# Unimolecular Equilibration of Isomeric Cation Radicals. Mechanism of Decomposition of Ionized Methyl Isobutyrate in the Gas Phase

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**Abstract:** The fragmentation of gaseous cation radicals of methyl isobutyrate has been investigated with the aid of ion cyclotron resonance, collisional activation, and field ionization kinetic techniques and by deuterium and $^{13}C$ labeling and deuterium isotope effect measurements. The results lead to the conclusion that the loss of $CH_3\cdot$ is preceded by a slow hidden hydrogen transfer from a $\beta$-methyl group to the carbonylic oxygen atom, and the resulting ion has the structure of protonated methyl acrylate. The elimination of $C_2H_4$, resulting in the ionized enol of methyl acetate, takes place by three distinct multistep pathways, each involving hydrogen migrations and skeletal rearrangements.

## Introduction

The development of powerful techniques for the investigation of structural and mechanistic characteristics of gas-phase ion reactions such as ion cyclotron resonance (ICR), collisional activation (CA), mass analyzed ion kinetic energy (MIKE), and field ionization kinetic (FIK) spectroscopy, stimulated reinvestigation of numerous fragmentation processes. These techniques together with extensive isotope labeling revealed that many seemingly simple fragmentations may in fact be the result of complicated multistep processes.

The 70-eV mass spectra of isobutyramide and of methyl isobutyrate were reported in the early days of organic mass spectrometry.[2] One noteworthy feature of these tabulated mass spectra is the presence of relatively intense *m/e* 59 (rel abundance (RA) = 26%) and 74 (RA = 2.8%) peaks, respectively. These peaks which represent $[M - C_2H_4]^{+\cdot}$ ions in both cases (confirmed by exact mass measurements) must result from an extensive rearrangement. Another interesting feature of the mass-spectral data of these compounds is the presence of relatively abundant $[M - CH_3]^+$ ions (RA ≈ 26%; $[M - CH_3]^+/[M^{+\cdot}] = 1.13$ for isobutyramide; RA = 15%; $[M - CH_3]^+/[M^{+\cdot}] = 1.34$ for methyl isobutyrate).[2] The high abundance of these ions is surprising for a simple cleavage of a C-C bond $\beta$ to a carbonyl function. For comparison, the loss of a methyl radical from the molecular ion of 2,4-dimethyl-3-pentanone is negligible (RA = 0.28%; $[M - CH_3]^+/[M^{+\cdot}] = 0.054$).[3]

We shall describe here the results of our study of the above two processes, namely, loss of $C_2H_4$ and $CH_3\cdot$ from the molecular ion of methyl isobutyrate.

## Loss of Methyl Radical

The mass-spectral data obtained in the present work at 70 eV for methyl isobutyrate (**1**) reveal that the $[M - CH_3]^+$ ion is one of the most abundant fragments (% $\Sigma_{39}$ = 8.3%, $[M - CH_3]^+/[M^{+\cdot}] = 5.2$). The leaving methyl group originates specifically from the isopropyl group, as shown by deuterium and $^{13}C$ labeling (Table I), both in the fast process taking place in the ion source and in the slow one occurring in the second field-free region of a reverse geometry mass spectrometer.

As stated above the relatively high abundance of the $[M - CH_3]^+$ ion is surprising for a simple cleavage of a carbon-carbon bond $\beta$ to a carbonyl group. Not less surprising is the high intensity of the metastable transition (1% of the normal *m/e* 87 ion measured by defocusing in the first field-free region, 77% of the total unimolecular fragmentation of the molecular ion in the second field-free region measured by the MIKES technique). Much more surprising is the great preference for the loss of $CD_3\cdot$ from methyl isobutyrate-$\beta$-$d_3$ (**6**), in which an equal opportunity exists for the elimination of $CH_3\cdot$ and $CD_3\cdot$. $CD_3\cdot$ is eliminated in this case 2.2 times faster than $CH_3\cdot$ in the ion source and 3.0 times faster (including some hydrogen exchange) in the second field region. This preference cannot be explained in terms of a secondary isotope effect because of its magnitude and direction. Secondary isotope effects are usually much smaller[4]—$k_H/k_D$ is slightly above unity, while here it equals 0.46 for the process occurring in the ion source.

The unusual features of this apparent large inverse isotope effect are consistent with a two-step mechanism for the loss of the methyl radical, shown in Scheme I for **6**.[5] In the rate-determining step a hydrogen atom is transferred from one of the $\beta$-methyl groups to the ionized carbonyl oxygen, thus generating the reactive intermediate A. The subsequent fast radical-induced homolysis gives rise to ion a, which has the structure of protonated methyl acrylate.

In the case of methyl isobutyrate-$\beta$-$d_3$ (**6**) (Scheme I) the rate-determining hydrogen transfer is expected to exhibit a *primary* deuterium isotope effect resulting in preferred formation of intermediate A′ and subsequently in a higher abundance of the *m/e* 87 ion a.

The abundance ratio [ion a]/[ion $a_1$] reflects the magnitude of the primary isotope effect $k_H/k_D$, which equals 2.2 for the process in the ion source and 3.0 for the process in the second field-free region of a reverse geometry mass spectrometer in which the decomposition of ions with lower internal energy is sampled.

The higher abundance of $[M - CH_3]^+$ than that of the $[M - C_2H_5]^+$ ion ($[M - CH_3]^+/[M - C_2H_5]^+ = 3.5$) from the ionized methyl ester of 2-methylbutanoic acid can also be explained by an initial hidden hydrogen transfer. Such a $\beta$-transfer is expected to be faster for the secondary H atom from the methylene than for the primary H atom from the

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**Table I.** Isotope Labeling Data for the Loss of Methyl Radical from the Molecular Ion of Methyl Isobutyrate[a]

| compd | $[M - CH_3]^+$ | $[M - CH_2D]^+$ | $[M - CHD_2]^+$ | $[M - CD_3]^+$ | $[M - {}^{13}CH_3]^+$ |
|---|---|---|---|---|---|
| $(CH_3)_2CHCO_2CH_3$ **1** | 100[b] (100)[c] | | | | |
| $(CH_3)_2CHCO_2CD_3$ **2**[d] | 100 (97) | (3) | | | |
| $(CD_3)_2CHCO_2CH_3$ **3**[d] | 0.3 | 0.9 (1.1) | 7.4[e] (14) | 91.3 (85) | |
| $({}^{13}CH_3)_2CHCO_2CH_3$ **4**[d] | | | | | 100 (100) |
| $({}^{13}CH_3)(CH_3)CHCO_2CH_3$ **5**[d] | (53) | | | | (47) |
| $(CH_3)(CD_3)CHCO_2CH_3$ **6**[e] | 30.4 (25) | 1.3[f] | 2.8[e,f] (9.0) | 65.8 (66) | |

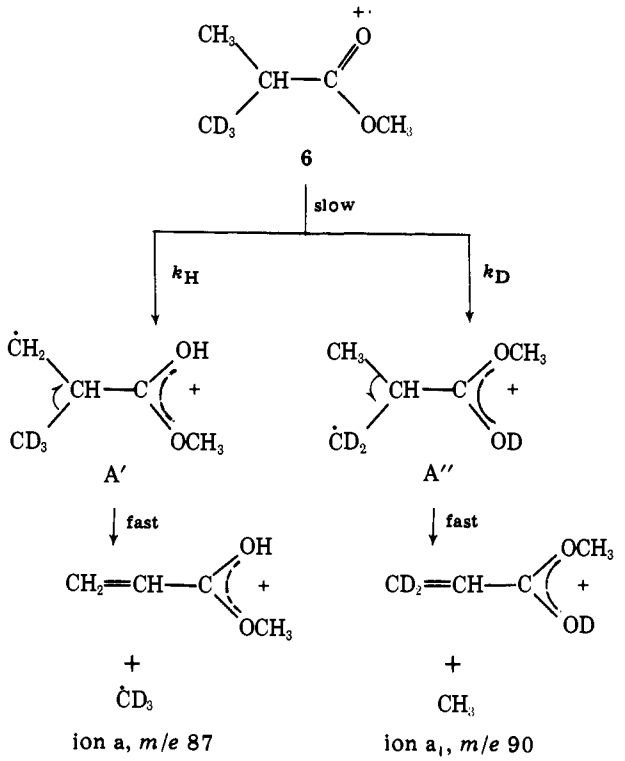
[a] All data are based on total methyl elimination (=100%). [b] Data for the process occurring in the ion source (normal peaks). [c] Data in parentheses: from MIKES measurements. [d] Corrected for noncomplete labeling. [e] Corrected for natural $^{13}C$ isotope contribution. [f] Not corrected for noncomplete labeling of **6**: 5.1% $d_2$ and 1.2% $d_1$.

**Table II.**[a] Collisional Activation Spectra of $C_4H_7O_2^+$ (*m/e* 87)

| CA fragments | **1**[b] $[M - CH_3]^+$ | **7**[b] $[M - C_2H_4 - CH_3]^+$ | **8**[c] $[MH]^+$ | **10**[b] $[M - CH_3]^+$ | **13**[b] $[M - CH_3]^+$ |
|---|---|---|---|---|---|
| 86 | 5.0 | 5.2 | 4.9 | 5.0 | 5.0 |
| 85 | 12 | 11 | 12 | 11 | 12 |
| 72 | 1.9 | 1.9 | 1.7 | 1.8 | 1.6 |
| 69 | 2.9 | 2.9 | 2.7 | 2.9 | 2.5 |
| 59 | 6.2 | 7.5 | 7.3 | 7.2 | 7.1 |
| 55 | 152 | 120 | 153 | 150 | 170 |
| 53 | 6.6 | 6.4 | 6.1 | 6.3 | 6.1 |
| 45 | 20 | 18 | 19 | 19 | 20 |
| 41 | 6.4 | 6.5 | 6.3 | 6.1 | 6.0 |
| 39 | 2.4 | 2.6 | 2.2 | 2.4 | 2.3 |
| 31 | 3.7 | 4.2 | 4.3 | 3.9 | 4.3 |
| 29 | 6.4 | 6.5 | 6.2 | 6.3 | 6.2 |
| 27 | 21 | 21 | 22 | 22 | 21 |
| 15 | 5.6 | 5.9 | 6.1 | 5.8 | 5.4 |

[a] Normalized to $\Sigma_{15}$ = 100% except for the fragment *m/e* 55, which is also produced unimolecularly. [b] Ion *m/e* 87 produced by electron impact ionization (70 eV). [c] Ion *m/e* 87 produced by chemical ionization ($H_3^+$).

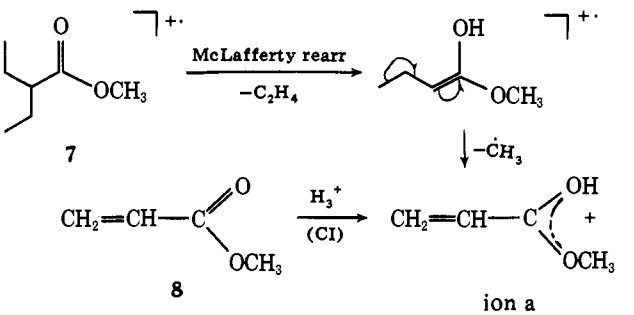
**Scheme I**




$k_H/k_D$ = 2.2 (3.0 by MIKES)

methyl group,[6] leading to a more pronounced loss of a methyl than an ethyl radical.

**Scheme II**




The protonated methyl acrylate structure of ion a is consistent with collisional activation (CA) results summarized in Table II.[7] The CA-induced fragmentation pattern of the *m/e* 87 ions a formed from methyl isobutyrate (**1**) is very similar to that of the *m/e* 87 ions obtained by fragmentation of methyl 2-ethylbutyrate (**7**) and by protonation of methyl acrylate (**8**) with $H_3^+$ under chemical ionization (CI) conditions (Scheme II).

The similarity clearly indicates that an identical structure should be considered for the *m/e* 87 ions obtained from the three different precursors (the same holds for other precursors, vide infra). The relatively abundant *m/e* 27 $[C_2H_3^+]$ ion formed by collision-induced decomposition from the *m/e* 87 ions can be easily explained by the protonated methyl acrylate structure of ion a, but not by the 1-carbomethoxyethyl cation structure b, which would result from a simple $\beta$-cleavage of **1**.

The mechanism suggested in Scheme I for the loss of $CH_3\cdot$ from methyl isobutyrate is also supported by the high intensity of the metastable transition mentioned above, which is indic-

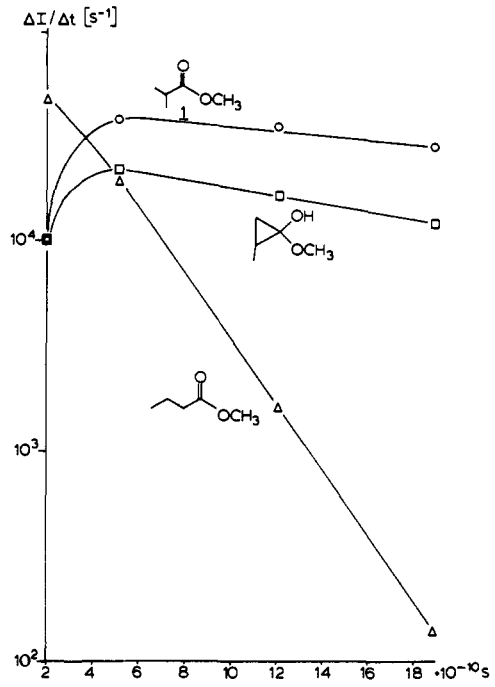
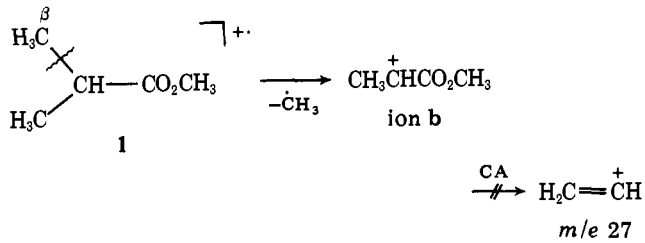



**Figure 1.** Relative rates of formation ($\Delta I/\Delta t$) of $C_4H_7O_2^+[M - CH_3]^+$ as a function of ion lifetime for methyl isobutyrate (**1**), 1-hydroxy-1-methoxy-2-methylcyclopropane (**13**), and methyl butyrate (**10**).




ative of a fragmentation involving rearrangement.[8] The peak shape analysis affords an additional support. Kinetic energy release ($T_{kin}$) in the unimolecular dissociation of metastable ions is usually greater for multistep processes than for simple bond cleavages provided that the dissociation is preceded by a rate-determining isomerization.[9] The measured value $T_{kin}$ = 0.9 kcal/mol seems to be at least an order of magnitude too large for a simple cleavage of a C-C bond;[10] however, it is in the range that is often observed for fragmentations in which stable product ions are generated, or for dissociations occurring via multistep processes.[11]

The results of a field ionization kinetic study (FIK)[12] of methyl isobutyrate (described later in detail) provide a further support for the two-step mechanism. The formation of the $[M - CH_3]^+$ ion is a relatively slow process. This ion is not observed at times shorter than $10^{-10}$ s, which indicates that its rate of formation is too slow for a simple bond cleavage. For comparison, the *m/e* 71 $[M - CH_3O]^+$ ion is very abundant at $2 \times 10^{-11}$ s, which is the shortest time that can be achieved. The relative rate of formation of the $[M - CH_3]^+$ ion as a function of the decomposition time shown in Figure 1 exhibits a maximum at $\sim 5 \times 10^{-10}$ s.

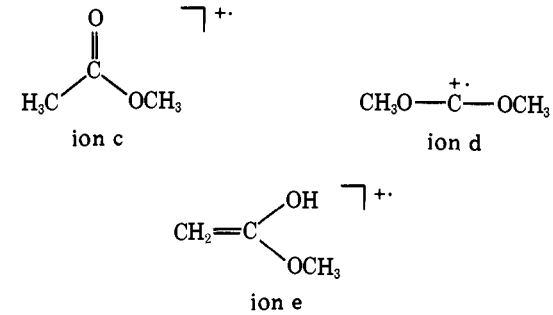
The presence of a maximum indicates that the methyl elimination involves at least two steps. It is interesting to note that the time interval corresponding to the maximum ($\sim 5 \times 10^{-10}$ s) is long even for a rearrangement.[13]

Noteworthy are the results of the time-dependence measurements for the loss of $CH_3\cdot$ and $CD_3\cdot$ from methyl isobutyrate-$\beta$-$d_3$ (**6**). At shortest measurable lifetimes, where energetic ions decompose, no (or a very small) isotope effect is observed: at $1.6 \times 10^{-10}$ s, $[M - CD_3]^+ = 47 \pm 8\%$, $[M - CH_3]^+ = 53 \pm 8\%$; at $4.7 \times 10^{-10}$ s, $[M - CD_3]^+ = 55 \pm 5\%$, $[M - CH_3]^+ = 45 \pm 5\%$. Only at longer times is the isotope effect observed (at $1.3 \times 10^{-6}$ s, $[M - CD_3]^+ = 69 \pm 3\%$, $[M - CH_3]^+ = 31 \pm 3\%$), which again indicates that a hydrogen migration is involved in the methyl elimination from $M^+\cdot$.

The methyl elimination from methyl isobutyrate is one of the few known cases of hidden hydrogen migrations preceding a bond cleavage. In such processes the migrating hydrogen atom originates and remains in the charge-carrying portion of the molecule, and therefore the hydrogen transfer cannot be directly detected by the mass shifts of deuterium-labeled analogues. Only indirect methods, as, for instance, isotope-effect measurement, stereospecificity, or ion structure determination, can reveal the true nature of such processes.[14]

### Elimination of Ethylene

A reasonable starting point for the investigation of the mechanism of elimination of ethylene from the molecular ion of methyl isobutyrate is the determination of the structure of the $[M - C_2H_4]^+\cdot$ ion. Three possible structures were considered in this context: (i) ionized methyl acetate, ion c, which

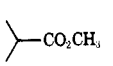
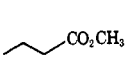
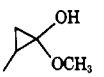
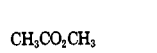
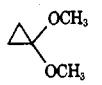



could arise by the migration of a methyl group to the carbonylic carbon atom; (ii) ionized dimethoxymethylene, ion d, by the transfer of a methyl to the carbonylic oxygen atom; (iii) the enolic form of ionized methyl acetate, ion e, which could be formed by a more complicated process. According to information accumulated in previous works[15] the energy of activation for the enol/ketone tautomerization of ions in the gas phase is high, and consequently ions c and e are not expected to be in equilibrium at the internal energies available to many of the nondecomposing ions. It is reasonable to assume that the same is true for ion d.

Ion c can be excluded on the basis of the very low abundance of the acetyl ion in the mass spectrum of methyl isobutyrate (less than 2% of the isobaric $C_3H_7^+$ ion). A positive structure assignment is provided by comparative studies of collisional activation (CA) spectra and of ion–molecule reactions by ion cyclotron resonance (ICR)[16] of $C_3H_6O_2^+\cdot$ ions from various precursors.

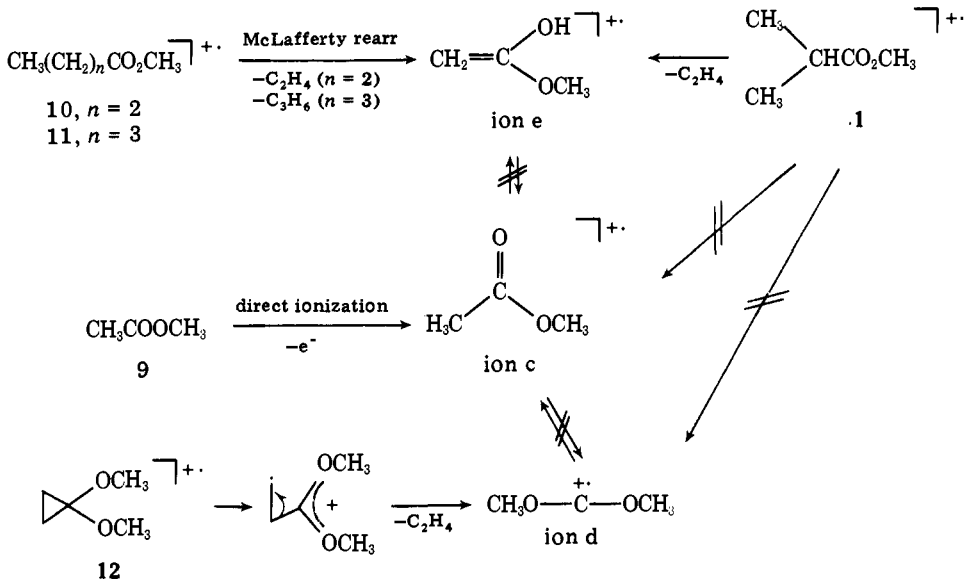
The results of the CA study are summarized in Table III. The CA spectra of the $C_3H_6O_2^+\cdot$ ions obtained from methyl acetate (**9**) (by ionization), methyl butyrate (**10**) and valerate (**11**) (by loss of ethylene or propene via McLafferty rearrangement), and 1,1-dimethoxycyclopropane (**12**) exhibit pronounced differences indicating different nonequilibrating structures. The $C_3H_6O_2^+\cdot$ ion formed from **10** and **11** can be securely assumed to have the enol methyl acetate structure (ion e), which does not equilibrate with ion c obtained by direct ionization of methyl acetate (**9**). The $C_3H_6O_2^+\cdot$ ion formed from 1,1-dimethoxycyclopropane (**12**), which can neither be nor equilibrate with ions c and e, attains presumably structure d (ionized dimethoxymethylene). The CA behavior of the $C_3H_6O_2^+\cdot$ ion obtained from methyl isobutyrate **1** is identical within experimental error with that of methyl butyrate (**10**) and valerate (**11**), leading to the conclusion that they have the enol methyl acetate (ion e) structure (see Scheme III). The data in Table III clearly indicate that the $[M - C_2H_4]^+\cdot$ ion

**Table III.**[a] Collisional Activation Spectra of $C_3H_6O_2^{+\cdot}$ (*m/e* 74)

| CA fragments |  **1** $[M - C_2H_4]^{+\cdot}$ |  **10**[b] $[M - C_2H_4]^{+\cdot}$ |  **13** $[M - C_2H_4]^{+\cdot}$ |  **9** $M^{+\cdot}$ |  **12** $[M - C_2H_4]^{+\cdot}$ |
|---|---|---|---|---|---|
| 73 | 2.5 | 2.2 | 2.4 | 0.6 | 2.1 |
| 60 | 2.0 | 1.8 | 1.9 | 0.7 | |
| 59 | 2.8 | 3.2 | 2.9 | 5.0 | 314 (76) |
| 58 | 8.8 | 8.5 | 8.5 | 3.8 | |
| 45 | 9.1 | 8.9 | 9.2 | 8.7 | 6.2 |
| 44 | 13 | 14 | 13 | 18 | 8.7 |
| 43 | 123 (100) | 216 (100) | 159 (100) | 358 (100) | 122 (24) |
| 42 | 29 | 29 | 28 | 28 | 17 |
| 31 | 15 | 15 | 14 | 16 | 9.7 |
| 30 | 4.8 | 4.7 | 4.9 | 4.3 | 7.5 |
| 29 | 5.3 | 5.0 | 5.2 | 5.7 | 8.6 |
| 28 | | | | | 6.4 |
| 27 | 2.2 | 2.2 | 2.3 | 2.0 | 2.2 |
| 15 | 4.9 | 4.5 | 5.2 | 5.1 | 29 |
| 14 | 1.5 | 1.5 | 1.6 | 1.8 | 2.6 |

[a] Normalized to $\Sigma_{14} = 100\%$ except for fragments which are also produced unimolecularly. The abundances of the pure metastable ion decompositions are given in brackets. [b] The CA spectrum of the $[M - C_3H_6]^{+\cdot}$ ion from methyl valerate (**11**) is identical within experimental error.

**Scheme III**




formed from 1-hydroxy-1-methoxy-2-methylcyclopropane (**13**) also has the enolic structure e.

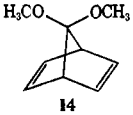
The assignment of structures of ions c, d, and e is supported by some specific collision-induced decompositions. Thus the highly energetic loss of $CH_2$ (*m/e* 60) is relatively pronounced for ions e generated from **1, 10, 11,** and **13,** while this process is of minor importance in the case of ion c and absent in d. The facile loss of $CH_3\cdot$ (*m/e* 59) is indicative for ion d obtained from **12**.

It should be stated that the structure assignments deduced from CA data hold for nondecomposing ions having lifetimes longer than $\sim 10^{-5}$ s.

The structure of ion e formed by the elimination of ethylene from the molecular ion of methyl isobutyrate is further supported by a proton-transfer investigation studied by ICR. The results of proton-transfer reactions of $C_3H_6O_2^{+\cdot}$ ions generated from various precursors to hexadeuterioacetone are listed in Table IV. The measured ratios of the intensities of the double resonance signals for the ion/molecule reaction

$$\underset{m/e\ 74}{C_3H_6O_2^{+\cdot}} + (CD_3)_2CO \rightarrow \underset{m/e\ 65}{(CD_3)_2C{=}\dot{O}H} + C_3H_5O_2\cdot$$

**Table IV.** Measurements of Proton Transfer from $C_3H_6O_2^{+\cdot}$ Ions Generated from Various Precursors to Hexadeuterioacetone[a]

| source of $C_3H_6O_2^{+\cdot}$ | partial pressure, Torr[b] | rel $dk/dE$ values[c,d] |
|---|---|---|
| $CH_3CO_2CH_3$ (**9**) | $2.0 \times 10^{-6}$ | 0.017 |
| $CH_3(CH_2)_2CO_2CH_3$ (**10**) | $6.0 \times 10^{-6}$ | 0.021 |
| $CH_3(CH_2)_3CO_2CH_3$ (**11**) | $1.6 \times 10^{-6}$ | 0.022 |
| $CH_3(CH_2)_4CO_2CH_3$ (**15**) | $1.5 \times 10^{-6}$ | 0.019 |
|  **14** | $1.4 \times 10^{-6}$ | 0.000 |
| $(CH_3)_2CHCO_2CH_3$ (**1**) | $6.0 \times 10^{-6}$ | 0.018 |

[a] Electron energy 15 eV. [b] Partial pressure of hexadeuterioacetone in all measurements was $0.5 \times 10^{-6}$ Torr. [c] These were obtained from the (negative) double resonance to single resonance signal intensity ratio. The double resonance intensity was measured for proton transfer from the $C_3H_6O_2^{+\cdot}$ ion to $(CD_3)_2CO$. [d] Estimated error $\lesssim 20\%$.

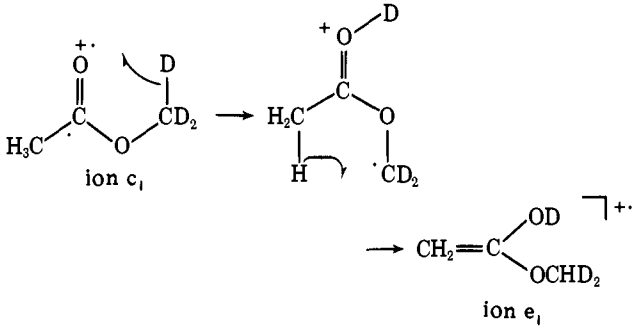
and the intensities of the *m/e* 74 peaks in the single resonance spectra are proportional to the variation of the rate constant

**Table V.** Relative $dk/dE$ Values of Proton Transfer from $C_3H_6O_2^{+\cdot}$ for Several Bases[a]

| base[b] | compd $CH_3COOCH_3$ **9** | compd $CH_3(CH_2)_2COOCH_3$ **10** |
|---|---|---|
| $(CD_3)_2CO$ | 0.017 | 0.021 |
| c-$C_3H_5CN$ | 0.027 | 0.024 |
| $CH_3(CH_2)_3CN$ | 0.018 | 0.018 |
| $CD_3OCD_3$ | 0.003 | −0.002[c] |

[a] These were obtained from the (negative) double resonance to single resonance signal intensity ratio. Error ≤20%. [b] Basicity decreases in the order $(CD_3)_2CO$ > c-$C_3H_5CN$ > $CH_3(CH_2)_3CN$ > $CD_3OCD_3$. [c] Positive double resonance signal.

Scheme IV



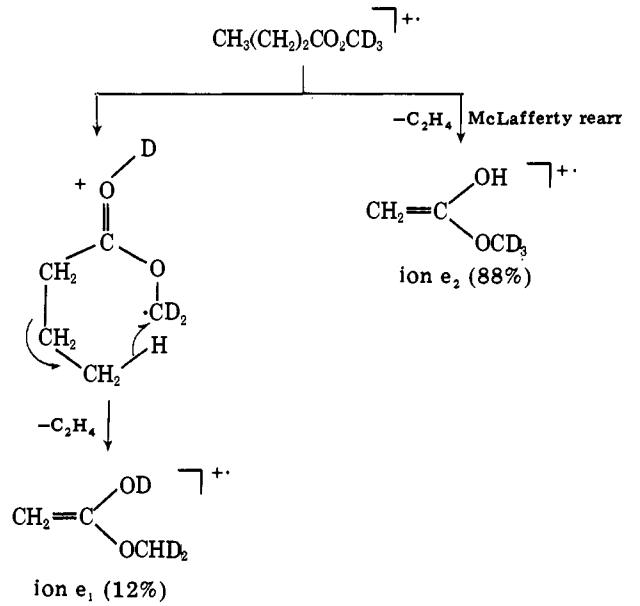

of this reaction with the translational energy of the reactant ions ($dk/dE$).

These values are identical within experimental error for the $C_3H_6O_2^{+\cdot}$ ions formed from methyl acetate, butyrate, valerate, caproate, and isobutyrate, but no proton transfer was observed for the $C_3H_6O_2^{+\cdot}$ ion formed from 7,7-dimethoxynorbornadiene (**14**). The latter ion obtained from **14** has undoubtedly the dimethoxymethylene structure (ion d). The distinct difference between methyl isobutyrate (**1**) and **14** clearly shows that the $C_3H_6O_2^{+\cdot}$ ion obtained from **1** cannot have the structure of ion d. The data of Table IV cannot, however, differentiate between ions c and e. No significant difference could be detected in their rates of proton transfer to other bases (see Table V).

The similarity of the behavior of the $C_3H_6O_2^{+\cdot}$ ion obtained from methyl acetate and the $C_3H_6O_2^{+\cdot}$ formed by the McLafferty rearrangement from methyl butyrate, valerate, caproate, and isobutyrate raises the question whether ions c and e are in equilibrium under ICR conditions where ions of higher internal energy are involved compared with CA. This problem has been solved by studying the proton and deuteron transfer reactions of methyl-$d_3$ acetate and butyrate. Methyl-$d_3$ acetate exhibits an exclusive transfer of $D^+$ to hexadeuterioacetone. This behavior clearly shows that no enolization of ion c occurs via a 1,3-hydrogen shift. It can be suggested that either ion c is an efficient protonating reagent, comparable in its rate with ion e, or ion c may undergo enolization by a two-step mechanism shown in Scheme IV.[17] The *m/e* 77 ions formed from methyl-$d_3$ butyrate transfer ~88% $H^+$ and ~12% $D^+$ to hexadeuterioacetone. The transfer of $H^+$ can be easily explained by the presence of ion $e_2$ formed by the McLafferty rearrangement. The transfer of $D^+$ shows that *m/e* 77 ions having a structure different from $e_2$ are also formed from methyl-$d_3$ butyrate. A possible pathway is shown in Scheme V.

Two possible structures exist for the neutral particle $C_2H_4$, namely, ethylene and ethylidene (methylcarbene). The appearance energy calculated for the reaction **1** → ion e + $CH_2{=}CH_2 + e^-$ is 234.5 kcal/mol:[17b] AP(ion e) = $\Delta H_f°$(ion e) + $\Delta H_f°(CH_2{=}CH_2) - \Delta H_f°$(**1**) = 110 + 12.5 − (−112) = 234.5 kcal/mol. The appearance energy calculated for the alternative reaction **1** → ion e + $CH_3CH{:} + e^-$ is at least 308 kcal/mol [$\Delta H_f°(CH_3CH{:})$ = 86 kcal/mol].[18] The measured appearance potential of ion e from methyl isobutyrate of 258 kcal/mol indicates that ethylene is formed in this process.

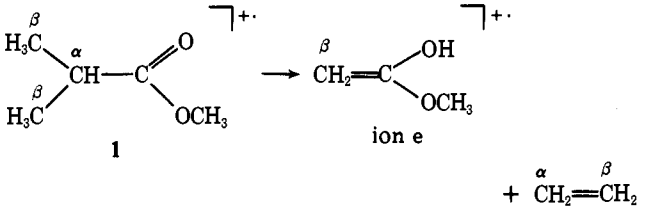
Scheme V




The question that remains is the detailed mechanism of this fragmentation. Extensive deuterium and $^{13}C$ labeling has been employed to solve it.

### Deuterium- and $^{13}C$-Labeling Results

The results of the labeling study are summarized in Table VI. The two $^{13}C$-labeled compounds **4** and **5** show that no carbon atom scrambling occurs in the course of the ethylene elimination. The α-C atom is completely lost with the ethylene, and consequently one of the β-carbon atoms is transferred to the carbonyl group and becomes C-2 in the resulting ion e.




The data presented in Table VI for the deuterium-labeled analogues clearly show that no hydrogen randomization takes place in this process. The abundance data for methyl isobutyrate-β-$d_3$ (**6**) eliminate the possibility of a β-methyl transfer group to the carbonyl group: 89% of ions e (85% in the second field-free region) are formed in this case by a transfer of two hydrogen atoms from one β-methyl group and one hydrogen from the other, together with one β-carbon atom. This hydrogen/deuterium distribution suggests that the major pathway (the labeling data show there must be more than one) starts with a transfer of one hydrogen atom from one of the β-methyl groups to the carbonyl function. Such a hydrogen transfer has been previously suggested as the first step in the formation of $[M - CH_3]^+$ (see Scheme I). A possible sequence of events leading to the elimination of ethylene is presented in Scheme VI, pathway I (a discussion concerning the reversibility of the individual isomerization steps is given later).

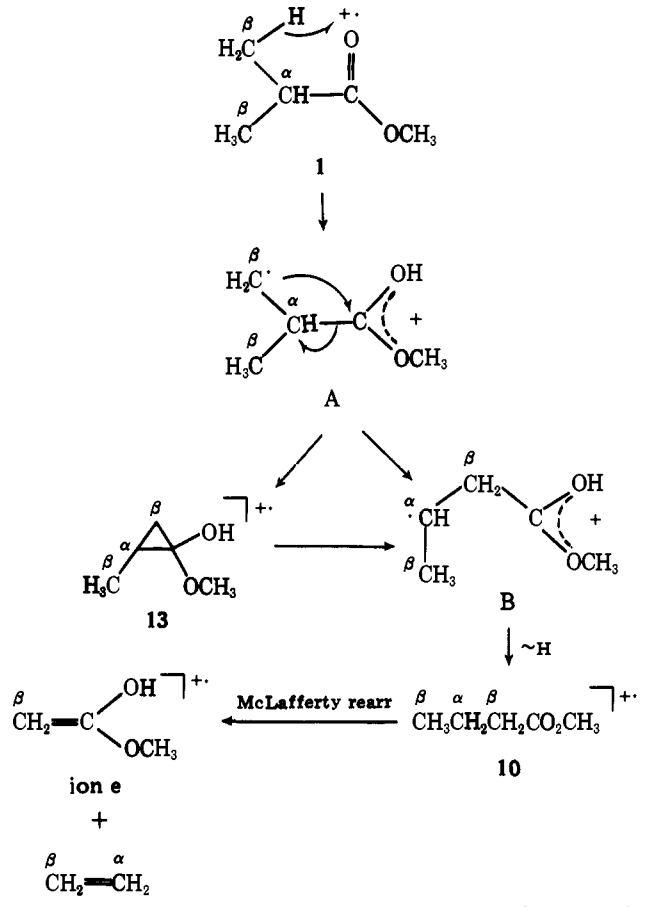
As stated above the substituted cyclopropane **13** gives rise to an $[M - C_2H_4]^{+\cdot}$ ion which has also the enolic structure e. The data in Table II show that **13** also loses $CH_3\cdot$ leading to ion a. These results indicate that **13** can be either an intermediate in the process A → **13** → B or an additional precursor of

**Table VI.** Abundance Data for the Elimination of Ethylene from Isotopically Labeled Methyl Isobutyrates

| compd | neutral fragment | obsd abundance[a] | | | calcd for randomization of | | |
|---|---|---|---|---|---|---|---|
| | | *m/e* | ion source[b] | 2nd FFR[c] | 10-H | 7-H[d] | 6-H[e] |
| $(^{13}CH_3)_2CHCO_2CH_3$ (**4**) | $^{13}CCH_4$ | 75 | 100 | 100 | | | |
| $(^{13}CH_3)(CH_3)CHCO_2CH_3$ (**5**) | $^{13}CCH_4$ | 74 | | 51 | | | |
| | $C_2H_4$ | 75 | | 49 | | | |
| $(CH_3)_2CHCO_2CD_3$ (**2**) | $C_2HD_3$ | 74 | 0 | 0 | 3.3 | | |
| | $C_2H_2D_2$ | 75 | 0 | 2 | 30 | | |
| | $C_2H_3D$ | 76 | 10 | 22 | 50 | | |
| | $C_2H_4$ | 77 | 90 | 76 | 16.7 | | |
| $(CD_3)_2CHCO_2CH_3$ (**3**) | $C_2D_4$ | 76 | 6 | 10 | | 42.9 | 0 |
| | $C_2HD_3$ | 77 | 78 | 74 | | 57.1 | 100 |
| | $C_2H_2D_2$ | 78 | 16 | 16 | | 0 | 0 |
| $(CH_3)_2CDCO_2CH_3$ (**16**) | $C_2H_3D$ | 74 | 85 | 75 | | 57.1 | 100 |
| | $C_2H_4$ | 75 | 15 | 25 | | 42.9 | 0 |
| $(CH_3)(CD_3)CHCO_2CH_3$ (**6**) | $C_2HD_3$ | 74 | 2.2 | 5 | 3.3 | 11.4 | 5 |
| | $C_2H_2D_2$ | 75 | 63 | 63 | 30 | 51.4 | 45 |
| | $C_2H_3D$ | 76 | 26 | 22 | 50 | 34.3 | 45 |
| | $C_2H_4$ | 77 | 9 | 10 | 16.7 | 3.9 | 5 |

[a] Percent of the total loss of ethylene. [b] Measured from the intensities of normal peaks (Varian MAT 711). [c] Measured by MIKES technique (Varian MAT 311 A). [d] Seven hydrogen atoms of the isopropyl group ($\alpha$ and $\beta$). [e] Six hydrogen atoms of the two $\beta$-methyl groups.

**Scheme VI.** Pathway I




the intermediate B. Both possibilities are shown in Scheme VI. MNDO calculations,[19] however, suggest that substituted cyclopropane cation radicals do not exist generally in potential minima. Consequently it is more likely that ionized **13** is an additional precursor of B rather than a true intermediate. In the following discussion only this possibility will be considered.

If pathway I in Scheme VI were the only route to the formation of ion e, methyl isobutyrate-$\beta$-$d_3$ (**6**) would yield only two ions: *m/e* 75 (loss of $C_2H_2D_2$) and 76 (loss of $C_2H_3D$). The abundance ratio of these two fragments would be expected to be 2.2 for the reaction occurring in the ion source and 3.0 for that in the second field-free region (based on the isotope effect, Scheme I) if the hydrogen transfer is the rate-determining step in this process too. The observed ratio (Table VI: 2.42 for normal and 2.86 for metastable ions) is not far from the expected value, but the presence of the *m/e* 77 and 74 ions, containing $D_3$ and $D_0$, indicates the operation of another pathway or more.

In methyl-$d_3$ isobutyrate (**2**) 10% of ions e generated in the ion source miss one deuterium atom from the methoxy group which has been lost with the ethylene. Analogously methyl isobutyrate-$d_6$ (**3**), which contains only one hydrogen atom in the isopropyl moiety, partially (16%) loses two hydrogen atoms with the neutral ethylene affording the *m/e* 78 ion (Table VI). These data show that there must exist a minor pathway II for the elimination of ethylene which involves a transfer of a hydrogen atom from the methoxyl to the isopropyl part of the molecule. This transfer may take place as the first step of the fragmentation with the intermediacy of the hydrogen transfer to the carbonylic oxygen (Scheme VII; compare also with the first step in Schemes IV and V).

The abundance of the *m/e* 78 ions in the mass spectrum of methyl isobutyrate-$d_6$ (**3**) which must be formed by a mechanism involving an H transfer from the methoxyl group is 16%. The analogous process yields 10% of the *m/e* 76 ion from **2**. These data show that the exchange of H by D in the methoxyl group results in a significant positive isotope effect ($k_H/k_D$ = 1.6). This result supports the suggested transfer in Scheme VII (pathway II).

In methyl isobutyrate-$d_6$ (**3**) the formation of the *m/e* 78 ion by pathway II involves the transfer of a hydrogen from the methoxyl to the isopropyl moiety, and a back-transfer of a hydrogen atom from one of the *$\beta$-methyl groups*. A back-transfer from the $\alpha$-carbon atom would be indistinguishable in this case, as it would results in an *m/e* 77 ion which is also formed by the major pathway I. In fact, the label distribution in methyl isobutyrate-$\alpha$-$d_1$ (**16**) (see Table VI) indicates the existence of an additional channel to ion e: the *m/e* 75 ion (15%) must result from the transfer of the deuterium atom from the $\alpha$ position to the methoxycarbonyl part of the molecular ion. This minor pathway III may be formulated as an alternative decomposition channel of the intermediate C as shown in Scheme VII. It cannot be excluded, however, that pathway III actually represents a partial H/D scrambling in any of the intermediates in the major pathway I (Scheme VI). Both pathways II and III lead to the *m/e* 76 ion in **2** (10%).

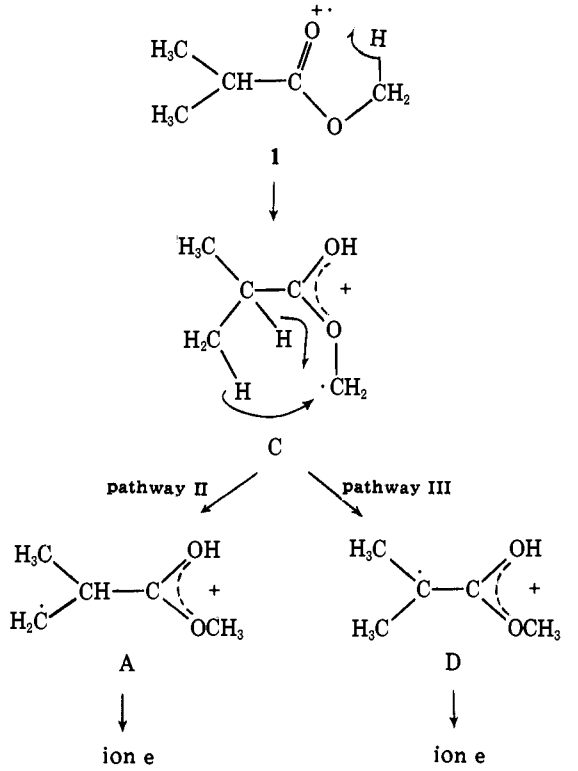
The *m/e* 78 ion in the mass spectrum of **3** (16%) is formed only by pathway II, and the *m/e* 75 ion in **16** (15%) only by pathway III. Thus the two minor pathways constitute 31% of

**Table VII.** Calculated and Observed Distribution of Labeled Ions e Formed from Methyl Isobutyrate-$\beta$-$d_3$ (**6**) under Electron Impact

| | calcd for pathway | | | | obsd | |
|---|---|---|---|---|---|---|
| *m/e* | I | II | III | total | ion source[a] | 2nd FFR[b] |
| 74 | 0 | 0 | 0.8 | 0.8 | 2.2 | 5 |
| 75 | 47 | 8 | 6.7 | 61.7 | 63 | 63 |
| 76 | 22 | 0 | 6.7 | 28.7 | 26 | 22 |
| 77 | 0 | 8 | 0.8 | 8.8 | 9 | 10 |

[a] Normal ions measured with Varian MAT 711. Not corrected for the contribution of $d_2$ and $d_1$ contaminants (5.5 and 1.2%, respectively). [b] Measured by MIKES technique with Varian MAT 311 A.

**Scheme VII**



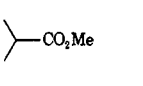
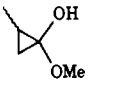
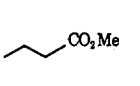

the total elimination of ethylene for compounds containing $OCH_3$, but only 10% for $OCD_3$. The isotope effect is therefore $k_H/k_D = 3.1$.

The three pathways I–III for the elimination of ethylene will now be employed in the explanation of the deuterium distribution data of methyl isobutyrate-$\beta$-$d_3$ (**6**). About 16% of the molecular ions are expected to undergo this process by pathway II and 15% by pathway III. Therefore only 69% will decompose by pathway I shown in Scheme VI, and, since the abundance ratio of ions *m/e* 75/76 is expected to be 2.2 due to the isotope effect, the abundances of these ions should be *m/e* 75 = 47% and *m/e* 76 = 22%. The fragmentation of 16% of the molecular ions by pathway II (Scheme VII) should result in ~8% of the *m/e* 75 and also ~8% of the *m/e* 77 ion. If pathway III occurs as shown in Scheme VII, the intermediate D′ (formed from **6** by pathway III) may be assumed to undergo scrambling of the six $\beta$-methyl hydrogen and deuterium atoms[20] resulting in the distribution shown in Scheme VIII. A similar distribution would be obtained if pathway III represents a partial H/D scrambling in the course of pathway I. The sum of the contributions of the three pathways summarized in Table VII is very close to the experimentally observed distribution of deuterium in the ions e formed from **6**.

### Detailed Mechanism of Decomposition of Methyl Isobutyrate

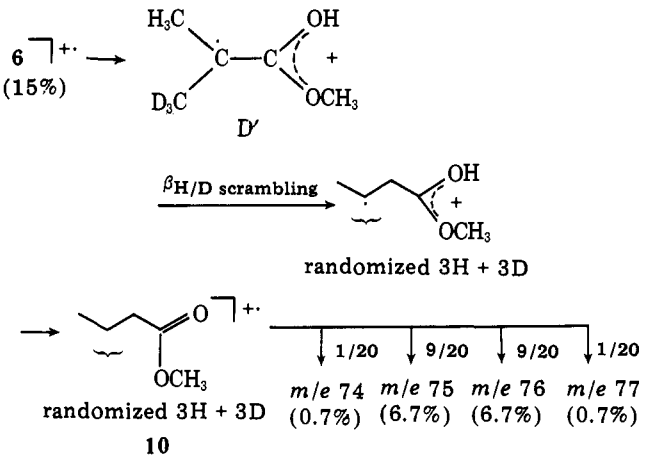
The multistep mechanism for the elimination of ethylene from ionized methyl isobutyrate (**1**) involves a number of intermediates in the three pathways (Schemes VI and VII). The

**Table VIII.**[a] Collisional Activation Spectra of $C_5H_{10}O_2^{+\cdot}$ (*m/e* 102)

| CA fragments |  **1** |  **13** |  **10** |
|---|---|---|---|
| 101 | 12 | 11 | 13 |
| 100 | 1.6 | 1.5 | 1.2 |
| 87[b] | 250 (74) | 218 (75) | 164 (42) |
| 74[b] | 43 (25) | 46 (26) | 322 (57) |
| 71 | 6.0 | 5.9 | 4.8 |
| 70[b] | 8.0 (1.0) | 7.4 (1.0) | 9.5 (1.5) |
| 69 | 6.0 | 6.3 | 6.0 |
| 59 | 10 | 10 | 9.5 |
| 55 | 13 | 13 | 11 |
| 53 | 2.8 | 2.6 | 2.4 |
| 45 | 8.0 | 8.5 | 7.1 |
| 43 | 10 | 11 | 16 |
| 41 | 12 | 12 | 10 |
| 39 | 5.6 | 5.2 | 4.8 |
| 31 | 2.4 | 2.2 | 3.6 |
| 29 | 2.8 | 3.0 | 2.4 |
| 27 | 5.2 | 4.8 | 4.8 |
| 15 | 3.2 | 3.7 | 3.6 |

[a] See footnote *a*, Table IV. [b] Fragments are also produced unimolecularly (MI data are given in brackets).

**Scheme VIII**




results of the CA and MIKES measurements of the molecular ions of **1** and **13** (Table VIII) show great similarity in their behavior; consequently it can be concluded that these ions give rise to one or more common intermediates. It is also of interest to note here the great similarity in the CA data of the $[M - CH_3]^+$ (Table II) and the $[M - C_2H_4]^{+\cdot}$ ions (Table III) of **1** and **13**. All these data lead to the conclusion that an equilibrium exists between the intermediates A and B, the structures of which have been given in Scheme VI.

The different CA data in Table VIII for **10** indicate, however, that the nondecomposing as well as the metastable molecular ion of **10** isomerizes only partially and therefore an equilibrium B $\rightleftarrows$ **10** (Scheme VI) is not attained.

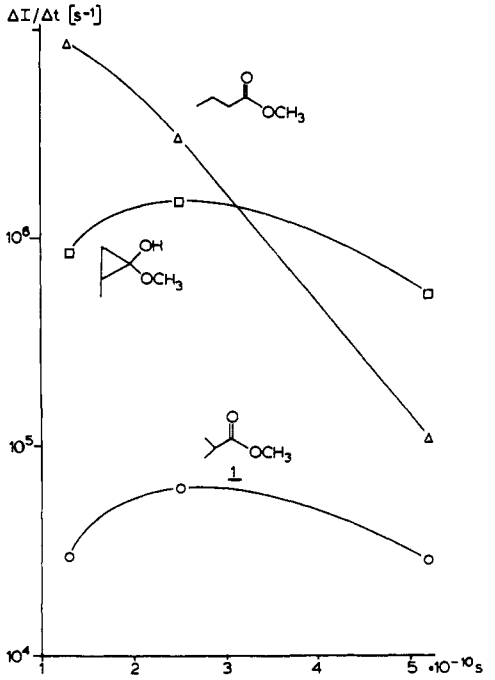



**Figure 2.** Relative rates of formation ($\Delta I/\Delta t$) of $C_3H_6O_2^{+\cdot}$[M − $C_2H_4$]$^{+\cdot}$ as a function of ion lifetime for methyl isobutyrate (**1**), 1-hydroxy-1-methoxy-2-methylcyclopropane (**13**), and methyl butyrate (**10**).

A more detailed picture is obtained from the analysis of the results of the field ionization kinetic study of the decomposing molecular ions. The relative rate of formation of ion e from methyl isobutyrate (**1**) and from **13** exhibits a maximum at ~2.5 × $10^{-10}$ s (Figure 2), which again indicates that the process consists of at least two steps. A decrease in the rate of ethylene elimination by a factor of 2.9 × $10^4$ for **1** and 8.6 × $10^5$ for **13** is observed in the time interval from 1.2 × $10^{-10}$ to 7 × $10^{-6}$ s. This decrease is relatively small compared with the McLafferty rearrangement of ionized methyl *n*-butyrate (**10**), for which the factor is ~$10^7$. The elimination of ethylene from ionized **1** and **13** must therefore involve a slow step in contrast to **10**.

Most informative for the evaluation of the fragmentation mechanism is the comparison of the time resolved field ionization mass spectra of **1, 10,** and **13** shown in Figure 3. At 1.6 × $10^{-10}$ s the three isomeric compounds exhibit an entirely different behavior. Methyl *n*-butyrate (**10**) fragments almost exclusively (98%) by the elimination of ethylene (McLafferty rearrangement). This fragmentation occurs to a very small extent (3.6%) in methyl isobutyrate (**1**), which exhibits a very abundant (94%) [M − $CH_3O$]$^+$ ion. **13** gives rise to both ions: [M − $C_2H_4$]$^{+\cdot}$ (76%) and [M − $OCH_3$]$^+$ (22%). The loss of a methyl radical is of little importance in all the three compounds. A dramatic change is observed in the behavior of **1** by increasing the molecular ion lifetime to 3.8 × $10^{-10}$ s. ([M − $CH_3O$]$^+$ drops from 94% to 18%, while [M − $C_2H_4$]$^{+\cdot}$ ion e and [M − $CH_3$]$^+$ ion a rise from 3.6 and 2.3% to 28 and 54%, respectively.) At 1.2 × $10^{-9}$ s the abundance of [M − $CH_3O$]$^+$ is already low for all the three isomers, but the other two ions a and e in **1** still exhibit an entirely different abundance relationship than in **10** and **13**. The different behavior cannot be attributed to different energy distribution function for the three compounds, because heating of the emitter is expected to result in a nearly equal energy distribution for the reacting isomers. At 1.3 × $10^{-6}$ s the field ionization mass spectra of **1** and **13** exhibit great similarity, and at 7.1 × $10^{-6}$ s the behavior of all the three isomers becomes identical within the experimental error.

The above results lead to the conclusion that under FIK conditions at 7.1 × $10^{-6}$ s a complete equilibrium as shown in Scheme IX is attained.

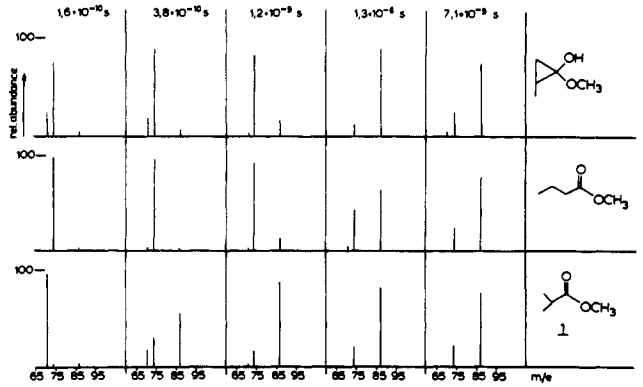
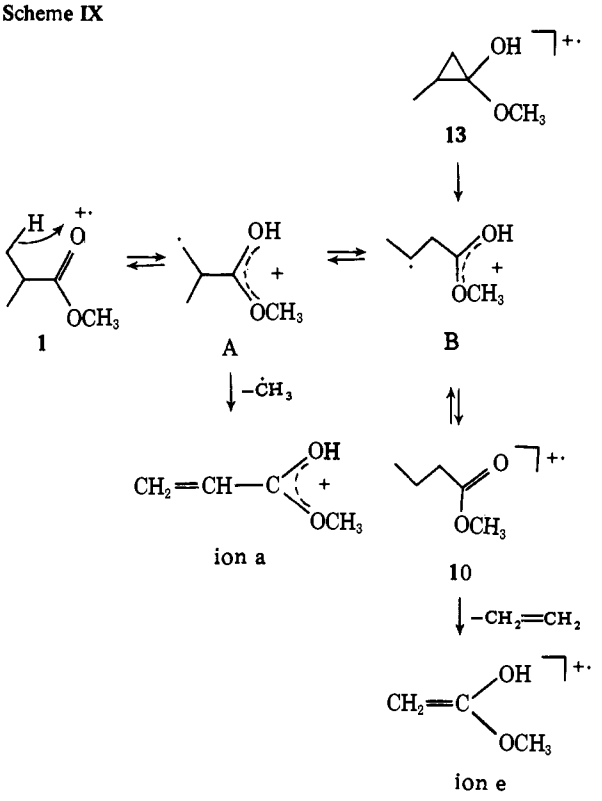



**Figure 3.** Partial field ionization mass spectra as function of the ion lifetime for methyl isobutyrate (**1**), 1-hydroxy-2-methoxy-2-methylcyclopropane (**13**), and methyl butyrate (**10**).

**Scheme IX**




It has been stated above that the CA and MIKE data (Table VIII) showed that **1** and **13** lead to common intermediates (A,B), whereas only a partial isomerization of **10** to A and B occurs. In addition, the data revealed that for **1** and **13** ionized by electron impact, $CH_3$ loss is the preferred process (~75 vs. 25% for $C_2H_4$ elimination) at lifetimes $t \sim 10^{-5}$ s (metastable ions); for ionized **10**, however, the elimination of $C_2H_4$ is dominant over $CH_3$ loss (57 vs. 42%). Under the conditions of FIK the prevailing dissociation pathway at longest ion lifetime ($t \sim 7.1 \times 10^{-6}$ s) is for all three precursors the formation of *m/e* 87 ($CH_3$ loss, Figure 3). Whether these remarkable differences in reactivities of ions of comparable lifetime ($t \sim 10^{-5}$ s) produced, however, by different ionization methods under different energetic conditions (electron impact vs. field ionization (using heated emitters)) indicate the existence of state-specific reactions of molecular ions cannot be unequivocally decided. Alternative explanations, e.g., the operation of entropic effects, are also possible, but presumably less likely.

## Experimental Section

**Materials. Methyl 2-methyl-$d_3$-propanoate-3,3,3-$d_3$ (3),[21] 1,1-dimethoxycyclopropane (12),[22] and 1-hydroxy-1-methoxy-2-methylcyclopropane (13)[23]** were synthesized following literature procedures. **7,7-Dimethoxynorbornadiene (14)** was kindly supplied by Professor R. W. Hoffmann, Marburg.

**Methyl-$d_3$ 2-methylpropanoate (2)** was prepared by adding methanol-$d_4$ to isobutyric acid chloride: $d_3$, 94%; $d_2$, 6%; $d_1$, 0.1%.

**Methyl [2-$^{13}$C]Methyl[3-$^{13}$C]propanoate (4).** Di($^{13}$C-methyl)malonic acid diethyl ester was synthesized by reacting 2 equiv of [$^{13}$C]methyl iodide (91% $^{13}$C content) with 1 equiv of diethyl malonate in the presence of 2.5 equiv of sodium ethylate in ethanol. Hydrolysis (KOH in EtOH/$H_2O$) followed by decarboxylation (heating the crystalline acid at 180 °C) yielded the [2-$^{13}$C]methyl[3-$^{13}$C]propanoic acid. Esterification with diazomethane gave the ester **4**: $^{13}C_2$, 81%; $^{13}C_1$, 18%; $^{13}C_0$, 1%.

**Methyl 2-Methylpropanoate-3,3,3-$d_3$ (6).** Propionic acid dianion sodium lithium salt was obtained following the literature procedure.[2] The addition of 1 equiv of methyl-$d_3$ iodide at 0 °C followed by diazomethane esterification yielded **6**: $d_3$, 93%; $d_2$, 5.5%; $d_1$, 1.2%; $d_0$, 0.1%.

**Methyl 2-Methylpropanoate-2-$d_1$ (16).** 2-Methylpropanoic-2-$d_1$ acid was prepared by acid-catalyzed ($D_3PO_4$–DCl obtained from $PCl_5$ and $D_2O$) exchange of isobutyric acid (four times). Transformation of the acid to the corresponding chloride ($SOCl_2$) followed by the addition of methanol resulted in **16**: $d_1$, 81%; $d_0$, 19%.

**Instrumental Details.** The high- and low-resolution mass spectra and the kinetic energy release were measured with a Varian MAT 711 mass spectrometer. Collisional activation (CA) spectra were obtained with a self-constructed double-focusing mass spectrometer of reversed geometry (magnetic sector preceding electrostatic field) equipped with a collision cell in front of the energy resolving slit (acceleration voltage, 8 kV; electron energy, 70 eV; electron beam, 20 μA; source temperature, ca. 150 °C). Samples were introduced via the gas inlet system kept at room temperature. Collisional activation spectra were taken using the following procedure. The magnetic and electrostatic fields were adjusted to pass the ions of interest. The target gas (helium) was then introduced into the collision cell via a variable leak valve and the leak rate increased until the precursor ion intensity decreased to 1/3 of its original value due to scattering and decomposition ($\sim 5 \times 10^{-5}$ Torr). CA spectra were obtained by scanning the electrostatic sector potential, recorded on an XY recorder and normalized to the sum of all fragments. Only peak heights were measured and the abundances were not corrected for reduced multiplier response. All CA spectra are the means of at least three measurements. The reproducibility was ±3 to ±8% depending on the abundance of the precursors. The unimolecular decompositions of metastable ions were recorded using the same technique without adding collision gas.

An instrument of identical geometry, but equipped with a nonfocusing field ionization source, was used for ion lifetime measurements. A potential of +7 kV was applied to the emitter, a tungsten wire of 8-μA diameter briefly activated with benzonitrile.[25] The slotted counterelectrode at a potential of −3.5 kV was placed 2 mm from the emitter. The decays of the molecular ions between the emitter and the counterelectrode ($\sim 10^{-11}$ to $2 \times 10^{-8}$ s) were determined by adjusting the electrostatic analyzer potential to transmit the molecular ion, increasing the acceleration voltage stepwise and scanning the magnet each time over the mass range of interest. Using this procedure it is possible to obtain complete mass spectra as a function of ion lifetime. For the registration of the ions a multichannel analyzer was used. The data of 80 individual scans were stored and the signal intensities were obtained by integrating the peak areas. Lifetime measurements in the time interval $10^{-8}$–$10^{-6}$ s were performed as described previously.[26] Abundances of metastable ions were corrected for reduced multiplier response. To reduce the influence of the high electric field on the internal energy distribution of the molecular ion, all measurements were carried out with a heated emitter (~700 °C) so that the internal energy of the field ionized molecular ion predominantly consisted of the thermal energy.

ICR mass spectra were recorded on a much-modified Varian V5903 instrument fitted with a 2-in. oil diffusion pump. Sample pressures were measured only approximately on an uncalibrated ionization gauge placed in a side arm of the main pumping line near the diffusion pump. The readings quoted are therefore expected to be too low by a factor of around 2 or 3, but the danger of gauge pyrolysis products causing the appearance of spurious signals is eliminated. The instrument is fitted with a four-section flat cell (cross section 26 × 12 mm) which has been constructed in our own workshop.

Except for double-resonance experiments it has been general practice to tune only the source region of the cell for maximum TIC, the subsequent regions then being tuned so as to maximize product ion formation. Double resonance has been done under tuning conditions given the minimum practicable ion sweep out (<5%) and at a constant rf voltage output level of 50 mV rms.

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# A Kinetic Investigation of the Insertion of Ketones into the Dioxygen Adduct $Pt(PPh_3)_2O_2$

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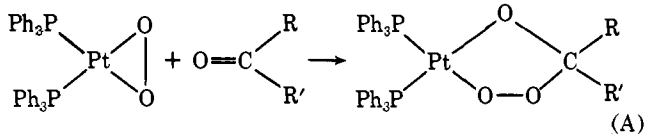
**Abstract:** The kinetics of the insertion reaction A have been studied with different ketones in different solvents. The experimental rate equation is in agreement with a dual pathway reaction mechanism. The major pathway involves precoordination of the ketone to the vacant axial coordination site of platinum followed by insertion. The minor pathway requires a prior activation of the dioxygen moiety. The nature of the transition states and the activated form of the dioxygen complex are discussed by means of an analysis of the activation parameters and solvent effects.

The synthesis and reactivity of dioxygen complexes with low oxidation state transition metal complexes have been investigated in recent years[1] since they could be related to the mechanisms of catalytic activation of dioxygen both on surfaces and in metal enzymes.[2] One interesting reaction involves the insertion into $Pt(PPh_3)_2O_2$ of an unsaturated group such as the carbonyl group of some organic molecules[3,4] or the double bond of activated olefins.[5] Such an insertion reaction can be considered to be a model for some of the important steps of catalytic selective oxidation such as the heterogeneous epoxidation of ethylene[6] or a particular metal-catalyzed olefin oxidation.[7]

Although a qualitative mechanistic study of this sort of reaction has been reported,[5] a detailed kinetic study is required to substantiate any proposed mechanism. We now describe the results of a kinetic investigation on the reaction A. These have



(A)

been reported in a preliminary way elsewhere.[8]

## Experimental Section

**Solvents and Reagents.** $Pt(PPh_3)_2O_2$ was obtained as previously reported;[9] solvents were distilled and dried over sodium or calcium hydride; ketones, all purchased commercially, were carefully distilled before use and their purity was checked by VPC.

**Kinetic Experiments.** All kinetics runs were carried out under pseudo-first-order conditions with a 50–1000 times excess of ketone with respect to the platinum complex whose concentration in solution was about $10^{-3}$ M. The reactions were carried out in dry, degassed solvents and were followed by monitoring absorbance changes at about 340 nm as a function of time. Good first-order plots were always obtained for up to 80% or more reaction of the platinum complex. Representative first-order kinetic plots are shown in Figure 1, where $[PtO_2]_0$ and $[PtO_2]_t$ are concentrations of $Pt(PPh_3)_2O_2$ at time = 0 and any other time, $t$. The results of the kinetic measurements are given in Tables IS, IIS, and IIIS.

## Results

Under the experimental conditions used the insertion reaction was found to be first order in the platinum complex for all the incoming ketones and in all the solvents investigated. Linear plots were obtained from plots of the pseudo-first-order constant, $k_{obsd}$, vs. different concentrations of the ketone (Figure 2). Such linear plots have a small intercept on the $y$ axis, which is independent of the nature of the ketone. These data suggest the following experimental rate law:

$$\text{rate} = k_{obsd}[PtO_2] = (k_A + k_B[\text{Ket}])[PtO_2] \qquad (1)$$

where Ket = ketone, $PtO_2 = Pt(PPh_3)_2O_2$. This equation was found to be valid for a series of nondonor solvents such as benzene, chloroform, or 1,2-dichloroethane as well as a donor solvent such as dimethylformamide (DMF).

For solvent mixtures containing DMF and benzene, the donor solvent has been found to play an important role in the overall kinetics since both the values $k_A$ and $k_B$ of the experimental rate equation (1) are dependent on the concentration of the donor solvent. This is illustrated in Figure 3 for different mixtures of $C_6H_6$/DMF with acetone as the incoming ketone. By plotting $1/k_A$ and $1/k_B$ vs. the DMF concentration, linear plots are obtained (Figure 4) which are of the general form[10]

$$1/k_A = (1/\mathbf{a})(1 + \mathbf{a}'[\text{DMF}])$$
$$1/k_B = (1/\mathbf{b})(1 + \mathbf{b}'[\text{DMF}]) \qquad (2)$$

These can be incorporated in the experimental rate law to give

$$\text{rate} = \left(\frac{\mathbf{a}}{1 + \mathbf{a}'[\text{DMF}]} + \frac{\mathbf{b}}{1 + \mathbf{b}'[\text{DMF}]}[\text{Ket}]\right)[PtO_2] \qquad (3)$$

The values of **a** and **b** from Figure 4 are $1.27 \times 10^{-4}$ s$^{-1}$ and

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