Methoxymethyl Cations. 3. Reactions of the Gaseous Ions with Acyl Compounds

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Methoxymethyl cations, produced by electron-impact (EI) cleavage of methyl ethers under ICR conditions, were found to react with neutral acyl compounds (AcXR) in various ways. Methyl transfer and loss of formaldehyde from the ion were evident in the reactions with acetamide and *N*-methyl- and *N*,*N*-dimethylacetamide. A competing reaction of wider generality led to ions of composition $RX^+{=}CH_2$. The latter reaction also was observed with ethyl, isopropenyl, and allyl acetates, thioacetates, diacetyl sulfide, and *N*-methyldiacetylimide. A third type of reaction was identified as a methoxylation reaction and gave product ions by elimination of $CH_2{=}X$. A fourth reaction led to ketene elimination and a fifth to 2-methylpropene elimination (R = *tert*-butyl). These reactions are explained as resulting from the dissociation of a collision complex formed by the attack of the reactant ion at the X atom of the acyl component, AcXR.

The chemistry of gaseous methoxymethyl cations 1 ($CH_3OCH_2^+$) has been the subject of several ion cyclotron resonance (ICR) studies in this laboratory and elsewhere,[1-6] and it is fair to say that more is now known about the chemistry of this ion in the gas phase than in condensed phase. Our interest in 1 stems in part from the recognition that some of its neutral precursors are carcinogens[7] and that the potential hazards of these compounds could be better understood if the chemical behavior of the ion were known. We also have an interest in the reactivity and reaction mechanisms of ions in the gas phase. Accordingly, we have investigated the behavior of gaseous methoxymethyl cations with numerous acyl compounds.

The ions in question were generated by electron-impact cleavage of methyl ethers CH_3OCH_2R, and the reactions of the ions with neutral acyl derivatives were followed by standard ICR techniques.[8,9] Isotopically labeled ions proved to be helpful in establishing the nature of the reactions involved, and for this purpose we have utilized labeled ethers $CH_3{}^{18}OCH_3$, $CD_3OCH_2CH_3$, and $CH_3OCD_2CD_3$ as sources of $CH_3{}^{18}OCH_2^+$, $CD_3OCH_2^+$, and $CH_3OCD_2^+$, respectively.

As will be described in the body of the paper, several different and often competing reactions take place when gaseous methoxymethyl cations encounter a neutral acyl compound. Overall, however, the reactions appear to be of three main types. One type is a straightforward methylation reaction which results only in the cleavage of the methyl-oxygen bond of the reactant ion (eq 1). Another more commonly observed reaction results in cleavage of bonds in both the ion and the neutral molecule (eq 2). In this event, the ion functions to *methoxylate* the acyl compound, but the actual products depend on the structure of the reactant. In some circumstances the acyl component retains the charge in the product (eq 2a), and, in others, the acyl group is incorporated into the neutral product (eq 2b). Finally, reactions occur with cleavage in the acyl component only. In most cases the neutral product is presumed to be ketene (eq 3a). In cases where R is *tert*-butyl, the neutral product is presumed to be 2-methylpropene (eq 3b).

$$AcXR + CH_3OCH_2^+ \longrightarrow (AcXR)CH_3^+ + CH_2{=}O \quad (1)$$

$$AcXR + CH_3OCH_2^+ \longrightarrow \begin{cases} (AcOCH_3)R^+ + CH_2{=}X & (2a) \\ AcOCH_3 + CH_2{=}XR^+ & (2b) \end{cases}$$

$$AcXR + CH_3OCH_2^+ \longrightarrow (CH_3OCH_2XR)H^+ + CH_2{=}C{=}O \quad (3a)$$

$$AcX\,t\text{-}C_4H_9 + CH_3OCH_2^+ \longrightarrow (CH_3OCH_2XAc)H^+ + C_4H_8 \quad (3b)$$

The unraveling of the various reaction channels 1-3 and the factors that contribute to their relative importance is the main subject of the discussion that follows. In spite of the apparent diversity of reactions 1-3, we attempt to show that each could be derived from the same ion-molecule collision complex.

Results and Discussion

Methylation and Methoxylation Reactions. Methoxymethyl cations in the gas phase have been shown to methylate neutral nucleophiles such as dimethyl sulfide, dimethyl disulfide,[6] dimethyl ether,[3] acetaldehyde, and acetone.[2] Comparable methylation of carboxylic acid derivatives was therefore anticipated and indeed found in some cases. For instance, the reactions of 1 with acetic acid, acetic anhydride, methyl and allyl acetates, acetamide, *N*-methylacetamide, and *N*,*N*-dimethylacetamide each gave a prominent (M + CH_3) product ion, presumably by loss of neutral formaldehyde. Although these reactions may appear to be straightforward methylation reactions (eq 1), there are several ways in which formaldehyde could be lost from an initially formed collision complex of the ion with the neutral molecule, as shown in structures **2a,b** and **3a,b** (X = O). (The elements of CH_2O are encircled.)

Reaction by way of **2a** or **2b** corresponds to *methyl transfer* from the ion to the neutral, as in eq 1, whereas reaction by way of **3a** or **3b** could achieve either *methyl transfer* (eq 1) or *methoxyl transfer* (eq 2a). Isotopic labels sometimes can be helpful in differentiating between alternative modes of reaction, but their use is not completely definitive in the present case. Thus, labeled ions $CD_3OCH_2^+$ and $CH_3{}^{18}OCH_2^+$ with acetamides and methyl acetate gave product ions of composition M + CD_3 and M + CH_3, respectively, corresponding to *methylation* by

(1) Dunbar, R. C.; Shen, J.; Melby, E.; Olah, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7200.
(2) van Doorn, R.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1978**, *13*, 527.
(3) Beauchamp, J. L.; Dunbar, R. C. *J. Am. Chem. Soc.* **1970**, *92*, 1477.
(4) Pau, J. K.; Kim, J. K.; Caserio, M. C. *J. Am. Chem. Soc.* **1978**, *100*, 3838.
(5) Pau, J. K.; Ruggera, M. B.; Kim, J. K.; Caserio, M. C. *J. Am. Chem. Soc.* **1978**, *100*, 4242.
(6) For Parts 1 and 2 see: Kim, J. K.; Bonicamp, J.; Caserio, M. C. *J. Org. Chem.* **1981**, *46*, 4230; **1981**, *46*, 4236.
(7) (a) Miller, J. A.; Miller, E. C. In "The Molecular Biology of Cancer"; Busch, H., Ed., Academic Press: New York, 1974. (b) Lawley, P. D. In "Chemical Carcinogenesis"; Searle, C. A., Ed.; American Chemical Society: Washington, DC, 1976; ACS Monogr. No. 173, 83. (c) Miller, E. C.; Miller, J. A. *Ibid.*, p 737.
(8) See: Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley: New York, 1976.
(9) Schoemaker, H. E.; Nibbering, N. M. M.; Cooks, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 4415.

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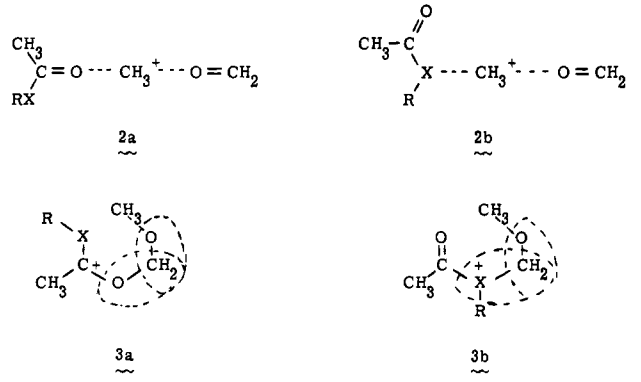


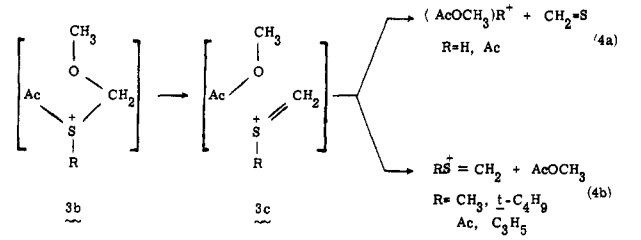
2a 2b

3a 3b

cleavage of the methyl–oxygen bond with loss of neutral formaldehyde *from the ion* (Table I). However, this result does not of itself differentiate between complexes **2a**, **2b**, **3a**, or **3b**, as each could dissociate by methyl transfer (eq 1). However, the observed methylations are closely related to the reactions of 1 with acetaldehyde and acetone which Nibbering and associates[2] have shown previously to give M + CH_3 ions by way of complexes akin to **2a** (RX = H, or CH_3). It would not then be unreasonable to conclude that the present methylations (RX = OCH_3, NR_2) involve **2a**. This may not be correct though because a number of other acyl derivatives were found to give M + CH_3 product ions by a *methoxylation* sequence that necessarily precludes the intervention of **2a**. Specifically, ^{18}O-labeled 1 with acetic acid, anhydride, or allyl acetate led to M + CH_3 ion in which *the ^{18}O label was retained in the ion.* This means that the oxygen lost as formaldehyde must originate from the acyl component, as in eq 2a, which implies formation and dissociation of either complex **3a** or **3b**.

At first glance, loss of either oxygen as formaldehyde from the acyl component in **3a** or **3b** (X = O) looks unusual, but there is some precedent for this in the work of Nibbering, Schoemaker, and Cooks,[9] who reported that ions of structure **3a** (RX = H) generated by EI cleavage of methoxymethyl isopropyl ether lose CH_2O to give $CH_3CH{=}OCH_3^+$ (m/z 59) in two ways: one by methoxylation and the other by methylation. The methoxylation channel has the higher activation energy.

Acylthio Compounds with $CH_3OCH_2^+$. A distinction between intermediates **3a** and **3b** is possible if the carbonyl oxygen can be distinguished isotopically or compositionally from X. The reactions of acylthio compounds illustrate this point. Thus, thioacetic and thiopropanoic *S*-acids and acetyl sulfide each reacted with 1 according to the methoxylation channel of eq 2a in which the sulfur atom was eliminated, presumably as thioformaldehyde. This result strongly suggests that the products are formed by the dissociation of complex **3b** (RX = SH, SAc) in which the reactant ion 1 is covalently bonded to sulfur. In order for **3b** to release neutral $CH_2{=}S$, the labile group at sulfur (R = H or Ac) must be transferred to the acyl group, possibly as shown in eq 4a. This is the expected result for thiol



3b 3c (4a) (4b)

acids (R = H) on the basis of thermochemistry because the proton affinity of methyl acetate is greater than the proton affinity of thioformaldehyde by about 11 kcal mol^{-1}.[10]

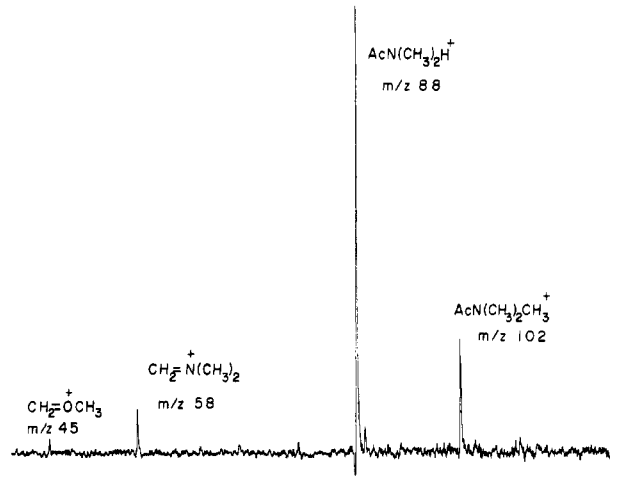


Figure 1. ICR mass spectrum of a mixture of *N,N*-dimethylacetamide (1×10^{-6} torr) and dimethyl ether (1.3×10^{-6} torr) after an 85-ms reaction time. The ion intensities are uncorrected for mass differences.

When, however, the R group at sulfur in the acylthio compound AcSR is other than hydrogen, the reaction takes an alternative course. Product ions of composition $RS^+{=}CH_2$ were observed in the reactions of 1 with thioesters (SR = SCH_3, S-*t*-C_4H_9, S–allyl) corresponding to the loss of neutral methyl ester $AcOCH_3$ and retention of charge (and the R group) by sulfur. This would be the normal result of dissociation of the complex **3c** *without* transfer of R from sulfur to oxygen, as in eq 4b. Although the relative importance of the two reaction channels 4a and 4b for R = H is undoubtedly governed by their relative enthalpies, there is insufficient thermochemical data in the cases of R≠H to support a similar conclusion. Nevertheless, in the case of acetyl sulfide (R = Ac) the reaction channels were competitive and gave m/z 117 of composition $(AcOCH_3)Ac^+$ and m/z 89 of composition $AcS^+{=}CH_2$ in the ratio of 60:40 (Table I), a result which quite possibly means that the acetyl affinities of methyl acetate and thioformaldehyde are comparable.

Cleavage of Amides and Esters with $CH_3OCH_2^+$. The incidence of **3b** in the reactions of 1 with acylthio derivatives suggests that related reactions of 1 with other acyl compounds AcXR (XR = OH, OR, NR_2) may also proceed by way of **3b**. Both the methylation and methoxylation channels can be explained in this way (see Scheme I). Methylation is shown as a type of cycloelimination. Furthermore, the reaction that leads to acyl cleavage and product ions $RX^+{=}CH_2$ turns out to be remarkably general. Thus, besides the methylation channel described previously, acetamide and its *N*-methyl derivatives each were cleaved on reaction with 1 to give $CH_2{=}NR_2^+$ (R = H, CH_3). Labeled reactant ions $CH_3OCD_2^+$ led to labeled product ions $CD_2{=}NR_2^+$, as expected (see Table I).

From the relative abundance of product ions of the type $(M + CH_3)^+$ and $CH_2{=}NR_2^+$, the ratio of methylation to methoxylation of acetamides is about 80:20 (see Figure 1). *N*-Methyldiacetylimide, representative of an imide, was also cleaved by 1 to give $CH_2{=}N(CH_3)Ac^+$ (m/z 86), but no methylation channel was evident.

(10) The proton affinity (PA) of methyl acetate is reported as 195.8 kcal mol^{-1} with reference to ammonia (PA = 202.3 kcal mol^{-1}): Wolf, J. F.; Staley, R. G.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417. The PA of thioformaldehyde is calculated to be 185 kcal/mol from heats of formation of $CH_2{=}S$ (24 kcal mol^{-1}) $CH_2{=}SH^+$ (205 kcal mol^{-1}), and H^+ (366 kcal mol^{-1}): Benson, S. W. *Chem. Rev.* **1978**, *78*, 23. Dill, J. D.; McLafferty, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 6526.

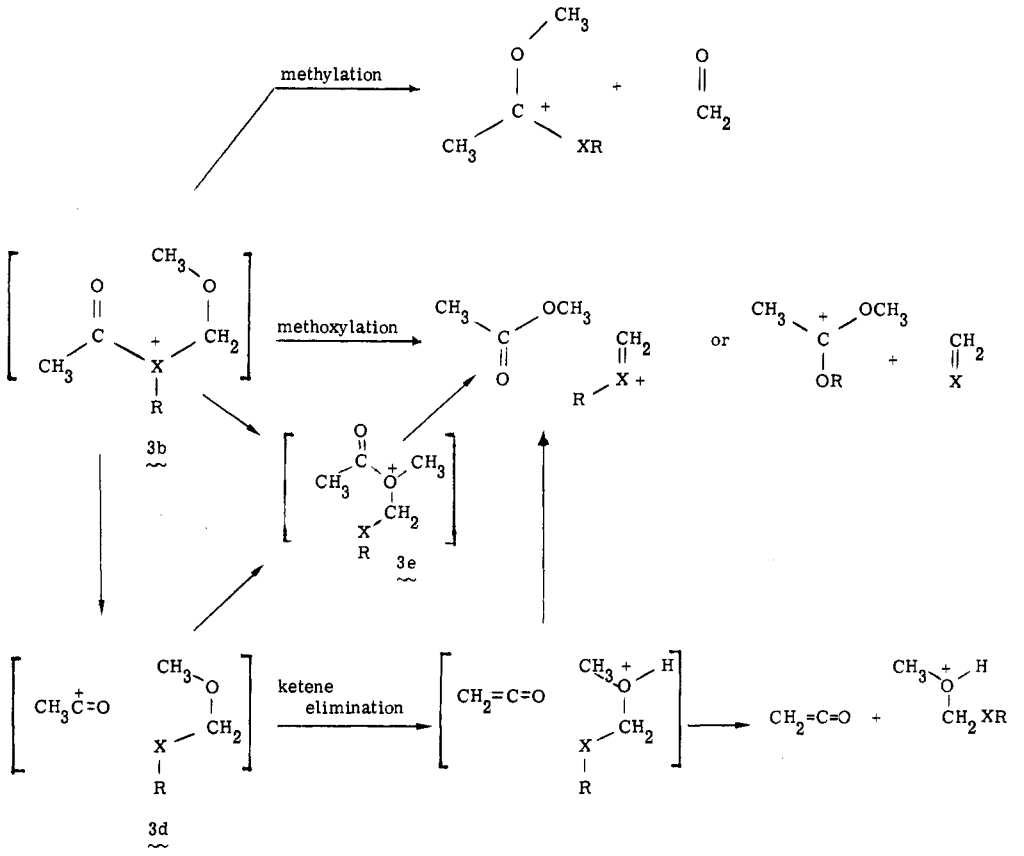
Table I. Summary of Reactions 1-3 of Methoxymethyl Cations with Acyl Compounds

reactants		productions (m/z, %) [ΔH, kcal mol^{-1}]		
AcXR[a]	ion (m/z)	eq 1	eq 2b	eq 3
$AcNH_2$	$CH_3OCH_2^+$ (45)	$(AcNH_2)CH_3^+$ (74) [-24]	$CH_2{=}NH_2^+$ (30) [-25]	
	$CD_3OCH_2^+$ (48)	$(AcNH_2)CD_3^+$ (77) [-24]	$CH_2NH_2^+$ (30) [-25]	
$AcNHCH_3$	(45)	$(AcNHCH_3)CH_3^+$ (88)	$CH_2{=}NHCH_3^+$ (44)	
	$CH_3OCD_2^+$ (47)	(88)	$CD_2{=}NHCH_3^+$ (46)	
$AcN(CH_3)_2$	(45)	$(AcN(CH_3)_2)CH_3^+$ (102, 84)	$CH_2{=}N(CH_3)_2^+$ (58, 16)	
	$CH_3{}^{18}OCH_2^+$ (47)	(102, 84)	(58, 16)	
$AcOCH_3$	(45)	$(AcOCH_3)CH_3^+$ (89, 100) [-20]		
	$CH_3{}^{18}OCH_2^+$ (47)	(89, 100) [-20]		
$AcOC_2H_5$	(45)		$CH_2{=}OC_2H_5^+$ (59, 100) [-3]	
	$CH_3{}^{18}OCH_2^+$ (47)		(59, 100) [-3]	
$AcSCH_3$	(45)		$CH_2{=}SCH_3^+$ (61, 100)	
	$CH_3{}^{18}OCH_2$ (47)		(61, 100)	
AcOH	$CH_3OCH_2^+$ (45)	$(AcOCH_3)H^+$ (75, 100) [-12]	$CH_2{=}OH^+$ (31, 0) [+18]	
	$CH_3{}^{18}OCH_2^+$ (47)	$(Ac^{18}OCH_3)H^+$ (77, 100) [-12]		
CH_3COSH	$CH_3OCH_2^+$ (45)	$(CH_3CO_2CH_3)H^+$ (75, 100) [-19]	$CH_2{=}SH^+$ (47, 0) [-8]	
C_2H_5COSH	(45)	$(C_2H_5CO_2CH_3)H^+$ (89, 100)	$CH_2{=}SH^+$ (47, 0) [-8]	
AcOAc	$CH_3OCH_2^+$ (45)	$(AcOCH_3)Ac^+$ (117, 100)		
	$CH_3{}^{18}OCH_2^+$ (47)	$(Ac^{18}OCH_3)Ac^+$ (119, 100)		
AcSAc	$CH_3OCH_2^+$ (45)	$(AcOCH_3)Ac^+$ (117, 60)	$CH_2{=}SAc^+$ (89, 40)	
$AcOCH_2CH{=}CH_2$	$CH_3OCH_2^+$ (45)	$(AcOCH_3)C_3H_5^+$ (115, 30)	$CH_2{=}OC_3H_5^+$ (71, 40)	$(CH_3OCH_2OC_3H_5)H^+$ (103, 30)
	$CH_3OCD_2^+$ (47)	$(AcOCH_3)C_3H_5^+$ (115, 30)	$CD_2{=}OC_3H_5^+$ (73, 40)	$(CH_3OCD_2OC_3H_5)H^+$ (105, 30)
	$CH_3{}^{18}OCH_2^+$ (47)	$(Ac^{18}OCH_3)C_3H_5^+$ (117, 30)	$CH_2{=}OC_3H_5^+$ (71, 40)	$(CH_3{}^{18}OCH_2OC_3H_5)H^+$ (105, 30)
$AcSCH_2CH{=}CH_2$	$CH_3OCH_2^+$ (45)		$CH_2{=}SC_3H_5^+$ (87, 100)	
$AcOCH{=}CH_2$	$CH_3OCH_2^+$ (45)			$(CH_3OCH_2OC_2H_3)H^+$ (89, 100)
	$CH_3{}^{18}OCH_2^+$ (47)			$(CH_3{}^{18}OCH_2OC_2H_3)H^+$ (91, 100)
$CD_3CO_2CH{=}CH_2$	$CH_3OCH_2^+$ (45)			$(CH_3OCH_2OC_2H_3)D^+$ (90, 100)
$AcOC(CH_3){=}CH_2$	$CH_3OCH_2^+$ (45)		$(CH_2OC_3H_5)^+$ (71, 20)	$(CH_3OCH_2OC_3H_5)H^+$ (103, 80)
	$CH_3{}^{18}OCH_2^+$ (47)		$CH_2{=}OC_3H_5^+$ (71, 20)	$(CH_3{}^{18}OCH_2OC_3H_5)H^+$ (105, 80)
	$CH_3OCD_2^+$ (47)		$CD_2{=}OC_3H_5^+$ (73, 20)	$(CH_3OCD_2OC_3H_5)H^+$ (105, 80)
	$CD_3OCH_2^+$ (48)		$CH_2{=}OC_3H_5^+$ (71, 20)	$(CD_3OCH_2OC_3H_5)H^+$ (106, 80)
Ac_2NCH_3	$CH_3OCH_2^+$ (45)		$CH_2{=}NAcCH_3^+$ (86, 60)	$(CH_3OCH_2NAcCH_3)H^+$ (118, 40)
$AcOC_4H_9$-t	$CH_3OCH_2^+$ (45)			$(AcOCH_2OCH_3)H^+$ (105, 100)
	$CH_3{}^{18}OCH_2^+$ (47)			$(AcOCH_2{}^{18}OCH_3)H^+$ (107, 100)
$AcSC_4H_9$-t	$CH_3OCH_2^+$ (45)		$CH_2{=}SC_4H_9$-t^+ (103, 70)	$(AcSCH_2OCH_3)H^+$ (121, 30)

[a] ΔH values were calculated from known heats of formation of ions and neutral compounds (see: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1). Values of $\Delta H(CH_3C(OCH_3)_2^+)$, $\Delta H(CH_3C(OCH_3)(OC_2H_5)^+)$, $\Delta H(C_2H_5OCH_2^+)$, $\Delta H(CH_3C(OCH_3)NH_2^+)$ as 67, 56, 148, and 108 kcal/mol, respectively, were estimated from methyl-cation affinity data derived from proton-affinity data.[10]

Acetate esters also gave ions of composition $CH_2{=}OR^+$. In the case of ethyl acetate, acyl cleavage (as in eq 2b) was the only reaction channel evident. Isopropenyl acetate and allyl acetate both gave product ions of the type $CH_2{=}OR^+$. The oxygen in the product ion clearly originates from the neutral reactant because $CH_3{}^{18}OCH_2^+$ with allyl acetate gave $CH_2{=}OCH_2CH{=}CH_2^+$ (m/z 71) showing no incorporation of the ^{18}O-labeled oxygen. The competing methoxylation channel of eq 2a gave m/z 117, showing complete retention of the oxygen label in the product ion. These results are entirely consistent with the description of the reactions given in Scheme I.

Scheme I



The reaction summary in Table I includes the reaction enthalpies where these can be estimated with some reliability. As already indicated for thiol acids, the relative importance of reaction channels 2a and 2b is clearly determined by their enthalpy differences whenever a labile proton is involved (RX = OH, SH, NH_2, $NHCH_3$). For other situations, the data are too limited to allow for firm conclusions, although it would appear from Table I that the R group must be reasonably labile (R = Ac, allyl) for channels 2a and 2b to compete.

Ketene Elimination. The third type of reaction of methoxymethyl cations with acyl compounds produces ions corresponding to the loss of 42 mass units, C_2H_2O or ketene (eq 3a). It is the dominant reaction channel for vinyl and isopropenyl acetates and is prominent in the ion chemistry of allyl acetate and *N*-methyldiacetylimide. The elements of the reactant ion are totally retained in the product ion because ions derived from the isotopically labeled ions $CH_3OCD_2^+$, $CD_3OCH_2^+$, and $CH_3{}^{18}OCH_2^+$ showed complete retention of the labels (Table I). The neutral product must therefore be lost from the neutral reactant. Moreover, the product ion retains *one* hydrogen originally in the acetyl methyl group because $CD_3CO_2CH{=}CH_2$ and 1 gave $(CH_3OCH_2OCH{=}CH_2)D^+$.

Loss of ketene can be readily understood if the collision complex has structure **3b**. Dissociation of the complex to an acetyl cation followed by proton transfer to the associated neutral would lead to $(CH_3OCH_2XR)H^+$ and ketene (Scheme I).[11]

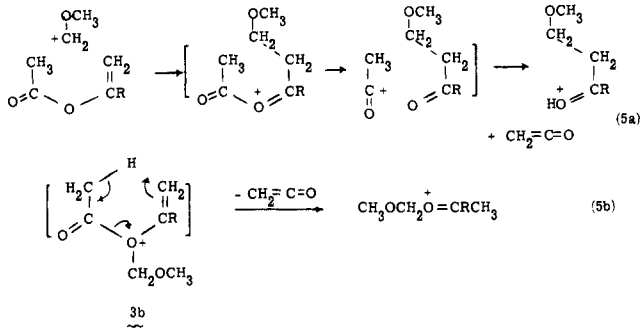
It is also possible that the methoxylation channel of eq 2a and 2b may occur along the same reaction coordinate as ketene elimination. That is to say, a complex of an acyl cation with the ether ($RXCH_2OCH_3$), shown as **3d** in Scheme I, besides eliminating neutral ketene could rearrange to **3e** by acyl migration to the ether oxygen. Dissociation of **3e** would lead to the products of reactions 2b or 2a. In view of the fact that methoxylation products derived directly from **3b** appear to involve a symmetry-forbidden, four-electron, four-center reaction, the alternative stepwise process of acyl cation transfer looks attractive.

Vinyl and *tert*-Butyl Esters with $CH_3OCH_2^+$. A special comment is in order regarding the reactions of vinyl and isopropenyl acetates with **1**. As Table I shows, ketene loss is a prominent reaction channel and, in fact, is the only reaction channel for vinyl acetate. In a separate paper on the ion chemistry of vinyl acetate and related esters, we reported that acylium ions Ac^+ attack the neutral esters at the terminal vinylic carbon.[12] By analogy, it is very possible that reaction of methoxymethyl cations with vinyl acetate similarly results in addition of the ion to the vinylic carbon, in which case ketene elimination could proceed as in eq 5a. Another possibility is that ketene is lost from a complex of **1** with the ester in a concerted cycloelimination (eq 5b).

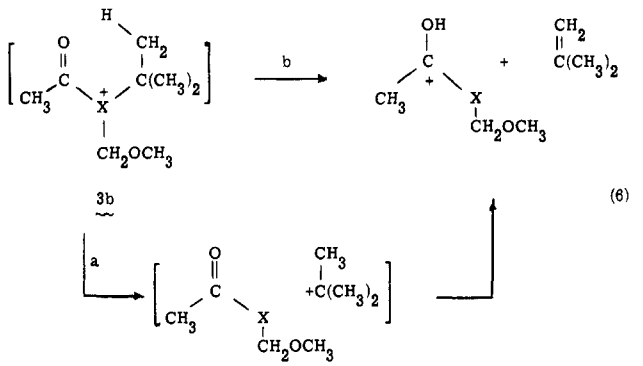
As indicated, most of the reactions in which only the neutral component suffered cleavage led to dissociation at the acyl–XR bond (i.e., ketene loss). However, in the case of *tert*-butyl acetate and thioacetate, the related reactions with **1** led to cleavage at the acyl X–R bond (C_4H_8 loss). Indeed, the reaction of **1** with *tert*-butyl acetate gave *only* m/z 105 by loss of C_4H_8. The reaction is a logical outcome of the reorganization of an intermediate complex **3b** into methoxymethyl acetate and a *tert*-butyl cation which, on proton transfer to the ester, leads to the observed

(11) Gas-phase proton transfer from CH_3CO^+ to oxygen bases of higher proton affinity is rapid [$k \approx (2\text{–}4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for ketones] even though proton transfer from carbon acids to oxygen bases can be slow in a condensed phase. See: Kumakura, M.; Sugiura, T. *J. Phys. Chem.* **1978**, *82*, 639.

(12) Kim, J. K.; Caserio, M. C. *J. Am. Chem. Soc.*, in press.



products (eq 6, route a). However, the alternative electrocyclic 1,5 hydrogen migration process (eq 6, route b) is certainly possible.



Conclusions

The results of this investigation leave no doubt that gaseous methoxymethyl cations react rapidly with representative carboxylic acids, esters, amides, imides, and thioesters. Apart from a few examples of methyl transfer (eq 1) and acyl X–R cleavage (eq 6), the most commonly observed reactions are those which cleave the neutral molecule at the acyl–X bond. Each of these reactions can be explained by assuming that the products arise from the dissociation of an intermediate complex, **3b**, formed by attack of the reactant ion at the X atom of the neutral molecule (X = O, S, or N). This pathway may not be the only one possible, especially in the case of vinylic esters, but it accounts for the results with the minimum number of postulated intermediates.

In some respects it is surprising that a cation would attack the X atom in preference to the acyl oxygen because the greater resonance stabilization in ions of type **3a** compared to **3b** implies that they should be energetically preferred. For example, the proton affinity of the acyl oxygen of acetic acid exceeds that of the hydroxyl oxygen by about 27 kcal mol^{-1}.[13] Also, the carbonyl oxygen of esters is more basic than the ether oxygen in the gas phase.[14] However, the relative stability of isomeric ions may be irrelevant to arguments on the relative importance of reaction intermediates. Thus, the incidence of **3a** or **3b** along the reaction pathway is more likely to be determined by the relative activation energies for the dissociation of **3a** and **3b** to the products than by the relative thermal energies of **3a** and **3b**. Regardless of whether complex **3a** is more or less stable than **3b**, dissociation of **3a** evidently requires greater internal reorganization than does **3b**. Most remarkable is the integrity of the acetyl group. Apart from proton loss from the methyl group in ketene elimination, the acyl group remains intact. That is, cleavage of the acyl carbonyl bond was not observed. As far as the implications for condensed-phase reactions of acyl compounds with $CH_3OCH_2^+$ are concerned, the feasibility of acyl cleavage is clearly established but remains to be documented for the specific cases cited in this paper.

Experimental Section

The pulsed ICR instrumentaion utilized a trapped-ion analyzer cell[15] and multiple inlet valves to admit the several gaseous neutral compounds at pressures maintained at about 10^{-6} torr. Ions were generated from the neutral molecules by electron impact at 19 eV. All reaction sequences were confirmed through double-resonance experiments and scans of ion abundance with time. All commercially available compounds employed in this study were purified before use until chromatographically pure. Isotopically labeled methyl ethers were prepared as described previously.[6] The synthesis of $CD_3CO_2CH{=}CH_2$ is described elsewhere.[12] *N*-Methyldiacetylimide was prepared from *N*-methylacetamide and isopropenyl acetate according to a published procedure;[16] bp 64–65 °C (5 mm) [lit.[16] bp 71 °C (7 mm)].

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Registry No. 1, 23653-97-6; $AcNH_2$, 60-35-5; $AcNHCH_3$, 79-16-3; $AcN(CH_3)_2$, 127-19-5; $AcOCH_3$, 79-20-9; $AcOC_2H_5$, 141-78-6; $AcSCH_3$, 1534-08-3; AcOH, 64-19-7; CH_3COSH, 507-09-5; C_2H_5COSH, 1892-31-5; AcOAc, 108-24-7; AcSAc, 3232-39-1; $AcOCH_2CH{=}CH_2$, 591-87-7; $AcSCH_2CH{=}CH_2$, 23973-51-5; $AcOCH{=}CH_2$, 108-05-4; $CD_3CO_2CH{=}CH_2$, 20630-89-1; $AcOC(CH_3){=}CH_2$, 108-22-5; Ac_2NCH_3, 1113-68-4; $AcOC_4H_9$-*t*, 540-88-5; $AcSC_4H_9$-*t*, 999-90-6; $CD_3OCH_2^+$, 78638-94-5; $CH_3OCD_2^+$, 78638-95-6; $CH_3{}^{18}OCH_2^+$, 81876-08-6; $(AcNH_2)CH_3^+$, 81876-09-7; $(AcNH_2)CD_3^+$, 81876-10-0; $(AcNHCH_3)CH_3^+$, 81876-11-1; $(AcN(CH_3)_2)CH_3^+$, 44546-69-2; $(AcOCH_3)CH_3^+$, 81876-12-2; $(AcOCH_3)H^+$, 39014-36-3; $(Ac^{18}OCH_3)H^+$, 81876-13-3; $(C_2H_5CO_2CH_3)H^+$, 39014-37-4; $(AcOCH_3)Ac^+$, 81876-14-4; $(Ac^{18}OCH_3)Ac^+$, 81898-52-4; $(AcOCH_3)C_3H_5^+$, 81876-15-5; $(Ac^{18}OCH_3)C_3H_5^+$, 81876-16-6; $CH_2{=}NH_2^+$, 28963-72-6; $CH_2{=}NHCH_3^+$, 51943-18-1; $CD_2{=}NHCH_3^+$, 81876-17-7; $CH_2{=}N(CH_3)_2^+$, 28149-27-1; $CH_2{=}OC_2H_5^+$, 51624-52-3; $CH_2{=}SCH_3^+$, 43431-07-8; $CH_2{=}OH^+$, 18682-95-6; $CH_2{=}SH^+$, 54043-03-7; $CH_2{=}SAc^+$, 81876-18-8; $CH_2{=}OC_3H_5^+$, 81876-19-9; $CD_2{=}OC_3H_5^+$, 81876-20-2; $CH_2{=}SC_3H_5^+$, 81876-21-3; $CH_2{=}NAcCH_3^+$, 81876-22-4; $CH_2{=}SC_4H_9$-t^+, 81876-23-5; $(CH_3OCH_2OC_3H_5)H^+$, 81876-24-6; $(CH_3OCD_2OC_3H_5)H^+$, 81876-25-7; $(CH_3{}^{18}OCH_2OC_3H_5)H^+$, 81876-26-8; $(CH_3OCH_2OC_2H_3)H^+$, 81876-27-9; $(CH_3{}^{18}OCH_2OC_2H_3)H^+$, 81876-28-0; $(CH_3OCH_2OC_2H_3)D^+$, 81876-29-1; $(CD_3OCH_2OC_3H_5)H^+$, 81876-30-4; $(CH_3OCH_2NAcCH_3)H^+$, 81876-31-5; $(AcOCH_2OCH_3)H^+$, 81876-32-6; $(AcOCH_2{}^{18}OCH_3)H^+$, 81876-33-7; $(AcSCH_2OCH_3)H^+$, 81876-34-8.

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