OCH_2]^+$ and of $[CH_3OCD_2]^+$ generated from CD_3OCH_3 with a variety of organic substrates have been studied to obtain this knowledge. Toluene appears to react with these ions in a highly specific way, as noted earlier.[9] In our experiments the collision complex decomposes to give $[C_8H_9]^+$ and CH_3OH, while the CH_3OH molecule appears to contain the original methyl group to at least 96% at 13 eV electron energy:

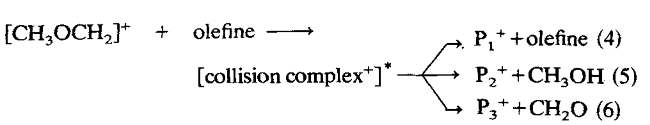
$$[CD_3OCH_2]^+ + C_6H_5CH_3 \rightarrow [C_8H_9]^+ + CD_3OH \quad (3a)$$

$$[CH_3OCD_2]^+ + C_6H_5CH_3 \rightarrow [C_8H_7D_2]^+ + CH_3OH \quad (3b)$$

Thus, it can be concluded that the *hydrogen atoms in non-decomposing methoxymethyl cations, generated with* 13 *eV electrons retain their identity to at least* 96%. This result should be borne in mind in the discussions which follow.

Reactions of the methoxymethyl cation with some olefines

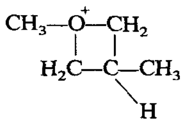
Methoxymethyl cations may react with olefines in the ICR cell by three types of reactions, as shown by double resonance experiments:

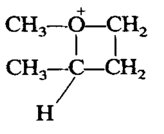


$$[CH_3OCH_2]^+ + \text{olefine} \longrightarrow [\text{collision complex}^+]^* \begin{cases} \rightarrow P_1^+ + \text{olefine} & (4) \\ \rightarrow P_2^+ + CH_3OH & (5) \\ \rightarrow P_3^+ + CH_2O & (6) \end{cases}$$

Reactions (4–6), which are not always observed simultaneously for any olefine studied, have been investigated further with $[CH_3OCD_2]^+$ and $[CD_3OCH_2]^+$, generated from CH_3OCD_3, and with $[CD_3OCD_2]^+$, generated from CD_3OCD_3.

Propene. If methoxymethyl cations react with propene by reaction (2), given in the introduction, two different collision complexes might, in principle, be formed:


f


g

If an open collision complex is formed, the methoxymethyl cations are expected to attack the methylene carbon atom of propene in view of charge density calculations[10] and the dipole moment of propene.[11] Such an attack should result in the formation of the following secondary carbenium ion as a collision complex:

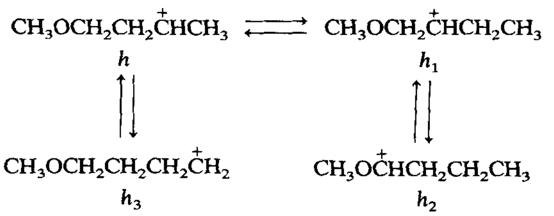
$$CH_3OCH_2CH_2\overset{+}{C}HCH_3$$

h

Collision complex *g* could eliminate ethylene by a cyclo-reversed ring opening, whereas *h* could lose ethylene by a concomitant methoxyl migration to the carbenium ion centre. This ethylene loss, however, is not observed under the experimental conditions. For the overall reaction (7) an exothermicity of 6.5 kcal mol^{-1} is calculated (see Appendix for all heats of formation used):

$$\underset{m/e\ 45}{[CH_3OCH_2]^+} + CH_3CH{=}CH_2 \rightarrow \underset{m/e\ 59}{CH_3O\overset{+}{C}HCH_3} + \underset{m/e\ 59}{CH_2{=}CH_2} \quad (7)$$

Moreover, the non-decomposing and hydrogen unscrambled methoxymethyl cations (*vide supra*) can have an internal energy of 58 kcal mol^{-1} according to a gas phase study of some simple oxonium ions.[8] This amount of internal energy would be sufficient to open reaction channel (7). Clearly, this cannot compete with the processes discussed below. One of these processes is that the collision complex of the methoxymethyl cation and propene decomposes into its initial products. This has become apparent from the ion–molecule reactions of labelled methoxymethyl cations with (un)labelled propenes. On the basis of relatively weak double resonance signals it has been found that $[CH_3OCD_2]^+$ and $[CD_3OCD_2]^+$ ions in reactions with unlabelled propene exchange one and two of their deuterium atoms for hydrogen atoms. The same is true for $[CD_3OCD_2]^+$ ions if they react with $CH_3CH{=}CD_2$, $CH_3CD{=}CH_2$ and $CD_3CH{=}CH_2$. Although the intensities of the double resonance signals are too weak to obtain reliable quantitative data, these observations seem to indicate that the hydrogen atoms of the methylene group and not of the methyl group of the methoxymethyl cation exchange with the hydrogen atoms of propene in the collision complex. Such an exchange can best be explained with collision complex *h*, rather than with collision complexes *f* and *g*, by assuming a series of reversible 1,2 hydrogen shifts in *h* to give the isomeric ions h_1–h_3 in Scheme 1, related to those proposed as intermediates in the elimination of ethylene from protonated propionaldehyde:[12]



$$\begin{tikzcd} \underset{h}{CH_3OCH_2CH_2\overset{+}{C}HCH_3} \arrow[r, shift left] \arrow[d, shift left] & \underset{h_1}{CH_3OCH_2\overset{+}{C}HCH_2CH_3} \arrow[l, shift left] \arrow[d, shift left] \\ \underset{h_3}{CH_3OCH_2CH_2CH_2\overset{+}{C}H_2} \arrow[u, shift left] & \underset{h_2}{CH_3O\overset{+}{C}HCH_2CH_2CH_3} \arrow[u, shift left] \end{tikzcd}$$

Scheme 1

The proposal that the initially generated collision complex *h* lives long enough to equilibrate to some extent with h_1–h_3 before it decomposes again in the methoxymethyl cation and propene, is further shown by the methanol loss from the collision complex [reaction (5)]. This reaction occurs in competition with the loss of formaldehyde [reaction (6)] and k_5/k_6 appears to be about 1.8.

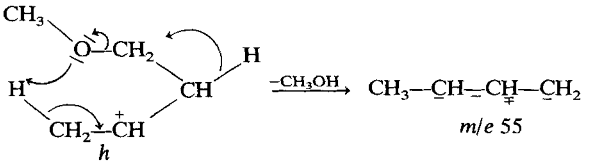
The label distributions in the neutral molecules, generated in reactions (5 and 6) from (un)labelled methoxymethyl cations and (un)labelled propenes, have been summarized in Table 1. They have been obtained from the intensities of double resonance signals[13] for the production of the ions $[P_2]^+$ and $[P_3]^+$in these reactions.

It is seen that the eliminated methanol molecule contains the original methyl group of the methoxymethyl cation and one of the hydrogen atoms of the original methyl group of propene to the extent of 80–90%. These data can best be explained by collision complex *h* and point to the following mechanism (Scheme 2) for methanol loss, tacitly assuming a concerted 1,2 hydrogen shift to obtain a more stable product ion:

Table 1. Label distribution[a,b] (in %) in the neutral molecules, generated from the ion–molecule reactions (5 and 6) of (un)labelled methoxymethyl cations with (un)labelled propenes at 13 eV[c]

Reactant ion	Substrate	Reaction (5) (methanol loss)				
		CH_4O	CH_3DO	CD_2H_2O	CD_3HO	CD_4O
$[CH_3OCD_2]^+$	$CH_3CH{=}CH_2$	86	8	6	—	—
$[CD_3OCH_2]^+$	$CH_3CH{=}CH_2$	—	3	9	88	—
$[CD_3OCD_2]^+$	$CH_3CH{=}CH_2$	—	4	5	86	5
$[CD_3OCD_2]^+$	$CH_3CH{=}CD_2$	—	6	2	87	5
$[CD_3OCD_2]^+$	$CH_3CD{=}CH_2$	—	7	6	79	8
$[CD_3OCD_2]^+$	$CD_3CH{=}CH_2$	—	11	6	6	77
		Reaction (6) (formaldehyde loss)				
		CH_2O	$CHDO$	CD_2O		
$[CH_3OCD_2]^+$	$CH_3CH{=}CH_2$	93	7	—		
$[CD_3OCH_2]^+$	$CH_3CH{=}CH_2$	—	2	98		
$[CD_3OCD_2]^+$	$CH_3CH{=}CH_2$	—	5	95		
$[CD_3OCD_2]^+$	$CH_3CH{=}CD_2$	—	2	98		
$[CD_3OCD_2]^+$	$CH_3CD{=}CH_2$	—	3	97		
$[CD_3OCD_2]^+$	$CD_3CH{=}CH_2$	—	5	95		

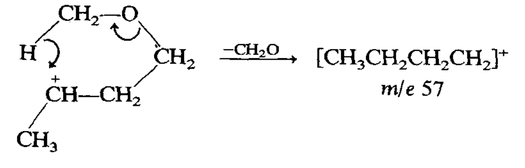
[a] Corrected for natural ^{13}C isotopic contributions and for incomplete labelling (see Experimental section).
[b] The limits of error in the values are estimated to be 10%.
[c] See Experimental section.



Scheme 2

The other 10–20% of the eliminated methanol molecules appear to contain the hydrogen and deuterium atoms at random, due to some H/D interchange in the methoxymethyl cations (*vide supra*) and in the collision complex (by occurrence of h_1–h_3). It is clear also from the data in Table 1 that the hydrogen atoms of the original methyl group of the methoxymethyl cation participate only to a negligible extent in the hydrogen exchange processes in the collision complex, as concluded from the propene elimination from *h*, described above. However, the elimination of the formaldehyde molecule from the collision complex appears to contain the hydrogen atoms of the original methyl group of the methoxymethyl cation to the extent of at least 95% (Table 1).

In view of the results obtained for methanol loss (*vide supra*), it is most likely that the major part of the formaldehyde molecules, if not all, are eliminated from collision complex *h* rather than from h_1–h_3 in the following way:



Scheme 3

Reactions (5 and 6) are calculated to be exothermic by 12 kcal mol^{-1} and 6 kcal mol^{-1}, using the heats of formation of the product ions (see Appendix) given in Schemes 2 and 3, and k_5/k_6 appears to be 1.8 (*vide supra*).

It is interesting to note that similar mechanisms to those in Schemes 2 and 3 have been found for the unimolecular decompositions of $[C_4H_9O]^+$ ions.[14]

Butene-2. For butene-2 all product ions $[P_1]^+$, $[P_2]^+$ and $[P_3]^+$, generated in reactions (4–6), are observed. As in propene, reaction (4) may give rise to its initial products in addition to the observed formation of $[C_3H_7O]^+$ ions by the elimination of C_3H_6 from the collision complex. This reaction channel is very suited to obtaining information about the collision complex, because the *m/e* values of the reactant and product ions are now different.

Table 2 summarizes the label distributions in the neutral molecules, generated in reactions (4–6) from

Table 2. Label distributions[a,b] (in %) in the neutral molecules, generated from the ion–molecule reactions (4–6) of labelled methoxymethyl cations with unlabelled *cis*-butene-2, at 13 eV[c]

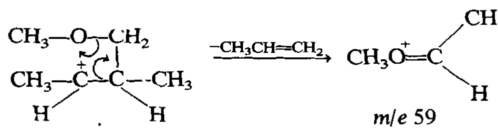
Reactant ion	Reaction (4) (propene loss)				
	C_3H_6	C_3H_5D	$C_3H_4D_2$		
$[CH_3OCD_2]^+$	6	75	19		
$[CD_3OCH_2]^+$	99	1	—		
$[CD_3OCD_2]^+$	—	76	24		
	Reaction (5) (methanol loss)				
	CH_4O	CH_3DO	CH_2D_2O	CD_3HO	CD_4O
$[CH_3OCD_2]^+$	92	8	—	—	—
$[CD_3OCH_2]^+$	—	3	4	93	—
$[CD_3OCD_2]^+$	—	—	—	93	7
	Reaction (6) (formaldehyde loss)				
	CH_2O	CHDO	CD_2O		
$[CH_3OCD_2]^+$	95	5	—		
$[CD_3OCH_2]^+$	—	3	97		
$[CD_3OCD_2]^+$	—	—	100		

[a] Corrected for natural ^{13}C isotopic contributions and for incomplete labelling (see Experimental section).

[b] The limits of error in the values are estimated to be 5%.

[c] see Experimental section.

labelled methoxymethyl cations and unlabelled *cis*-butene-2, and based on the intensities of double resonance signals.[13] These data show again that loss of propene from the collision complex is accompanied with hydrogen scrambling, predominantly occurring between those of the original methylene group of the methoxymethyl cation and those of butene-2. Therefore, a collision complex with an open chain structure like *i* is much more likely than one with a 4-membered ring structure, as discussed above for propene. The loss of propene from *i* may then occur by a methoxyl shift to the carbenium ion centre, as shown in Scheme 4:



Scheme 4

The data in Table 2 show also that methanol, eliminated from the collision complex, contains the original methyl hydrogen atoms of the methoxymethyl cation to the extent of >90%. The same is true for the formaldehyde molecule, eliminated from the collision complex. The mechanisms for these eliminations are similar to those given for propene in Scheme 2 and 3. For *cis*-butene-2 $k_5/k_6 = 8.3$ and $k_5/k_4 = 1.1$. The $\Delta H_{reaction}$'s of reactions (4–6) are calculated to be 7 kcal mol^{-1} exothermic for reaction (4) and 19 kcal mol^{-1} exothermic for reactions (5 and 6), using the heat of formation of the product ion given in Scheme 4 and the heats of formation of the ions, generated through the mechanisms given in Schemes 2 and 3 (see Appendix for heats of formation of the ions and neutral molecules). For *trans*-butene-2 the same reactions are observed, while $k_5/k_6 = 8.6$ and $k_5/k_4 = 2.3$

Vinyl methyl ether. In the ICR spectrum of a mixture of dimethyl ether and vinyl methyl ether product ions with *m/e* 71 = $[P_2]^+$ and *m/e* 73 = $[P_3]^+$, generated in reactions (5 and 6), are observed. Double resonance experiments have shown that there is also a small contribution to the product ions with *m/e* 75 generated in reaction (4), resulting from ethylene loss from the collision complex. The ratio k_5/k_6 appears to be about 1. The ion–molecule reactions (5 and 6) between pentadeuteromethoxymethyl cations and unlabelled vinyl methyl ether molecules lead to product ions at *m/e* 72–78, according to double resonance experiments. Assuming that dk_5/dE and dk_6/dE behave similarly, the relative intensities of the double resonance signals for the generation of the ions *m/e* 72–78 appear to be:

m/e 72	1%	*m/e* 76	27%
m/e 73	28%	*m/e* 77	13%
m/e 74	17%	*m/e* 78	8%
m/e 75	6%		

These data point to an extensive scrambling between the hydrogen and deuterium atoms in the collision complex with *m/e* 108 before methanol and formaldehyde are eliminated.

In view of $k_5/k_6 \approx 1$, however, there is also a regularity in these data, namely: the relative intensity of *m/e* 73, corresponding to the loss of CD_3HO from the collision complex, is the same as that of *m/e* 76, corresponding to the loss of CD_2O from that complex. The same is true for *m/e* 74 (CD_2H_2O loss) versus *m/e* 77 (CHDO loss) and for *m/e* 75 (CH_3DO loss) versus *m/e* 78 (CH_2O loss).

If a complete scrambling is assumed between the five deuterium atoms and the six hydrogen atoms in the collision complex prior to the equal loss of methanol and formaldehyde, the following relative intensities are calculated for the ions *m/e* 72–*m/e* 78:

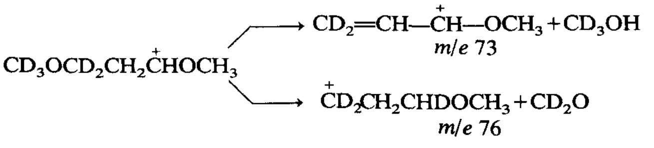
m/e 72	1%	*m/e* 76	11%
m/e 73	9%	*m/e* 77	27%
m/e 74	23%	*m/e* 78	14%
m/e 75	15%		

Subsequently, if 55% of the collision complexes have suffered from a complete hydrogen/deuterium scrambling prior to the equal loss of methanol and formaldehyde, while the other 45% show specific loss of trideuteromethanol and dideuteroformaldehyde with equal probability, the following relative intensities for the ions *m/e* 72–*m/e* 78 are predicted:

m/e 72	1%	*m/e* 76	28%
m/e 73	27%	*m/e* 77	15%
m/e 74	13%	*m/e* 78	8%
m/e 75	8%		

It can be seen that these predicted values agree well with the observed values.

Therefore, it seems justifiable to interpret the specific loss of trideuteromethanol and dideuteroformaldehyde as coming from the hydrogen/deuterium unscrambled open chain collision complexes *j* rather than from any 4-membered ring complex, such as shown in Scheme 5.

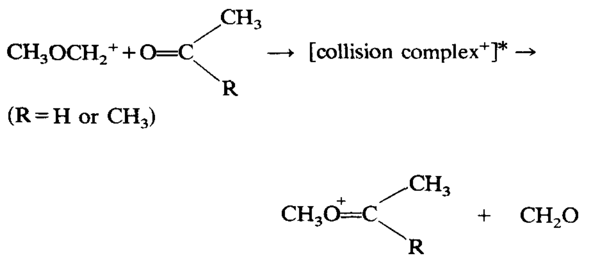


Scheme 5

The other collision complexes in which a complete randomization of the five deuterium atoms and six hydrogen atoms occurs prior to the loss of methanol and formaldehyde might also have the structure of *j*, because this has a symmetrical carbon skeleton. The methanol and formaldehyde expulsions from ion *j* in Scheme 5 have also been observed as unimolecular decompositions of the $[M{-}C_2H_5O]^+$ ions from 1,2,4-trimethoxybutane.[15] Deuterium labelling of the methoxy group at C-2 has further shown that the corresponding labelled ions *j* lose CH_3OH and CD_3OH in the ratio of 73.1:26.9; the last molecule is assumed to be eliminated after a 1,3 hydride shift from C-4 to C-2 (the ratio is based on the intensities of normal peaks due to $[j-CH_3OH]^+$ and $[j-CD_3OH]^+$ ions; intensities of corresponding metastable peaks have not been reported[15]). The absence of H/D randomization in ions *j*, generated by EI, as opposed to the complete H/D randomization in collision complexes *j* prior to decomposition, is probably due to differences in internal energy of the ions. Unlabelled *j* ions generated by EI eliminate methanol and formaldehyde in the ratio of 2:1,[15] while unlabelled collision complexes *j* eliminate these molecules in the ratio of 1:1 (*vide supra*). The increased loss of formaldehyde from collision complexes *j*—which requires a lower activation energy than the loss of methanol[15]—indicates that the collision complexes *j* have a lower internal energy than the ions *j* generated by EI from 1,2,4-trimethoxybutane. Therefore, the former may suffer more readily from H/D randomization prior to decomposition than the latter, because a lower internal energy usually favours H/D randomization processes with respect to decomposition processes of ions.

Reactions of the methoxymethyl cation with acetaldehyde and acetone

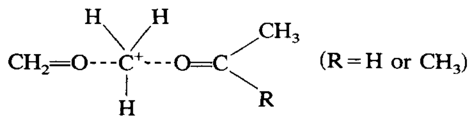
Methoxymethyl cations appear to react with acetaldehyde and acetone with the expulsion of formaldehyde:



(8)

Three different collision complexes are, in principle, possible for this reaction:

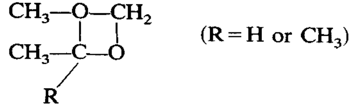
(a) A methyl cation bonded complex, like *k*.



k

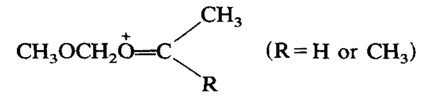
Reaction (8) may then be regarded as a methyl cation transfer reaction, which tacitly has been assumed earlier in the reaction of $[CH_3OCH_2]^+$ with acetone.[16]

(b) A 4-membered ring complex, like *l*.



l

(c) An open chain collision complex, like *m*.



m

In order to differentiate between these possible collision complexes *k–m*, reactions of (un)labelled methoxymethyl cations with unlabelled acetaldehyde, acetone and acetone-^{18}O have been studied. The results, obtained from the intensities of double resonance signals, have been summarized in Table 3. They show that the formaldehyde molecule, eliminated from the collision complex, contains entirely the original methylene group and oxygen atom (based on the experiment with acetone-^{18}O) of the methoxymethyl cation. Therefore, the intermediacy of collision complex *l* in these ion–molecule reactions can be fully excluded.

To differentiate between collision complexes *k* and *m*, the previous investigation of the EI induced elimination of formaldehyde from the $[M-CH_3]^+$ ion of

Table 3. Generation of (un)labelled formaldehyde[a] from the ion–molecule reactions of (un)labelled methoxymethyl cations with unlabelled acetaldehyde, acetone and acetone-^{18}O, at 14 eV[c]

Reactant ion	Substrate	Formaldehyde lost		
		CH_2O	CD_2O	$CH_2{}^{18}O$
$[CH_3OCD_2]^+$	CH_3CHO	—	X	—
$[CD_3OCH_2]^+$	CH_3CHO	X	—	—
$[CD_3OCD_2]^+$	CH_3CHO	—	X	—
$[CH_3OCD_2]^+$	$(CH_3)_2CO$	—	X	—
$[CD_3OCH_2]^+$	$(CH_3)_2CO$	X	—	—
$[CD_3OCD_2]^+$	$(CH_3)_2CO$	—	X	—
$[CH_3OCH_2]^+$	$(CH_3)_2C^{18}O$	X[b]	—	—

[a] Corrected for natural ^{13}C isotopic contributions and for incomplete labelling (see Experimental section).

[b] This number remains unchanged over an electron energy range of 14–50 eV.

[c] See Experimental section.

methoxymethyl isopropyl ether is important.[7] This ion has the same structure as *m*, if R = H. From combined deuterium and ^{18}O labelling in methoxymethyl isopropyl ether it has been found that the $[M-CH_3]^+$ ion eliminates formaldehyde in two ways:[7] (i) by a methoxyl migration to the carbenium centre. The eliminated formaldehyde then contains the original methylene group and the oxygen atom of the isopropoxy group; (ii) by a methyl migration to the oxonium centre. In that case the formaldehyde molecule contains the original methylene group and the oxygen atom of the methoxy group.

It should be noted further that the $[M-CH_3]^+$ ions decompose in the ion source by 90% and 60% methoxyl migration at 70 and 11 eV respectively. Similar observations are made in the single resonance ICR spectra of methoxymethyl-^{18}O isopropyl-d_7 ether, taken at 12 to 50 eV electron energies. Metastable $[M-CH_3]^+$ ions, however, fragment by >99% methyl migration.[7] If these results are compared with the data given in Table 3 for acetone and acetone-^{18}O, this would mean that only the methyl migration is operative when reaction (8) proceeds through collision complex *m*. This might be the case if, for example, the reaction coordinate diagram for the ion–molecule reaction of the methoxymethyl cation with acetaldehyde is considered. In this diagram, indicated in Fig. 1, the energies of the reactants, intermediates and products are shown.

The heats of formation of the reactants and products have been taken from the literature (see Appendix). The heat of formation of the collision complex has been computed using the appearance potential value, determined for the formation of the $[M-CH_3]^+$ ion from methoxymethyl isopropyl ether (see Appendix). In the ionization efficiency curve for loss of formaldehyde from this $[M-CH_3]^+$ ion, generated from *m/e* 59, a break point is observed about 0.4 eV above the corresponding appearance potential value (measured to be 0.7 eV above the appearance potential value of the $[M-CH_3]^+$ ion of methoxymethyl isopropyl ether); this break point has been assumed to correspond with the onset for the methoxyl shift in the $[M-CH_3]^+$ ion, which has been shown to require a higher activation energy than the methyl shift in the elimination of formaldehyde.[7]

From Fig. 1 it can be seen that the reaction between the methoxymethyl cation and acetaldehyde is exothermic, but route B (i.e. methoxyl migration in the collision complex) requires an activation energy as opposed to route A (i.e. methyl migration in the collision complex). A similar diagram can be constructed for the reaction of the methoxymethyl cation with acetone.

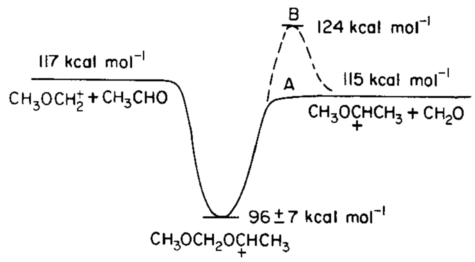


Figure 1. Reaction coordinate diagram illustrating the energetics of the possible reaction between the methoxymethyl cation and acetaldehyde. Route A corresponds to a methyl shift and route B corresponds to a methoxyl shift in the collision complex, prior to formation of the products (see text).

Channel B in Fig. 1 will not be accessible if the methoxymethyl cations are in their ground state. However, their internal energy may be 58 kcal mol^{-1} before scrambling of the hydrogen atoms starts and 83 kcal mol^{-1} before decomposition by loss of methane will occur, according to a gas phase study of some simple oxonium ions.[8] The value of 58 kcal mol^{-1} is in reasonable agreement with our value, determined by the ICR method: ion–molecule reactions of methoxymethyl cations, generated with 12–50 eV electrons, with acetone have indeed shown that part of the collision complexes eliminate formaldehyde containing the original hydrogen atoms of the methoxymethyl cations at random, as indicated by the labelling results given in Table 4. Appearance potential measurements with the ICR technique have shown that the onset for H/D scrambling (1,3 H shifts) in these methoxymethyl cations is about 2.3 eV above the appearance potential value for formation of methoxymethyl cations from dimethyl ether (see Experimental section). This value is in excellent agreement with the height of the barrier for isomerization of $CH_3—CH=\overset{+}{O}CH_3$ to $CH_3CH_2\overset{+}{O}=CH_2$ by a 1,3 hydrogen shift, determined to be 58 kcal mol^{-1} ≃ 2.5 eV.[8] Therefore, reaction channel B should certainly become accessible when higher electron energies are used to generate methoxymethyl cations. The observation that the reaction between the methoxymethyl cation and acetone-^{18}O does not result in any loss of $CH_2{}^{18}O$ from the collision complex over an electron energy range of 14–50 eV (see Table 3) may thus be taken as evidence against the occurrence of collision complex *m*. Apparently, reaction (8) proceeds through collision complex *k* and may be regarded as a nucleophilic displacement reaction. Such a type of reaction has been observed earlier in the field of gas phase ion–molecule chemistry.[17]

EXPERIMENTAL

Instruments

The ion cyclotron resonance spectra were recorded on a considerably modified Varian V5903 instrument. A four-section cell was used and high vacuum was obtained using a 2 in oil diffusion pump. The single resonance spectra were obtained using grid or field modulation; in the double resonance experiments a square wave modulated radiofrequency signal was applied to the drift plates of the source or reaction region of the cell (radiofrequency output generally 50 mV RMS).

Electrons were produced by heating a tungsten filament and accelerated by a potential difference between the filament and the trapping plate. The poten-

Table 4. Label distributions[a,b] (in %) in the neutral formaldehyde generated from the ion–molecule reactions of (un)labelled methoxymethyl cations with (un)labelled acetone as a function of the electron energy[c]

Reactant ion	Substrate	Formaldehyde lost	Electron energy (eV) 12	13	14	15	20	50
$[CH_3OCD_2]^+$	$(CH_3)_2CO$	CH_2O	0	4	7	9	16	13
		$CHDO$	0	1	10	12	18	19
		CD_2O	100	95	83	79	66	67
$[CD_3OCH_2]^+$	$(CH_3)_2CO$	CH_2O	100	97	90	83	71	74
		$CHDO$	0	2	7	11	19	18
		CD_2O	0	1	3	6	10	8
$[CH_3OCH_2]^+$	$(CD_3)_2CO$	CH_2O			100			>99
		$CHDO$			0			<1
		CD_2O			0			0

[a] Corrected for natural ^{13}C isotopic contributions and for incomplete labelling (see Experimental section)

[b] The limits of error in the values are estimated to be 5%.

[c] The electron energy scale is not calibrated (see Experimental section).

tial difference between the centre of the filament and the earth was used as a measure for the electron energy, which was only calibrated for ionization/appearance potential measurements. Drift and trapping plate potentials were $\leq 1V$. All experiments were carried out at room temperature and total pressures were between 5×10^{-6} and 2×10^{-5} Torr, as determined from an ionivac Leybold Heraeus ionization gauge. Ionization/appearance potential measurements of ions from methoxymethyl isopropyl ether were carried out on a Varian MAT 711 instrument. Benzene was used as standard, and the data were obtained using the semi-log plot method.[18] The intensities of the signals were plotted down to 0.1% of the intensities at 50 eV. The break point for the loss of CH_2O from the $CH_3OCH_2O^+CHCH_3$ ions was found in the ionization efficiency curve, obtained by the extrapolated difference determination (EDD) method.[19] The appearance potential for scrambling of H and D atoms in the long-lived methoxymethyl cations was measured by ICR from calibration of the appearance potential value for the formation of the product ions of the reaction of $[CD_3OCH_2]^+$ ions with acetone by loss of CHDO (see Table 4), against the appearance potential value for the formation of $[CD_3OCH_2]^+$ ions and the ionization potential value of $[CD_3OCH_3]^+$,[20] taken to be identical with the known ionization potential value of $[CH_3OCH]_3]^+$ ions. Plots of the intensities of the corresponding ICR signals versus the electron energy were obtained, while detection of the various ions was accomplished by changing the frequency of the marginal oscillator only, leaving all other variables unchanged.

Materials

Dimethyl-1,1,1-d_3 ether was prepared by the action of methyl-d_3 iodide on sodium methoxide in methanol, according to standard procedures.[21] There was no evidence for isotopic impurities. Dimethyl-d_6 ether was prepared by introducing methanol-d_4 to a mixture of sulphuric acid-d_2 and methanol-d_4, according to standard procedures.[21] The label content was 97.5% d_6 and 2.5% d_5. Propene-1,1-d_2 (98% pure) and propene-3,3,3-d_3 (98% pure) were Merck, Sharp and Dohme products. Propene-2-d_1 was prepared by the gas phase pyrolysis of propyl-2-d_2 acetate,[22,23] which was made from propanol-2-d_2, synthesized earlier.[24]

Acetone-^{18}O was obtained from Bio-Rad Laboratories (California, USA). The label content appeared to be 71,3% ^{18}O and 28.7% ^{16}O. The preparation of methoxymethyl isopropyl ether and methoxymethyl-^{18}O isopropyl-d_7 ether has been described earlier.[7] Dimethyl ether was a Fluka product; propene, butene-2 and vinyl methyl ether were obtained from Matheson Gas Products. All other compounds and starting materials were obtained from standard sources and used without further purification.

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APPENDIX

Sources of heats of formation

The last reported[25] value of the heat of formation of the methoxymethyl cation is 157 kcal mol^{-1}, which is intermediate between the earlier reported values of 144 kcal mol^{-1} [8] and 167 kcal mol^{-1}.[26] The value of 157 kcal mol^{-1} has been used as the most realistic one in the calculations of the heats of reactions presented here. With the difference of 10 kcal mol^{-1} between this value and the value of 167 kcal mol^{-1},[26] the reported heat of formation of the $CH_3\overset{+}{O}CHCH_3$ ion[26] can be corrected, resulting in a value of 143 kcal mol^{-1} for this ion. The values used for the heats of formation of the $[C_4H_7]^+$ ion (198 kcal mol^{-1}),[27] $[C_4H_9]^+$ ion (184 kcal mol^{-1})[28] and the $[C_5H_{11}]^+$ ion (164 kcal mol^{-1}),[28] are based on photoionization experiments, which are considered to give the most precise results. For the $[C_5H_9]^+$ ion a value of 184 kcal mol^{-1} has been used, as obtained from theoretical calculations.[29]

Heats of formation of all neutrals have been taken from the compilation of ionization potential, appearance potential and ΔH_f values by Franklin *et al.*[20] The heat of formation of the $CH_3OCH_2\overset{+}{O}CHCH_3$ ion from methoxymethyl isopropyl ether was computed from the appearance potential value, as measured in our laboratory on a Varian MAT 711 instrument (see Experimental section).