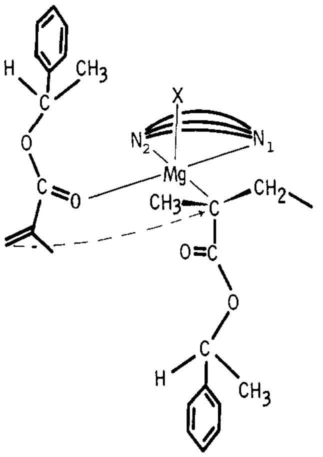
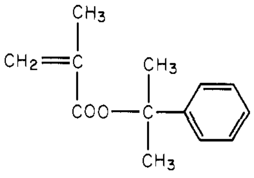


Figure 10. Schematical structure of an active center. The monomer is (*R*)-MBMA.

side of **1** is more sterically hindered than the right-hand side. Therefore, the existence of the bulky growing end at the right-hand side seems more favorable.

According to the above mechanism, one cannot expect polymerization of α,α-dimethylbenzyl methacrylate (**7**) with the Grignard reagent–**1** catalysts. Actually, this monomer showed no reactivity in the copolymerization with (*RS*)-MBMA by cHexMgCl-**1** in toluene at −78 °C.[6c]



7

The cavities of **5** and **6** are less hindered than that of **1**. Therefore, most Grignard reagent complexes of these ligands initiated the polymerization of MBMA, but enantiomer selection became low compared with that of the complexes of **1**. The activity and selectivity of the catalysts are very sensitive to the ligands and the cations. Highly asymmetric selective polymerization of vinyl monomers seems to be attainable only under restricted conditions.

Acknowledgment. A part of this work was supported by a Grant-in-Aid for Scientific Research by the Ministry of Education.

Registry No. **1**, 90-39-1; EtMgBr-**1**, isomer 1, 82335-32-8; EtMgBr-**1**, isomer 2, 82335-33-9; *t*-BuMgCl-**1**, isomer 1, 82281-69-4; *t*-BuMgCl-**1**, isomer 2, 82335-34-0; Et_2Mg-**1**, 82281-70-7; **2**, 446-95-7; EtMgBr-**2**, 82281-68-3; **3**, 82209-19-6; EtMgBr-**3**, 82281-67-2; **4**, 82263-24-9; EtMgBr-**4**, 82281-66-1; **5**, 2130-67-8; **5** $2HClO_4$, 82209-20-9; **6**, 82209-21-0; *c*-HexMgCl, 931-51-1; *t*-BuMgCl, 677-22-5; EtMgBr, 925-90-6; *i*-PrMgBr, 920-39-8; *i*-BuMgBr, 926-62-5; *c*-HexMgBr, 931-50-0; PhMgBr, 100-58-3; *c*-HexMgI, 931-52-2; Et_2Mg, 557-18-6; (±)-MBMA, 19321-42-7; ethyl bromide, 74-96-4; benzyl bromide, 100-39-0.

Acyl Transfer Reactions in the Gas Phase. Ion–Molecule Chemistry of Vinyl Acetate

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Abstract: An ion cyclotron resonance study of the ion–molecule reactions of vinyl acetate with methanol in the gas phase has revealed the formation of structurally different ions having the composition of protonated vinyl acetate. Deuterium-labeled reactants ($CD_3CO_2CH{=}CH_2$ with CH_3OH or CD_3OD) gave product ions showing incorporation of up to two deuteriums in the vinyl group, indicating coexistence and interconversion of O-protonated and C-protonated vinyl acetate. Evidence was also obtained for a third MH^+ ion for which the proposed structure is protonated 3-oxobutanal. This ion is believed to be formed by attack of CH_3CO^+ at the terminal vinylic carbon with loss of the ester acyl group as ketene. The ion reacts with methanol to give *m/z* 101 by loss of water. In contrast, protonated vinyl acetate reacts with methanol by an acyl transfer process to give $(AcOCH_3)H^+$, *m/z* 75. The related ion chemistry of vinyl propanoate, vinyl 2,2-dimethylpropanoate, and isopropenyl acetate is also described. Each of the acyl transfer reactions observed is consistent with formation of intermediate acylium ion complexes rather than tetracovalent addition complexes. Attempts were made to generate tetracovalent intermediates by an independent route from ortho esters of vinyl acetate. Dissociation of the ortho ester $CH_3C(OCH{=}CH_2)_2(OCH_3)$ to dioxacarbocations was the dominant reaction, but the product ions were unreactive with H_2O, CH_3OH, or *t*-C_4H_9OH. The mechanistic implications of these results are discussed.

Acyl transfer reactions are among the most important reactions in organic and bioorganic chemistry and, for this reason, have been studied intensively with respect to their scope and mechanisms. A wealth of data exists on acid-catalyzed bimolecular acylation of nucleophiles ($A_{Ac}2$ in the Ingold notation) that supports an addition–elimination pathway involving tetrahedral addition intermediates.[1] Related ion–molecule reactions occur in the gas phase and have been the object of several investigations by ion-cyclotron resonance (ICR) techniques.[2] Recently, we reported evidence that $A_{Ac}2$ reactions in the gas phase under ICR conditions do not involve tetrahedral addition intermediates but rather proceed by way of acyl cation transfer, as in eq 1.[3] With one

$$HY + AcXH^+ \rightarrow [HY\cdots Ac^+\cdots XH] \rightarrow AcYH^+ + HX \qquad (1)$$

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[1] (a) Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1953; Chapter 14. (b) For a review, see: Euranto, E. K. In "The Chemistry of Carboxylic Acids and Esters"; S. Patai, Ed.; Interscience: New York, 1969; Chapter 11.

[2] (a) Tiedemann, P. W.; Riveros, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 185. (b) McMahon, T. B. *Can. J. Chem.* **1978**, *56*, 670. (c) Beauchamp, J. L. *NATO Adv. Study Inst. Ser., Ser. B* **1975**, *8*, 418–436.

[3] (a) Kim, J. K.; Caserio, M. C. *J. Am. Chem. Soc.* **1981**, *103*, 2124. (b) Pau, J. K.; Kim, J. K.; Caserio, M. C. *Ibid.* **1978**, *100*, 3831.

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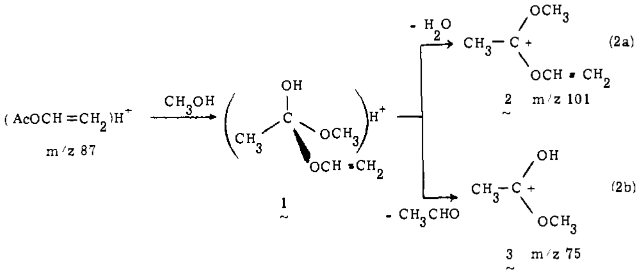
apparent exception, all of the reactions investigated of protonated acyl compounds ($AcXH^+$) with nucleophiles resulted in the cleavage of the Ac–X bond. The exception concerns the ion chemistry of protonated vinyl acetate [$(AcOCH{=}CH_2)H^+$] with methanol, which gave product ions having *m/z* 75 and 101, corresponding respectively to the elimination of acetaldehyde and water from the ion–molecule collision complex. Loss of water to give *m/z* 101 suggests that the acyl C–O bond is broken, and it is difficult to account for this circumstance unless a tetrahedral addition complex, **1**, is formed (eq 2). But, it is equally difficult

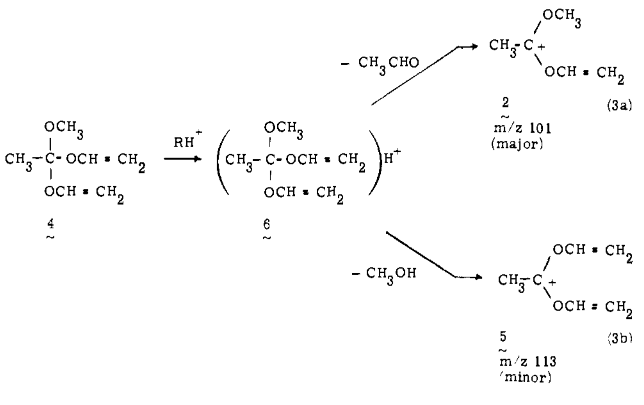


to accept that vinyl acetate should be unique among acyl compounds in its reactions with methanol, and we sought therefore to find an alternative explanation for the formation of *m/z* 101. This paper describes the ion chemistry of vinyl acetate and related compounds in some detail and presents the evidence that revealed an unsuspected reaction channel for the production of *m/z* 101 from vinyl acetate and methanol. Possibly the most interesting aspect of this work is the finding that protonated vinyl acetate and ions of related structure evidently rearrange by a facile electrocyclic process, which complicates their ion–molecule chemistry.

We begin with a discussion of the gas-phase ion–molecule reactions of ortho esters insofar as they relate to that of vinyl acetate.

Results and Discussion

Ion Chemistry of Ortho Esters of Vinyl Acetate. There is often an element of doubt as to the structure of an ion generated in an ICR experiment because mass spectral techniques in general only give direct information on relative ion abundance and ion mass. Structure is usually inferred from the elemental composition deduced from the ion mass and the mode of ion formation. It is entirely possible that the ion of *m/z* 101 detected in the ion chemistry of vinyl acetate and methanol has a different structure from that of **2** proposed in eq 2a. Evidence of ion structure, other than from collisional activation mass spectrometry,[4] can sometimes be obtained by generating the ion of interest in alternate ways and observing whether the ion chemistry is the same or different. For this purpose, we prepared the ortho ester **4** in anticipation that under ICR conditions it would generate **2** by the reaction shown in eq 3a. As expected, **2** (*m/z* 101) and **5** (*m/z* 113) were the only major product ions formed from **4**. Their ionic precursors were acidic ions produced by electron impact fragmentation of **4**. The protonated parent ion **6** is presumably an intermediate, but it evidently dissociates as fast as it forms because no MH^+ ions were detected. Also, the relative abundance of *m/z* 101 and 113 indicates (after statistical correction) that **6** dissociates to **2** about 2.6 times faster than to **5**.



Now, if eq 2 is a valid description of the reaction between vinyl acetate and methanol, formation of the intermediate **1** by the reverse reaction of addition of water to **2** should lead to **3**, *m/z* 75. However, mixtures of the ortho ester and $H_2{}^{18}O$ gave **2** (*m/z* 101) in abundance, but no product ions of *m/z* 77 of composition $(Ac^{18}OCH_3)H^+$ were detected.

By similar reasoning, the minor product ion *m/z* 113 of reaction 3b may possibly be converted to the major product *m/z* 101 in the presence of methanol by the sequence **5** + $CH_3OH \rightarrow$ **6** $\rightarrow$ **2** + CH_3CHO. A test for this sequence with mixtures of the ortho ester **4** with $CH_3{}^{18}OH$ failed to show any ^{18}O-labeled ions equivalent to **2** (*m/z* 103).

In short, mixtures of **4** with either $H_2{}^{18}O$, $CH_3{}^{18}OH$, or *tert*-butyl alcohol gave *no* products derived from reaction of either of the ions **2** or **5** with either of the neutral hydroxylic compounds. This result contrasts sharply with solution chemistry, where ortho esters solvolyze readily under acidic conditions by way of ions like **2** or **5**.[5] The gas-phase results show very clearly that tetrahedral intermediates such as **1** or **6**, when formed, rapidly dissociate to dioxacarbocations. The reverse step is *slow*,[6] probably because it is energetically unfavorable and therefore presents the would-be reaction with an insurmountable barrier. Although these results are partly negative and do not prove that methanol cannot add to protonated vinyl acetate, they lend no support to that idea.

Structural Isomers of Protonated Vinyl Acetate. Isotopically labeled reactants are valuable aids in establishing which bonds are broken as the result of reaction. With respect to reaction 2, we observed that vinyl acetate with ^{18}O-labeled methanol gave product ions *m/z* 103 and 77, and with CD_3OD gave ions *m/z* 104 and 78 and 79, all derived from protonated and deuterated vinyl acetate. (See Figure 1A–C and Table I.) These results confirmed that the methoxyl group is incorporated wholly into the product ions equivalent to **2** and **3** and that the oxygen eliminated as the neutral product originates from vinyl acetate, all of which is consistent with the process of eq 2.

However, the results obtained with vinyl acetate-d_3 and methanol have some curious features that are inconsistent with the pathway of eq 2. As may be seen from the mass spectrum of Figure 1B, the two major reactant ions of vinyl acetate-d_3, MH^+ and MD^+ at *m/z* 90 and 91, give rise to product ions *m/z* 104 (expected of reaction 2a) and *m/z* 78/79 (expected of reaction 2b). Surprisingly, though, the double resonance responses clearly indicated that *m/z* 104 came mostly from *m/z* 91 whereas *m/z* 78/79 came mostly from *m/z* 90 (see Figure 2). According to the reaction pathway of eq 2, the product ions *m/z* 78, 79, and 104 are shown to be formed by the dissociation of a common intermediate **1** and they should therefore show the same dependence on the precursor ions MH^+ (*m/z* 90) and MD^+ (*m/z* 91). The fact that they exhibit quite different dependencies means that they are *not* formed from the same intermediate complex and that the precursor ions, *m/z* 90 and 91, must be structurally as well as isotopically *different*.

Rearrangement of Protonated Vinyl Acetate. Regarding the protonated and deuterated parent ions, double resonance experiments showed that *m/z* 46, CD_3CO^+, is the precursor to MD^+, *m/z* 91 but that both *m/z* 46 *and* 91 are precursors to MH^+, *m/z* 90 by the sequence

$$CD_3CO^+ \xrightarrow{M} MD^+ \xrightarrow{M} MH^+$$

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[4] McLafferty, F. W.; Kornfeld, R.; Haddon, W. F.; Levsen, R.; Sakai, I.; Bente, P. F., III; Tsai, S.-C.; Schuddemage, H. D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3886.

[5] Capon, B.; Grieve, D. McL. A. *J. Chem. Soc., Perkin Trans. 2* **1980**, 300.

[6] A similar result was observed in the ion–molecule chemistry of 1,1,1-trimethyoxyethane, which produced 1,1-dimethoxyethyl cations that were unreactive toward hydroxylic nucleophiles (see ref 3a).

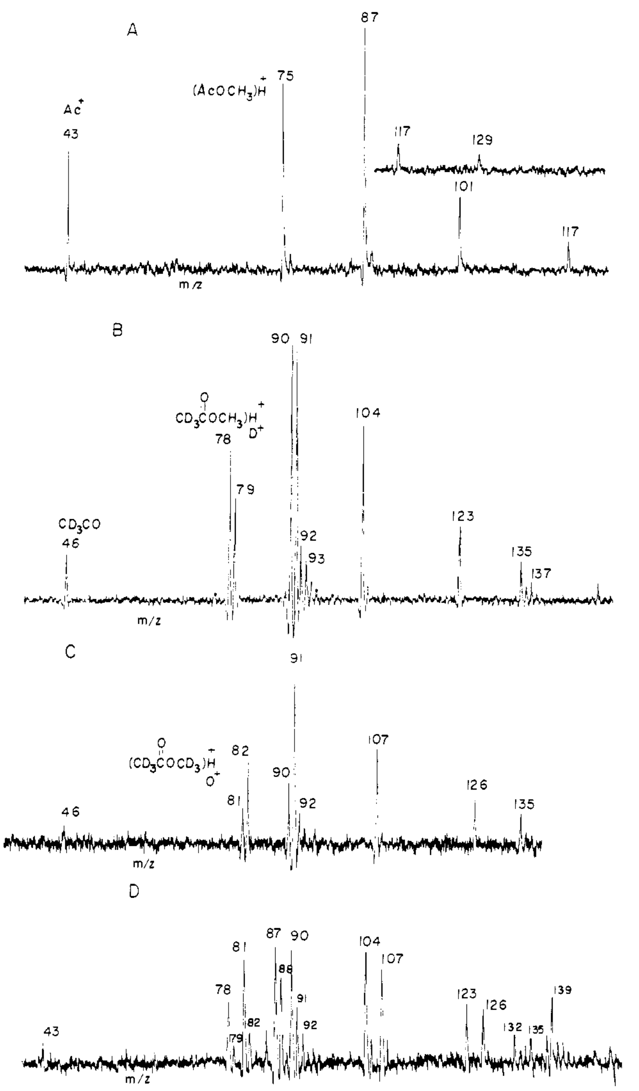


Figure 1. ICR mass spectrum: (A) vinyl acetate (M_r 86) and methanol at 1.6 × 10^{-6} torr after 85-ms reaction time; (B) vinyl acetate-d_3 (M_r 89) (9 × 10^{-7} torr) and methanol (1 × 10^{-6} torr) after 85 ms; (C) vinyl acetate-d_3 (M_r 89) (8 × 10^{-7} torr) and methanol-d_4 (1 × 10^{-6} torr) after 85 ms; (D) vinyl acetate-d_3 (9 × 10^{-7} torr), acetic acid (M_r 60) (1 × 10^{-6} torr), and methanol-d_4 (1 × 10^{-6} torr). Ions of m/z 61/62 and 103 derived from acetic acid and ions from the fragmentation of methanol are evident only at shorter reaction times.

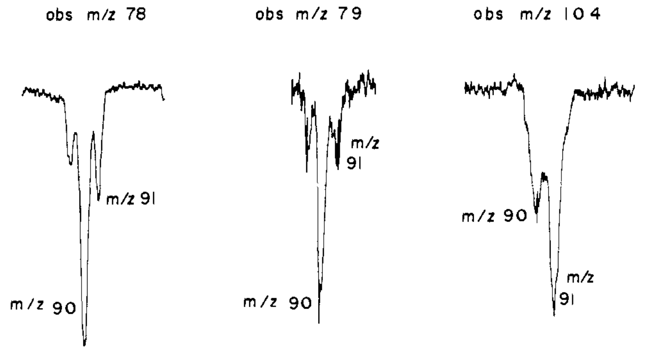
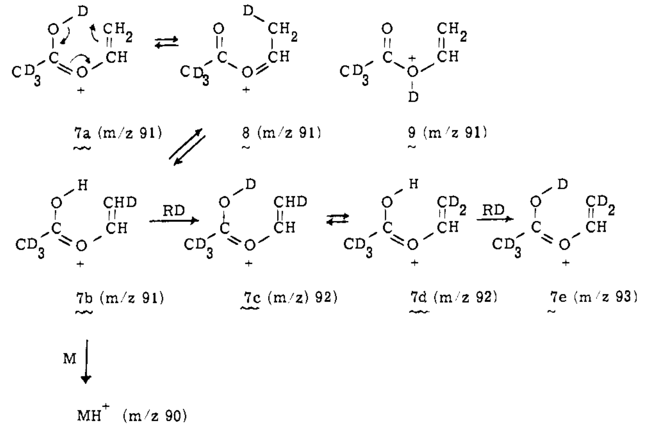
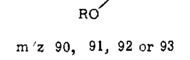


Figure 2. Double resonance response from ions m/z 78, 79, and 104 on irradiation at the cyclotron frequency of m/z 90 and 91 in the ion chemistry of a mixture of vinyl acetate-d_3 (9 × 10^{-7} torr) and unlabeled methanol (1 × 10^{-6} torr) after 85 ms.

It is not immediately obvious how the deuterated parent MD$^+$ could transfer a *proton* to the neutral ester to give MH$^+$ unless there is some internal rearrangement that exchanges hydrogen for deuterium. Of the three obvious possibilities for the structure of MD$^+$, **7**, **8**, and **9** (corresponding respectively to deuteration at the acyl oxygen, the vinylic carbon, and the ester oxygen), **7** and **8** appear to be easily interconvertible by a [1,5] sigmatropic rearrangement. By reversible hydrogen transfers of the kind **7a** ⇄ **8** ⇄ **7b**, m/z 91 could be either a proton or deuterium donor, which would explain why m/z 91 is a precursor to MH$^+$ m/z 90. Formation of multiply deuterated ions at m/z 92 and m/z 93, which are evident in the spectra of Figure 1B,C, can also be explained by a sequence of inter- and intramolecular H/D exchanges, **7b** → **7c** → **7d** → **7e**.



Further support for the proposed intramolecular H/D exchange is evident in the ICR spectra of vinyl acetate-d_3 alone, with CH_3OH, and with CD_3OD. Formation of certain ions can only be understood as the result of multiple deuterium incorporation in the vinyl group of the ester. This is particularly noticeable in the cluster of ions at m/z 135, 136, and 137 in the spectrum of Figure 1B,C. These ions are products of acyl transfer between neutral and protonated or deuterated forms of vinyl acetate-d_3 and have been proposed to occur by way of the cluster ion shown in eq 4.[3] In the absence of deuterium transfer to the vinyl group of the reactant ions, only m/z 135 would be formed. The fact that m/z 136 and 137 are clearly evident in the mass spectra of Figure 1B,C means that deuterium transfer to the vinyl group must occur, and up to two deuteriums can be retained in the vinyl group (i.e., R = CH=CH$_2$, CH=CHD, and CH=CD$_2$ in eq 4). Alternative collapse of the intermediate cluster ion in eq 4 to eliminate ketene accounts for the formation of MH$^+$ and MD$^+$ ions at m/z 90, 91, 92, and 93. As expected, the abundance of the labeled ions m/z 92/93 and 136/137 relative to ions m/z 91 or 135 increases with reaction time.



(4)

Product ions of vinyl acetate-d_3 and methanol that do *not* retain the vinyl group accordingly do *not* show isotopic variants. For example, the sequential acyl transfers of eq 5 lead to the formation of **11**.

$$(AcOCH{=}CH_2)H^+ \xrightarrow{ROH} (AcOR)H^+ \xrightarrow{AcOCH{=}CH_2} \underset{\mathbf{11}}{(AcOR)Ac^+} + CH_3CHO \qquad (5)$$

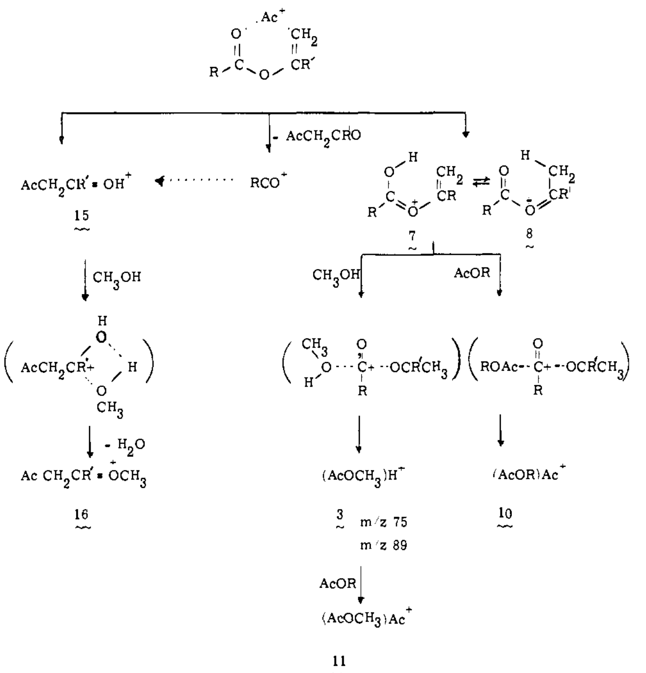
Ac = CH_3CO, m/z 87	R = CH_3, m/z 75	m/z 117
Ac = CD_3CO, m/z 90	R = CH_3, m/z 78	m/z 123
Ac = CD_3CO, m/z 90	R = CD_3, m/z 81	m/z 126

Table I. Summary of Reactant and Product Ions (m/z) in the Ion-Molecule Reactions of Vinyl Acetate with Methanol

product ions[a]	$CH_3CO_2CH{=}CH_2$, CH_3OH		$CH_3CO_2CH{=}CH_2$, CD_3OD		$CH_3CO_2CH{=}CH_2$, $CH_3{}^{18}OH$		$CD_3CO_2CH{=}CH_2$, CH_3OH		$CD_3CO_2CH{=}CH_2$, CD_3OD		$CD_3CO_2CH{=}CH_2$, CD_3OD, CH_3CO_2H	
	product	precursor[b,g]	product	precursor	product	precursor	product	precursor	product	precursor	product	precursor
7, 8	87	43	87, 88	43	87	43	90 91[f]	46, 91 46	90 91[f]	46, 91 46	90 91[f]	43, *46*, 91 43, *46*
15	87	43	87, 88	43	87	43	90, 91	46	90, 91	46	87 88	*43*, 46, 88 *43*, 46
2/16	101	87	104	87, 88	103	87	104[c]	90, *91*	107[d]	90, *91*	104[c] 107[d]	87, *88* 90, *91*
3	75	87	78, 79	87, 88	77	87	78, 79	*90*, 91	81, 82	90, 91	78, 79[e], 81, 82	61, 62[e], 90, 91
10	129	87	135	87, 88	129	87	135, 136, 137	90, 91	135, 136, 137	90, 91	132, 135	87, 88, 90, 91
11	117	75	120	78, 79	119	77	123	78, 79	126	81, 82	123 126	78, 79 81, 82

[a] For assigned structures, see Scheme I. [b] Determined by double resonance experiments. Unless otherwise indicated, only the major parent precursor ions are listed. When two or more precursor ions are listed, the m/z value in italic is the major contributor. [c] m/z 105 is also a minor product. [d] m/z 108 is also a minor product. [e] Produced by the reaction of $(AcOH)H^+$, m/z 61, and $(AcOH)D^+$, m/z 62, with methanol-d_4. [f] m/z 92 and 93 are also formed as minor product ions. [g] m/z 31, CH_2OH^+, an acidic ion produced in the EI fragmentation of methanol, contributes to the formation of protonated vinyl acetate. Proton transfer is so rapid that m/z 31 is not detectable after about 50-ms reaction time.

Scheme I



of **11** m/z 117 from unlabeled reactants, m/z 123 from vinyl acetate-d_3 and methanol, and m/z 126 from vinyl acetate-d_3 and CD_3OD (Figure 1A–C). The absence of other ions one unit different in mass confirms there are no reversible H/D exchanges involving methyl groups of the ester or methanol.

Origin of m/z 101. There is little doubt, on the basis of the evidence presented thus far, that product ions **2** (m/z 101) or isomers thereof are *not* formed in the ion chemistry of vinyl acetate and methanol by way of addition intermediates of type **1**. Yet despite evidence of electrocyclic rearrangement of protonated vinyl acetate, **7** ⇄ **8**, neither structure adequately accounts for the formation of ions equivalent to **2**. We have yet to explain why MD^+ (m/z 91) from vinyl acetate-d_3 gives mainly **2** (m/z 104) on reaction with methanol whereas MH^+ (m/z 90) and methanol gives mainly **3** (m/z 78, 79).

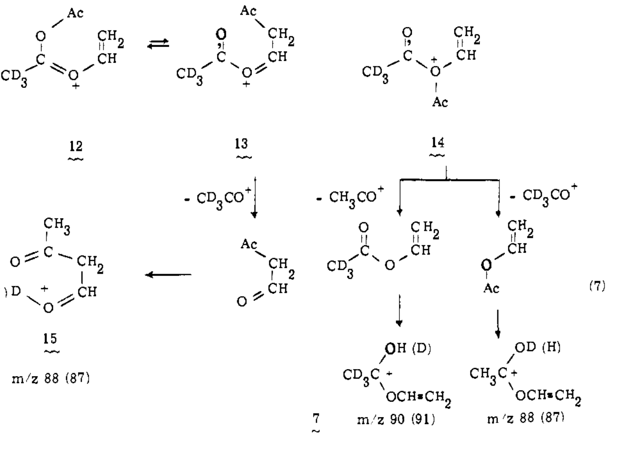
The solution to the problem came unexpectedly from a study of the ion chemistry of vinyl acetate-d_3 with acetic acid. In addition to MH^+ and MD^+ m/z 90 and 91, from vinyl acetate-d_3, ions were formed of m/z 87 and 88 corresponding in composition to MH and MD^+ from *unlabeled* vinyl acetate. The precursor to m/z 87 and 88 was m/z 43 CH_3CO^+, which is both a primary fragment ion (from electron impact cleavage of acetic acid) and a product ion of a displacement reaction with CD_3CO^+. That is,

$$CD_3CO^+ + CH_3CO_2H \rightarrow CH_3CO^+ + CD_3CO_2H$$

These results imply that the acetylium ion m/z 43 reacts with neutral vinyl acetate-d_3 to incorporate the elements of CH_3CO into the products at the expense of the acyl group from the ester, which is eliminated as ketene-d_2 (eq 6).

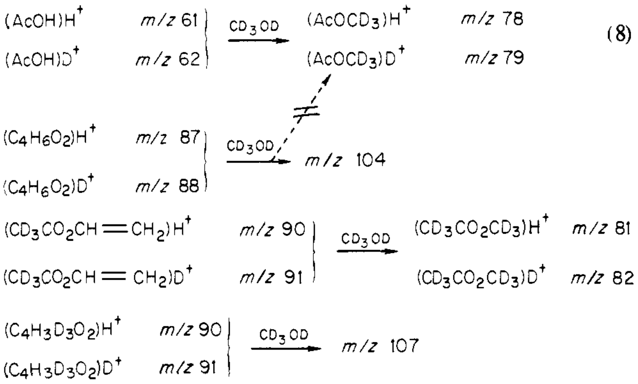
$$CH_3CO^+ + CD_3COOCH{=}CH_2 \rightarrow \underset{m/z\ 88}{CD_2{=}C{=}O + (C_4H_6O_2)D^+} \xrightarrow{RH} \underset{m/z\ 87}{(C_4H_6O_2)H^+} \quad (6)$$

The displacement of ketene-d_2 in reaction 6 can be accounted for in several ways. The three most likely structures of an intermediate complex of CH_3CO^+ with vinyl acetate-d_3 are **12**, **13**, and **14**. Of these, only **13** and **14** appear well suited to lose CD_3CO^+ (or ketene). Most importantly, **14** would be expected to collapse to protonated vinyl acetate **7** whereas **13** could lead to protonated 3-oxobutanal, **15** (m/z 87/88), by the route shown in eq 7.



The key question is whether there are ions of m/z 87 and 88 from the acetate–acetic acid mixture that are indeed structurally different from m/z 90 and 91 produced by proton or deuterium transfer to vinyl acetate-d_3, as implied in eq 7. To probe this question, we investigated the ion chemistry of mixtures of $CD_3CO_2CH{=}CH_2$, CH_3CO_2H, and CD_3OD with the idea of seeing whether m/z 87(88) behaved similarly or differently from m/z 90(91) with CD_3OD. The resulting ICR mass spectrum is complex because of the numerous isotopically labeled ions formed from the three-component system (Figure 1D). Nevertheless, double resonance experiments proved to be very helpful in sorting out which product ions were formed from the variously labeled MH^+/MD^+ ions. Figure 1D and Table I show that the mass spectrum of the three-component mixture is a composite of all product ions expected from $CD_3CO_2CH{=}CH_2 + CD_3OD$ (i.e., m/z 81, 82, 90, 91, 92, 107, 126, 135), and from acetic acid + CD_3OD (i.e., 61, 62, 78, 79, 103, 104). Additional ions (m/z 78, 79, 87, 88, 104, 123, 132) could conceivably come from $CH_3CO_2CH{=}CH_2 + CD_3OD$, and this is the point that must be addressed.

The crucial finding (from double resonance experiments) was that ions m/z 87/88, produced in reaction 6, were *not* the precursors to ions m/z 78 and 79, which came instead from m/z 61/62 (eq 8). Ions m/z 87/88 cannot then have the vinyl acetate structure $(CH_3CO_2CH{=}CH_2)H^+$ m/z 87, or $(CH_3CO_2CH{=}CH_2)D^+$ m/z 88, because the latter ions, when formed by direct H^+/D^+ transfer to vinyl acetate, react rapidly with CD_3OD to give m/z 78/79. Accordingly, $(CD_3CO_2CH{=}CH_2)H^+$ m/z 90 and $(CD_3CO_2CH{=}CH_2)D^+$ m/z 91 led to m/z 81/82 on reaction with CD_3OD, as expected.



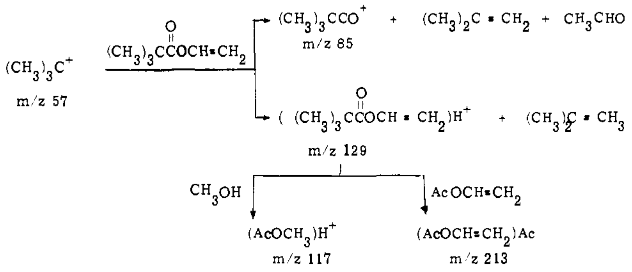
(8)

These results leave no doubt that m/z 87/88 must be structurally different from m/z 90/91 (of vinyl acetate structure) in this three-component mixture. Nevertheless, m/z 87/88 and m/z 90/91 were observed as precursors to m/z 104 and 107, respectively, as anticipated from the methanolysis of vinyl acetate to give product ions equivalent to **2**. We conclude that d_0-, d_3-, and d_6-labeled ions (m/z 101, 104, and 107) equivalent to **2** must actually be formed by a different reaction channel than ions equivalent to **3** (m/z 75, 78/79, 81/82). That is, the pathway given for reactions 2a and 2b must be modified.

A reasonable explanation of these events is given in Scheme I, which shows that the initial collision complex of an acylium cation with neutral vinyl acetate may have some degree of covalency between the acyl oxygen and the terminal vinylic carbon. This complex may also be viewed as interconverting ions **12** and **13**—but the important point is that the complex can partition in at least three ways. One route leads to protonated vinyl acetate **7** or **8**, another to protonated 3-oxobutanal **15**, and the third to displacement of an acylium ion RCO^+. On reaction with methanol, ions **7** or **8** gives the acyl-transfer product **3** (m/z 75), whereas ion **15** could conceivably give **16** m/z 101, which is isomeric with **2**.

Scheme I accounts for the double resonance results summarized in Table I. It may be understood that, in the three-component mixture ($CD_3CO_2CH{=}CH_2$, CD_3OD, CH_3CO_2H), ions of m/z 87/88 have the 3-oxobutanal structure **15**, which lead to d_3-labeled **16** m/z 104. On the other hand, m/z 90/91 can have both the 3-oxobutanal structure *and* the MH^+/MD^+ structure of vinyl acetate-d_3 leading, respectively, to d_6-labeled **16** m/z 107 and labeled **3** m/z 81/82. The scheme also offers an explanation for the puzzling fact that in the ion chemistry of $CD_3CO_2CH{=}CH_2$ with CH_3OH, MH^+ ions (m/z 90) react differently from MD^+ ions (m/z 91). Most of the ions having m/z 91 probably have structure **15** and, on reaction with CH_3OH, lead to m/z 104. On the other hand, most of the ions having m/z 90 are probably formed by direct proton transfer to vinyl acetate-d_3 from acidic fragment ions derived from methanol (i.e., $CH_2{=}OH^+$ m/z 31) and therefore have structure **7** or **8**. These ions react with methanol to give m/z 78/79.

Scheme II



We attempted to verify the proposed reaction channel involving **15** with methanol by preparing 3-oxobutanal in the hope that its ion chemistry with methanol could be studied directly. Unfortunately, we were unsuccessful in isolating the compound as it polymerized rapidly on acidification of solutions of its alkali metal salts. Despite numerous reports in the literature on this compound, it is evidently so reactive that it has not been prepared in a pure state.[7] Its spontaneous condensation–polymerization in neutral-to-acid solution lends some credibility to the proposed condensation of **15** with methanol in the gas phase. We also attempted to generate gaseous ions of structure **15** by EI clevage of 4-hydroxy-2-pentanone, $CH_3COCH_2CH(OH)CH_3$, but the hoped-for fragmentation of a methyl group did not take place. Instead, the molecular ion fragmented mostly by loss of water.

Although direct confirmation of the condensation of **15** with methanol has eluded us, comparable reactions have been documented for ICR generated ions of the type $RCH{=}OR^+$ in the presence of alcohols and thiols.[8] At this point, the proposed scheme remains plausible even though direct proof is lacking.

Reactions of Related Esters. The reactions of methanol with vinyl propanoate, vinyl 2,2-dimethylpropanoate, and isopropenyl acetate were also investigated by ICR techniques. Unlike vinyl acetate, isopropenyl acetate did not react with CH_3OH to form ions equivalent to **2** or **16** although, in other respects, the observed reactions were very similar. Ions of type **3**, **10**, and **11** were formed, presumably by the routes shown in Scheme I ($R = CH_3$, $R' = C(CH_3){=}CH_2$). Incorporation of up to two deuteriums in the vinyl group of product ions was evident in the presence of CD_3OD, which suggests that the protonated isopropenyl ester undergoes hydrogen migration similar to that of **7** or **8** in Scheme I. Less certain is the formation of ions equivalent to **15** by acylium ion attack on the vinyl group. The product of this process would be protonated acetylacetone (m/z 101). However, m/z 101 generated directly from authentic acetylacetone does not condense with methanol to eliminate H_2O. In this respect, the behavior of m/z 101 from acetylacetone is no different from that of m/z 101 from isopropenyl acetate. Unfortunately, though, there is no way to establish whether the ions have the same structure.

The behavior of vinyl propanoate with methanol is entirely comparable to that of vinyl acetate with methanol and includes all the equivalent reaction channels summarized in Scheme I. However, the dehydration pathway to give **16** ($R = CH_3$, $Ac = CH_3CH_2CO$, m/z 117) is relatively minor. Labeling studies with $CH_3{}^{18}OH$ and CD_3OD and unlabeled ester were consistent with

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[7] George, W. O.; Mansell, V. G. *J. Chem. Soc. B* **1968**, 132. Most references to 3-oxobutanal describe the compound as its enolate salts or as the neutral compound in solution. It rapidly oxidizes and polymerizes even in solution (see ref 16).

[8] Pau, J. K.; Kim, J. K.; Caserio, M. C. *J. Am. Chem. Soc.* **1978**, *100*, 3838.

the pathways suggested in Scheme I.

Vinyl 2,2-dimethylpropanoate and methanol gave somewhat different results from the other vinyl esters because the acylium ion $(CH_3)_3CCO^+$, m/z 85, was unreactive. Rather, the major fragment ion was $(CH_3)_3C^+$, m/z 57, from which the subsequent reactions were derived (as summarized in Scheme II). The most abundant product ions were m/z 117 and 213, corresponding to the acylation of both methanol and the neutral ester by the protonated ester, respectively. It is worth noting that the bulky *tert*-butyl group in $(CH_3)_3CCO_2CH{=}CH_2$ evidently does not inhibit the acyl transfer reactions of Scheme II, because these reactions were equally as rapid as the comparable reactions of vinyl acetate.[9] It will be recalled that strong retarding steric effects are manifest in acid-catalyzed esterification and hydrolysis reactions of carboxylic compounds in solution, and these effects have been attributed to steric inhibition in the addition step to produce tetracovalent intermediates.[10] This being so, the *absence* of any noticeable steric effects in the gas-phase reactions is more consistent with acyl transfer by way of acylium ion complexes (eq 1) than it is by way of tetrahedral addition intermediates.

Experimental Section

The ICR instrumentation and techniques have been described previously[8] and employed a pulsed-ion cyclotron resonance spectrometer equipped with multiple inlets and a trapped-ion analyzer cell.[11] Commercially available compounds utilized in this study were purified prior to use until chromatographically pure. Other compounds were prepared as follows.

Vinyl Acetate-*d*$_3$. To a cold slurry (0 °C) of mercuric diacetaldehyde, $Hg(CH_2CHO)_2$[12] (14.3 g, 60 mmol), in 10 mL of 1,2-dimethoxyethane was added CD_3COCl[13] slowly with vigorous stirring (the reaction is quite exothermic). After the mixture was refluxed for 30 min, the product was flash distilled along with the solvent. Fractional distillation gave 3.7 g (88%) of vinyl acetate-d_3 boiling at 72 °C. NMR ($CDCl_3$) δ 4.7 (m, 2 H), 7.2 (m, 1 H). **Vinyl propanoate** was similarly prepared from C_2H_5COCl and $Hg(CH_2CHO)_2$ in tetrahydrofuran in 90% yield: bp 92–93 °C; NMR ($CDCl_3$) δ 1.15 (t, J = 7 Hz, 3 H, CH_3), 2.34 (q, J = 7 Hz, 2 H, CH_2), 4.4–4.9 (m, 2 H, $=CH_2$), 7.0–7.3 (m, 1 H, $=CH$). **Vinyl 2,2-dimethylpropanoate** was likewise prepared from $(CH_3)_3CCOCl$ and $Hg(CH_2CHO)_2$ in 1,2-dimethoxyethane (82% yield; bp 108–109 °C); NMR ($CDCl_3$) δ 1.20 (s, 9 H $(CH_3)_3C$), 4.4–4.95 (m, 2 H, $=CH_2$), 7.0–7.35 (m, 1 H, $=CH-$).

1,1-Divinyloxy-1-methoxyethane (divinyl methyl orthoacetate) was prepared from 1-((2-chloroethyl)oxy)ethanimine hydrochloride $[CH_3C(OCH_2CH_2Cl){=}N^+H_2Cl^-]$, which was obtained in 70% yield from acetonitrile (41 g, 1 mol), 2-chloroethanol (95 g, 1.2 mol), and gaseous HCl (35–36 g, 1 mol) following the procedure of Sah:[14] NMR (CD_3NO_2) δ 2.50 (s, 3 H, CH_3), 3.92 (t, J = 6.5 Hz, 2 H, CH_2Cl), 4.80 (t, J = 6.5 Hz, 2 H, OCH_2), ~11.4 (br d, 2 H, N^+H_2). A mixture of the acetaldimino salt (46 g, 0.3 mol) and anhydrous methanol (90 mL) was stirred at room temperature for 7 days. Ammonium chloride separated and was removed by filtration. Addition of 100 mL of ether caused more NH_4Cl to precipitate. The supernatant liquid was separated and vacuum distilled to give 14 g of trimethyl orthoacetate. The involatile residue was added slowly to a boiling solution of potassium *tert*-butoxide in *tert*-butyl alcohol (1 M in 400 mL). After the mixture was refluxed for 1 h and cooled to room temperature, 800 mL of water was added. Extraction with three 100-mL portions of ether followed by drying over anhydrous Na_2SO_4, evaporation, and fractional distillation gave a fraction, bp 56–62 °C (50 mm) (14 g), which was further purified by preparative GLC to give pure orthoacetate: bp 63–64 °C (50 mm); NMR ($CDCl_3$) δ 1.56 (s, 3 H, CCH_3), 3.33 (s, 3 H, OCH_3), 4.2–4.7 (AB of ABX, J_{AX} = 13.9 Hz, J_{BX} = 6.33 Hz, J_{AB} = 1.14 Hz, 4 H, $=CH_2$), 6.35–6.6 (X of ABX, 2 H, $=CH$).

4-Hydroxy-2-pentanone was prepared according to a literature procedure[15] and had bp 109–111 °C (90 mm) (lit.[15] bp 74–75 °C (18 mm)). **3-Oxobutanal** was prepared by the procedure described by George and Mansell[7] but could not be isolated from the reaction mixture as the pure compound. Condensation trimerization to 1,3,5-triacetylbenzene occurred.[16]

Acknowledgment. We gratefully acknowledge support for this work in part by Grant CHE 7807993 awarded by the National Science Foundation and in part by the donors of the Petroleum Research Foundation, administered by the American Chemical Society.

Registry No. 4, 82190-84-9; $Hg(CH_2CHO)_2$, 82190-85-0; CD_3COCl, 19259-90-6; C_2H_5COCl, 79-03-8; $(CH_3)_3CCOCl$, 3282-30-2; $CH_3C(OCH_2CH_2Cl){=}NH$-4Cl, 82190-86-1; CH_3OH, 67-56-1; CD_3OD, 811-98-3; $CH_3{}^{18}OH$, 5770-05-8; CH_3CO_2H, 64-19-7; vinyl acetate-d_3, 20630-89-1; vinyl propanoate, 105-38-4; vinyl 2,2-dimethylpropanoate, 3377-92-2; acetonitrile, 75-05-8; trimethyl orthoacetate, 1445-45-0; isopropenyl acetate, 108-22-5.

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(9) Rate studies gave k_2 for the methanolysis of protonated vinyl acetate as 6.0×10^{-11} cm^3 s^{-1} molecule^{-1}, of protonated vinyl propanoate as 5.0×10^{-11} cm^3 s^{-1} molecule^{-1}, and of protonated vinyl 2,2-dimethylpropanoate as 8.0×10^{-11} cm^3 s^{-1} molecule^{-1}.

(10) See ref 1a, pp 776–778.

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(13) Prepared from CD_3CO_2H and C_6H_5COCl.

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