Unimolecular Chemistry of Methyl Formate Cation Radical. A Combined Theoretical and Experimental Study

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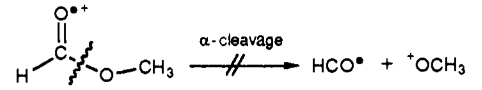
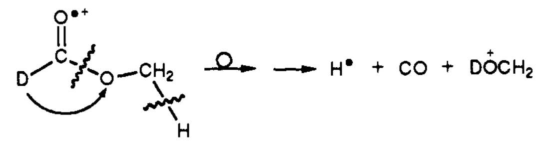
Abstract: The unimolecular chemistry of solitary methyl formate cation radical (**1**) has been studied by a combination of ab initio molecular orbital calculations executed at the MP3/6-31G**//6-31G*+ZPVE level of theory and mass spectrometry based experiments. The minimal energy requirement path corresponds to the loss of CO to produce $CH_3OH^{\bullet+}$ via a remarkably atom-specific process. The calculations indicate that the reaction proceeds via the hydrogen-bridged complex $CH_3OH\cdots C{=}O^{\bullet+}$ (**5**). The lowest energy pathway for the formation of **5** has been calculated to occur via a methoxy shift and simultaneous H transfer to the migrating moiety. The minimum rate for the loss of CO from **5** is small, and an intense metastable peak is produced. At slightly higher internal energies another process becomes energetically feasible: The dissociation to CH_2OH^+ + $HCO^\bullet$, which too is a remarkably atom-specific reaction. Our calculations indicate that this dissociation follows a multistep path. First **1** rearranges via a hydrogen 1,4-shift to the distonic ion $HC(OH)OCH_2^{\bullet+}$, **2**, which in turn isomerizes to the hydrogen-bridged complex $HC{=}O\cdots H\cdots O{=}CH_2^{\bullet+}$, **6**. The rate-determining step for this sequence, **2** → **6**, is calculated to lie 4.4 kcal/mol above the dissociation limit. According to ^{18}O-labeling experiments, the oxygen atoms retain their positional integrity, and so ions **6** do not undergo a degenerate isomerization via a hydrogen 1,5-shift. At still higher energies (those corresponding to the 70-eV electron impact mass spectrum) another process leads to CH_2OH^+ ions, namely, the consecutive fragmentation $HC(O)OCH_3^{\bullet+} \rightarrow CO + CH_3OH^{\bullet+} \rightarrow CH_2OH + H^\bullet$. Contrary to earlier suggestions, methoxy ions, CH_3O^+, are not produced from methyl formate ions. The sequence **1** → **2** → **6** → CH_2OH^+ + $HCO^\bullet$ is mechanistically related to that of the higher homologue; i.e., ionized methyl acetate, $CH_3C(O)OCH_3^{\bullet+}$, which inter alia prior to dissociation to $^\bullet CH_2OH/CH_3C{=}O^+$ isomerizes to $CH_3C{=}O\cdots H\cdots O{=}CH_2^{\bullet+}$.

Introduction

The unimolecular chemistry of gas-phase methyl formate cation radicals, $HC(O)OCH_3^{\bullet+}$, is very intriguing for a number of reasons.[1] The methyl formate cation radical is a textbook example[2a] of a dissociating species where isotopic labeling can lead to totally unexpected results.[2b] The major dissociation is the loss of $HCO^\bullet$, leading to the base peak in the 70-eV electron impact mass spectrum at *m/z* 31, and the process could, very reasonably, be viewed as a simple bond-breaking reaction as depicted in eq 1.

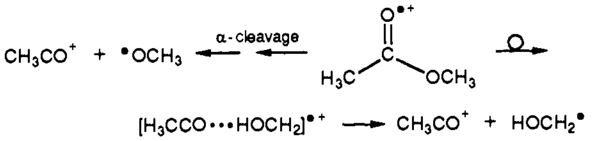


(1)


(2)

However, it was established 30 years ago, by the now time-honored technique of isotopic labeling, that the reaction is not due to one simple bond fission, because the corresponding peak for $DC(O)OCH_3$ is clearly shifted to *m/z* 32, $[H_2,D,C,O]^+$, and the mechanism in eq 2 was proposed. Thus, the daughter ion cannot be CH_3O^+, but rather corresponds to O-protonated formaldehyde, CH_2OH^+.[2b] This parallels observations being recently made for decomposing metastable methyl acetate ions, $H_3CC(O)OCH_3^{\bullet+}$, as far as the competition of direct bond cleavage versus extensive rearrangements prior to subsequent fragmentation is concerned.[2c]

In a recent paper on the mechanism of CH_3CO^+ formation from ionized methyl acetate, we reported on the importance of the hydrogen-bridged intermediate $[H_3CCO\cdots HOCH_2]^{\bullet+}$ as the direct precursor for $HOCH_2^\bullet$ loss. By means of ab initio MO calculations it was shown that this species could easily be generated below the threshold of the competing α-cleavage process, giving rise to the formation of CH_3CO^+ by the loss of the isomeric $HOCH_2^\bullet$ radical (eq 3).



(3)

The remarkable thermochemical stability of the H-bridged complex, being 0.5 kcal/mol more stable than ionized methyl acetate and being stabilized toward decomposition by 14.7 kcal/mol (MP2/6-31G*//3-21G+ZPVE), inspired us to investigate the importance of the corresponding process and the stability of the H-bridged complex, in particular, for the unimolecular chemistry of ionized methyl formate as the lower homologue of methyl acetate. Concerning the $[H_3,C,O]^+$ cation, it has become evident from recent theoretical and experimental studies[3] that singlet CH_3O^+ is a transient species (which spontaneously dissociates into $HCO^+ + H_2$) lying 91,[3a] 78 ± 5,[3b] or 76 ± 6 kcal/mol[3c] above O-protonated formaldehyde, $HOCH_2^+$ ($\Delta H_f[HOCH_2^+] = 169$ kcal/mol).[4] In contrast, the triplet of CH_3O^+

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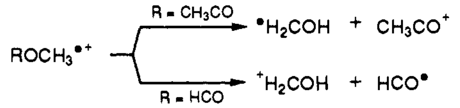
Table I. Absolute and Relative Energies As Obtained for Different Basis Sets

	6-31G*// 6-31G*	E_{rel}, kcal/ mol	MP2/6-31G**// 6-31G*	E_{rel}, kcal/ mol	MP3/6-31G**// 6-31G*	E_{rel}, kcal/ mol	ZPVE, kcal/ mol	E_{rel}, kcal/mol (MP2/6-31G**// 6-31G*+ZPVE)	E_{rel}, kcal/mol (MP3/6-31G**// 6-31G*+ZPVE)
1	−227.456 452	0.0	−228.034 076	0.0	−228.058 739	0.0	36.8	0.0	0.0
2a	−227.458 233	−1.1	−228.057 733	−14.9	−228.075 057	−10.3	36.4	−15.3	−10.7
2b	−227.462 423	−3.8	−228.061 660	−17.3	−228.079 131	−12.8	36.1	−18.0	−13.5
3	−227.418 858	23.6	−228.028 416	3.6	−228.041 567	10.8	34.8	1.6	8.8
4	−227.447 389	5.7	−228.051 520	−11.0	−228.066 485	−4.9	34.1	−13.7	−7.6
5	−227.442 574	8.7	−228.028 449	3.5	−228.050 032	5.5	33.7	0.4	2.4
6	−227.438 336	11.4	−228.041 786	−4.9	−228.055 993	1.7	34.1	−7.6	−1.0
7	−227.418 070	24.1	−228.032 398	1.1	−228.044 284	9.1	32.0	−3.7	4.3
TS **1/2**	−227.396 580	37.6	−228.014 519	12.3	−228.029 854	18.2	34.1	9.6	15.5
TS **2/3**	−227.358 193	61.8	−227.981 071	33.3	−227.990 595	42.8	32.3	28.8	38.3
TS **3/4**	−227.408 727	30.0	−228.017 983	10.1	−228.029 177	18.6	33.2	5.5	14.2
TS **1/5**	−227.417 819	24.3	−228.002 474	19.9	−228.021 660	23.3	33.3	15.4	18.8
TS **1/3**	−227.342 528	71.6	−227.971 107	39.6	−227.981 178	48.8	32.4	35.2	44.4
TS **2/6**	−227.403 259	33.4	−228.000 539	21.1	−228.016 452	26.6	33.7	18.0	23.5

has been generated in small yields by collision-induced two-electron detachment from CH_3O^-,[3b] but its generation by dissociation of positive ions has, as far as we are aware, never been proven.[5] We will demonstrate in this work, inter alia, that the $[H_3,C,O]^+$ ions generated from ionized methyl formate are indeed CH_2OH^+, which are formed, in part, directly from the molecular ion.

Another important peak in the mass spectrum of methyl formate is m/z 32, $[H_4,C,O]^{\bullet+}$, formed by loss of CO. This reaction is the sole process occurring in the microsecond metastable time window, and this indicates that the minimum rate constant for this reaction is quite small.[1] This, despite the fact that the phase space of the dissociating ion and the activation energy of the process (ca. 0.4 eV) are very small. Thus, RRKM/QET does not predict properly the metastable behavior for **1**.[1] These and other problems associated with the dissociation of ionized methyl formate have most recently been addressed and discussed in detail by Nishimura et al.[1] who concluded that the RRKM/QET calculated rates were a factor of 10^4 higher than the observed one. These researchers suggest that this large discrepancy may be the result of nonstatistical behavior and/or a fragmentation mechanism involving an isomerization process. Indeed, one can be confident that, in order to lose CO, ionized methyl formate must undergo a rearrangement of some sort. Consistent with all available labeling data is a hydrogen 1,2-shift, followed by CO loss, and this is the view that has prevailed until now. Invariably, however, such hydrogen 1,2-shifts are frequently associated with large energy requirements,[6,7] much larger than 0.4 eV, the measured activation energy for decarbonylation of $\mathbf{1}^{\bullet+}$. Rather, it appears from the recent literature that several other mechanisms may be operative which can slow down a unimolecular process sufficiently for it to produce an intense metastable peak.[5] These are (i) fragmentation involving ion/dipole complexes;[8] (ii) dissociation by tunneling through a barrier;[9] (iii) reactions involving nonadiabatic processes;[10] and (iv) spin-controlled decompositions.[3b] Baer et al.[8] argue that an intermediate ion/dipole complex (item i) can slow down a reaction, not necessarily by virtue of the complex's favorable heat of formation, but more appropriately by its ability to accommodate a large number of densities of states due to its extreme anharmonic potential well.

The present paper summarizes the results of a combined study, where various mass spectrometric techniques and extensive labeling experiments as well as high-level ab initio MO calculations have been used to elucidate the unimolecular fragmentation mechanism of $HC(O)OCH_3^{\bullet+}$, aimed at resolving the existing discrepancies. The results are compared with those obtained for the higher homologue, i.e., ionized methyl acetate. As will be shown below, the two systems are comparable, indeed, with respect to the energetics and electronic structures of intermediates being involved in the rearrangement steps although the fragmentation finally leads to a different charge and spin distribution in the $HOCH_2$ species being generated, respectively.



$$ROCH_3^{\bullet+} \begin{cases} \xrightarrow{R\,=\,CH_3CO} {}^{\bullet}H_2COH + CH_3CO^+ \\ \xrightarrow[R\,=\,HCO]{} {}^{+}H_2COH + HCO^{\bullet} \end{cases} \quad (4)$$

Experimental Section

All experiments were performed on the VG Instruments ZAB-2F mass spectrometer at the University of Utrecht, on the VG Instruments ZAB-HF-3F mass spectrometer at the Technical University Berlin, and on the McMaster VG Instruments ZAB-R instrument as described in detail elsewhere.[11] Helium was used as the collision gas in order to make comparisons possible with previous results. Details of the experiments are given in the appropriate sections below. The labeled compounds were synthesized and purified by standard laboratory procedures and their purities checked by GC/MS.

Computational Details

Ab initio MO calculations were carried out using the GAUSSIAN 82 series of programs.[12] For geometry optimization, a split valence 6-31G* basis set[13] was used. All stationary points were characterized to correspond either to local minima or to transition structures by calculating the Hessian matrix and checking for the number of negative eigenvalues. From the analytical force constants, the vibrational frequencies were obtained; zero-point vibrational energies (ZPVE) were scaled by 0.89 to correct for the overestimation at the Hartree–Fock level.[14] All open-shell species were treated within the unrestricted Hartree–Fock (UHF) formalism.[15] To account for valence electron correlation effects, Møller–Plesset perturbation theory[16] (terminated at third order) was applied on the basis of a 6-31G** wave function.[13] Thus, unless otherwise stated, the level of theory used for energy comparison corresponds to MP3/6-31G**//6-31G*+ZPVE.

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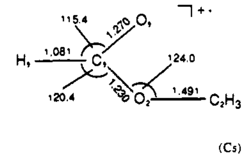
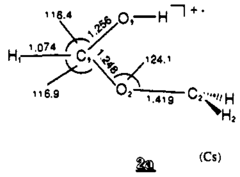
Chart I. Calculated Geometries of Structures Relevant to Scheme I: Bond Length (Å), Bond Angle (deg)



1

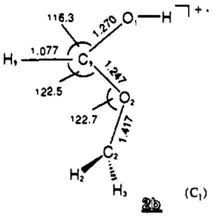
Charge density	Spin density
H_1 +0.31	O_1 1.11
C_1 +0.70	
C_2 -0.10	
O_1 -0.10	
O_2 -0.47	



2a

Charge density	Spin density
H_1 +0.30	C_2 1.28
C_1 +0.70	
C_2 -0.01	
O_1 -0.45	
O_2 -0.45	
H_2 +0.23	

<) $H_2C_2O_2C_1$ 84.9

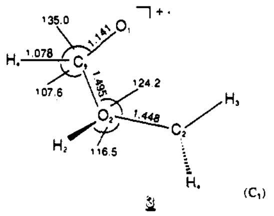


2b

Charge density	Spin density
H_1 +0.27	C_2 1.29
C_1 +0.72	
C_2 +0.05	
O_1 -0.45	
O_2 -0.47	
H_2 +0.20	

<] $H_2C_2O_2C_1$ 29.1

<) $H_3C_2O_2C_1$ 178.7

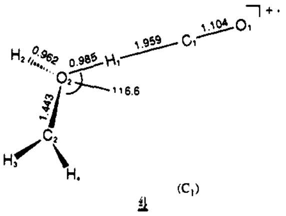


3

Charge density	Spin density
H_1 +0.27	C_2 1.29
C_1 +0.64	
C_2 +0.06	
O_1 -0.32	
O_2 -0.59	
H_2 +0.24	
H_4 +0.45	

<) $H_4C_2O_2C_1$ 213.9

<) $H_2O_2C_2C_1$ 186.9



4

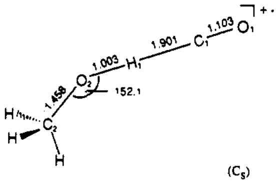
Charge density	Spin density
H_1 +0.46	C_2 1.29
C_1 +0.31	
C_2 +0.05	
O_1 -0.21	
O_2 -0.52	
H_2 +0.46	

<) $C_2O_2C_1H_1$ 239.6

<) $H_3C_2O_2C_1$ 326.0

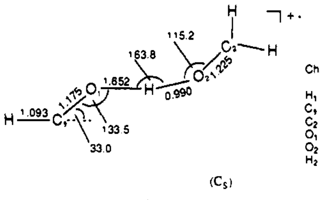
<) $H_4C_2O_2C_1$ 184.2

<) $H_2O_2C_2C_1$ 221.6



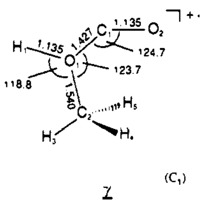
5

Charge density	Spin density
H_1 +0.47	O_2 1.13
C_1 +0.31	
C_2 -0.14	
O_1 -0.21	
O_2 -0.17	



6

Charge density	Spin density
H_1 +0.22	C_2 1.02
C_1 +0.34	
C_2 +0.31	
O_1 -0.50	
O_2 -0.38	
H_2 +0.49	



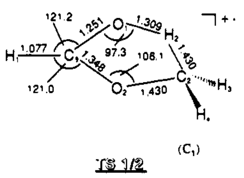
7

Charge density	Spin density
O_1 -0.69	O_1 0.34
C_2 -0.23	C_7 1.19
H_1 +0.30	
H_4 +0.29	
H_5 +0.29	
C_1 +0.75	
O_2 -0.28	

<) $H_1O_1C_2H_3$ -39.3

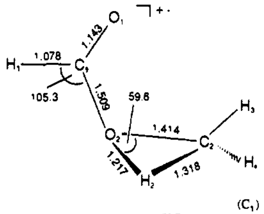
<) $C_1O_1C_2H_3$ 156.0

<) $O_2C_1O_1C_2$ -9.2



TS 1/2

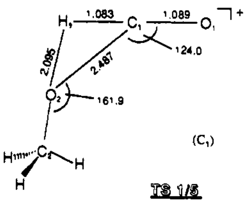
Charge density	Spin density
H_1 +0.31	C_2 0.71
C_1 +0.71	O_1 0.74
C_2 -0.07	
O_1 -0.38	
O_2 -0.45	
H_2 +0.33	
H_3 +0.27	



TS 1/3

Charge density	Spin density
H_1 +0.29	O_2 0.58
C_1 +0.61	C_2 0.92
C_2 -0.05	
O_1 -0.31	
O_2 -0.52	
H_2 +0.44	

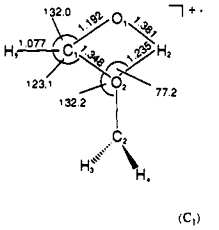
<) $H_2O_2C_2C_1$ 255.4



TS 1/5

Charge density	Spin density
H_1 +0.45	O_2 1.10
C_1 +0.63	
C_2 -0.07	
O_1 -0.11	
O_2 -0.42	

<) $O_2C_1O_1H_1$ 200.0



TS 2/3

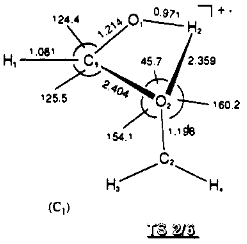
Charge density	Spin density
H_1 +0.30	C_2 1.29
C_1 +0.69	
C_2 -0.07	
O_1 -0.46	
O_2 -0.62	
H_2 +0.55	
H_3 +0.23	
H_4 +0.24	

<) $H_2O_1C_1$ 77.4

<) $H_3C_2O_2C_1$ 60.4

<) $H_4C_2O_2C_1$ 208.2

<) $H_2O_2C_1H_1$ 180.2



TS 2/5

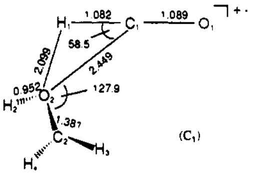
Charge density	Spin density
H_1 +0.29	C_1 1.10
C_1 +0.52	
C_2 +0.28	
O_1 -0.32	
O_2 -0.35	
H_2 +0.47	

<) $O_2C_2H_1O_1$ 245.9

<) $C_2O_2C_1H_1$ -32.6

<) $H_3C_2O_2C_1$ 11.0

<) $H_4C_2O_2C_1$ 190.9



TS 3/5

Charge density	Spin density
H_1 +0.44	C_2 1.31
C_1 +0.63	
C_2 +0.03	
O_1 -0.12	
O_2 -0.69	
H_2 +0.39	
H_3 +0.15	
H_4 +0.17	

<) $C_2O_2C_1H_1$ 265.6

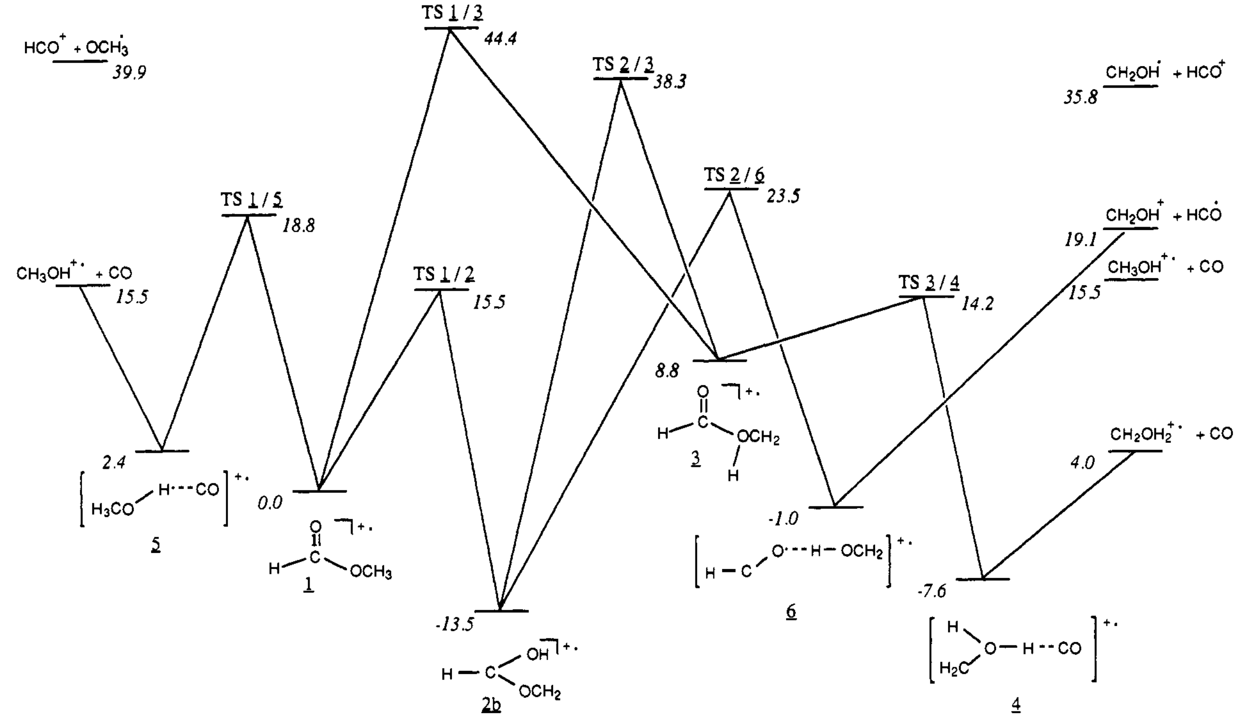
<) $H_2O_2C_2C_1$ 168.9

Results and Discussion

Theoretical Part. The optimized geometries of the seven minimum structures and the corresponding transition structures which are relevant for a discussion of the unimolecular decomposition of ionized methyl formate are shown in Chart I. The absolute and relative energies as obtained for the different basis sets are given in Table I.

Structure **1** corresponds to the methyl formate ion and has been taken as the energetic reference point (see Scheme I). The distonic ion[17] **2b** is predicted to be 13.5 kcal/mol more stable than

Scheme I. Calculated Hypersurface for Rearrangement and Dissociation Reactions of Ionized Methyl Formate (MP3/6-31G**//6-31G*+ZPVE) (Energies are give in kcal/mol)



1. The spin density maximum resides on C_2, whereas most of the positive charge is located on C_1. The two rotamers **2a** and **2b**, the former being 2.8 kcal/mol less stable than the latter, may freely communicate well below any threshold for further isomerization.[18] In the present context, however, **2a** has to be interpreted as the directly resultant structure of a H 1,4-shift from **1**, whereas **2b** acts as the starting conformation for isomerizations to species **3** and **6**, respectively, as will be detailed below. The two isomers **1** and **2b** are separated by a low-energy barrier of 15.5 kcal/mol (TS (transition state) **1/2**) corresponding to a 1,4-shift from the methyl group in **1** to the carbonyl oxygen.

The distonic ion **3** turns out to be 8.8 kcal/mol less stable than **1**. The spin density maximum still resides on C_2 as in **2**, but the bond distances are quite different from those calculated for species **2**. **3** shows a very short C_1–O_1 distance of 1.141 Å. For comparison, the C–O double bond distance in ionized methyl formate is 1.270 Å. The C–O distance connecting the HCO and $HOCH_2$ moieties is 1.495 Å and may already give an indication for a weak bonding. If this distance is elongated stepwise, rearrangement takes place rather than dissociation into the components HCO^+ and $HOCH_2^\bullet$. The dipolar $HOCH_2^\bullet$ radical is found to migrate along the positively charged rod of the formyl cation, and a transition structure (TS **3/4**) could be isolated, lying 5.4 kcal/mol above structure **3** which connects the distonic ion with the hydrogen-bridged complex **4** between distonic $CH_2OH_2^{\bullet+}$ and CO.

Beyond TS **3/4**, the formyl hydrogen is simultaneously shifted toward the migrating $HOCH_2$ moiety, reflecting the latter's higher proton affinity as compared to CO as indicated by eq (5).

$$\begin{array}{lcccccccc} & HCO^+ & + & {}^\bullet HOCH_2 & \longrightarrow & CO & + & CH_2OH_2^{\bullet+} & \\ \Delta H_f^\circ & 194.0^{19} & & -6.2^{20} & & -27.2^{21a} & & -195.0^{22} & (5) \end{array}$$

$$\Delta H_R^{theo} = -31.8\ \text{kcal/mol} \quad \Delta H_R^{exp} = -20.0\ \text{kcal/mol}$$

The dissociation of **3** into HCO^+ and $HOCH_2^\bullet$ is thermochemically less favored than the formation of $HCO^\bullet + HOCH_2^+$. However, the latter process even if it would occur without a barrier cannot compete with the rearrangement to **4**. Structure **4** serves as a well-suited precursor for CO loss; this dissociation channel corresponds to the energetically most favored one. We also note the remarkable stability of **4**, being 7.6 kcal/mol more stable than ionized methyl formate, **1**, and being 11.6 kcal/mol stabilized toward dissociation into its components! The distonic ion **3** which might dissociate to the ylide ion $CH_2OH_2^{\bullet+}$ via **4** can be thought to be generated either directly from **1** via TS **1/3** by a H 1,2-shift or as a result of a two-step mechanism of consecutive H and 1,4- and H 1,3-shifts (TS **1/2** and TS **2/3**, respectively) via intermediate **2**. According to Scheme I, the two-step mechanism is energetically more favorable. The rate-determining TS **2/3** is 6.1 kcal/mol lower in energy than TS **1/3** corresponding to the direct interconversion. Thus, the hypothetical formation of distonic $CH_2OH_2^{\bullet+}$ from ionized methyl formate would require an activation energy of 38.3 kcal/mol.

What is the fate of the distonic ion **2**? In the case of ionized methyl acetate, the corresponding species $[H_3CC(OH)OCH_2]^{\bullet+}$ was postulated to serve as the precursor for the electrostatically bound complex $[CH_3CO\cdots HOCH_2]^{\bullet+}$ which gave rise to the formation of CH_3CO^+ and $HOCH_2^\bullet$. The energetic demands for the same reaction sequence in ionized methyl formate are quite similar. Elongation of the C–(OCH_2) bond is followed by a migration of the almost uncharged OCH_2 moiety within the electrostatic field of the remaining $HCOH^{\bullet+}$ moiety to form the hydrogen-bridged complex **6**. At a late point on this reaction coordinate beyond the transition structure TS **2/6** a H transfer takes place, reflecting the differences in the proton affinities of either subunits as indicated by eq 6.

$$\begin{array}{lcccccccc} & HCOH^+ & + & {}^\bullet OCH_2 & \longrightarrow & HCO^\bullet & + & CH_2OH^+ & \\ \Delta H_f^\circ & 235.0^{23} & & -27.1^{21a} & & 7.8^{24} & & 168.0^{21b} & (6) \end{array}$$

$$\Delta H_R^{theo} = -24.1\ \text{kcal/mol} \quad \Delta H_R^{exp} = -32.1\ \text{kcal/mol}$$

The resulting complex **6** being 1.0 kcal/mol more stable than **1** dissociates into its components on a continuously endothermic path. Again, the stabilization of **6** toward decomposition of 20.1 kcal/mol is remarkably high. Note, that the spin and charge distribution in **6** already reflects the energetically favored decomposition products. This is in contrast to the corresponding structure on the methyl acetate ion surface where charge and spin redistribution has to occur during dissociation to generate the energetically favored products $CH_3CO^+ + CH_2OH^\bullet$ (see Scheme

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(17) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805.

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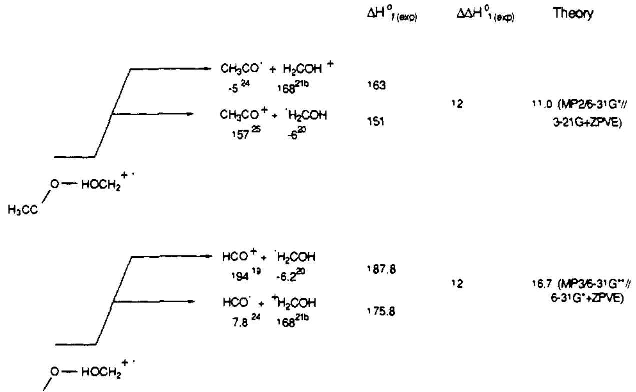
Scheme II. Comparison of the Heats of Formation (kcal/mol) of Some Dissociation Products As Derived from Methyl Acetate and Methyl Formate (for Details See Text)



II). The effect of replacing the formyl hydrogen of **6** by a methyl group is not very pronounced with respect to charge and spin distribution. The different dissociation behavior results from the methyl group effect on the resultant fragments and their stability. This can simply be rationalized in terms of the ordering of the respective ionization energies, i.e., $IE_{HCO^\bullet} = 186.2$ kcal/mol > $IE_{CH_2OH^\bullet} = 178.2$ kcal/mol > $IE_{CH_3CO^\bullet} = 162.0$ kcal/mol, which were calculated using the following heats of formation: $\Delta H_f°(HCO^\bullet) = 7.8$,[24] $\Delta H_f°(HCO^+) = 194.0$,[19] $\Delta H_f°(CH_2OH^\bullet) = -6.2$,[20] $\Delta H_f°(CH_2OH^+) = 168.0$,[21b] $\Delta H_f°(CH_3CO^\bullet) = -5.0$,[24], and $\Delta H_f°(CH_3CO^+) = 157.0$.[25]

We now return to the discussion of the chemistry of **1**. Common textbooks have it that ionized esters and carbonyl compounds tend to dissociate via α-cleavage processes. For metastable decomposing ions, however, this is not true in general as we have demonstrated in a series of previous studies.[2c,26] When the C–(OCH_3) bond in ionized methyl formate is cleaved, well below the threshold for decomposition of 39.9 kcal/mol (given by the sum of the relative energies of HCO^+ and $OCH_3^\bullet$), a shift of the dipolar radical component $^\bullet OCH_3$ is predicted to occur. Followed by simultaneous hydrogen transfer, a complex **5** of "classical" $CH_3OH^{\bullet+}$ and CO is formed. The corresponding transition structure TS **1/5** lies 18.8 kcal/mol above **1**. **5** is 2.4 kcal/mol less stable than **1** and 10.0 kcal/mol less stable than the comparable complex **4** of distonic $CH_2OH_2^{\bullet+}$ and CO. Thus, comparing the two species **4** and **5**, the difference in stability of the two isolated $[C,H_4,O]^{\bullet+}$ ions of 11.5 kcal/mol (see discussion below) in favor of the distonic ion is almost retained upon complexation. **5** subsequently decomposes without reverse activation energy.

A further distonic ion $[OCO(H)CH_3]^{\bullet+}$, **7**, has been found being 4.3 kcal/mol above **1**. Ion **7** might rearrange into **5** upon C–O bond cleavage. However, its formation can be thought to occur either via a H 1,2-shift from **1** or via a H 1,3-shift from **3**. Both rearrangements are expected to proceed via relatively high-lying transition structures. Therefore, it seems most unlikely that these interconversions are capable to compete with the low-energy processes involving TS **1/5** or TS **3/4**, respectively; consequently, the transition structures associated with the formation of **7** were not considered further.

Comparing MP3/6-31G**//6-31G*+ZPVE and MP2/6-31G**//6-31G*+ZPVE results (Table I), it turns out that both levels of theory lead to the same qualitative interpretation; the ordering of the respective transition structures is not affected.

According to the results presented above, low-energy methyl formate ions are predicted to preferentially decompose to $CH_3OH^{\bullet+}$ upon decarbonylation. Below the rate-determining barrier of this process, the two species **1** and **2** may nearly freely interconvert. This low-energy equilibrium, however, cannot be proven by labeling experiments as no positional exchanges with other hydrogens occur. On the basis of the theoretical predictions, a difference in the appearance energies should be detectable for $CH_3OH^{\bullet+}$ formation if **1** or **2** is specifically generated: starting from **2**, a higher activation energy for the $CH_3OH^{\bullet+}$ formation is required, reflecting the stability difference of **1** and **2**.

From a structural point of view, the case of decomposing methyl formate ions is a further striking example for ion/dipole formation prior to unimolecular decomposition of ions in the gas phase. With the exception of TS **1/2** for the H 1,4-shift, all transition structures which separate conventional covalently bound ion/dipole complexes are lower in energy than those connecting the covalent species. The dissociation behavior is highly influenced by the relative proton affinities of the components interacting in the complexes. This might be seen as a special behavior of cation radicals as charged and open-shell electron-deficient species: charge as a prerequisite for strong electrostatic interactions, and open-shell electron deficiency as a prerequisite for a weakened covalent bonding situation. Whereas in neutral closed-shell species covalency is the driving force in bonding and in closed-shell dications, electrostatic interaction (charge alternation) becomes the dominant factor in binding and reactivity.[27] The chemistry of charged open-shell species benefits from both features.

Summarizing the results the following conclusions can be drawn.

(1) Metastable methyl formate ions are predicted to dissociate to $CH_3OH^{\bullet+}$ + CO in an atom-specific process. This involves an $OCH_3^\bullet$ shift by a simultaneous H transfer to form the H-bridged complex $[CH_3OH^{\bullet+}\cdots CO]$, **5**, which subsequently decomposes into its components. The formation of the thermochemically more stable distonic ion $CH_2OH_2^{\bullet+}$ is calculated to have a much higher energy requirement. The rate-determining step for the latter reactions involves TS **2/3** which is 19.5 kcal/mol above TS **1/5**.

(2) For the reaction sequence $\mathbf{1} \rightarrow \mathbf{2} \rightarrow \mathbf{6} \rightarrow CH_2OH^+ + HCO^\bullet$, a slightly higher energy requirement is predicted. The rate-determining step corresponds to the interconversion $\mathbf{2} \rightarrow \mathbf{6}$, the respective transition structure TS **2/6** lying 23.5 kcal/mol above **1**. This process is predicted to be highly atom specific in that only the original atoms of the methoxy group will appear in the hydroxy methyl cation.

Experimental Part. We will discuss results obtained for the following processes: (i) the slow (average rate constant 5×10^4 s^{-1})[28] spontaneous reactions of ionized methyl formate as monitored by mass-analyzed ion kinetic energy spectroscopy; (ii) the collision-induced reactions of long-lived ions (CA spectroscopy[29]); and (iii) the fast reactions (rate constant greater than 10^6 s^{-1}) induced by electron impact (the ordinary mass spectrum). The above order reflects that of the internal energy content of the methyl formate ions.

Slow Reactions of Ionized Methyl Formate. The MI spectrum of ionized methyl formate is dominated by a peak at m/z 32, corresponding to loss of 28 amu. The MI spectrum of naturally ^{13}C-labeled m/z 61, which contains one ^{13}C atom in either possible position, shows two peaks at m/z 32 and m/z 33 of equal intensity and so the neutral lost from the unlabeled ion is CO, not C_2H_4,

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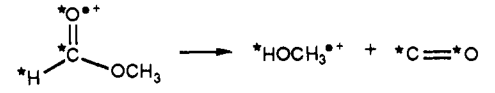
(28) Burgers, P. C.; Holmes, J. L. *Int. J. Mass Spectrom. Ion Processes* **1984**, *58*, 15.

(29) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77.

confirming results from earlier specific labeling experiments.[2b] Hence, the daughter ions generated from metastable parent ions have the elemental composition $[H_4,C,O]$. Theory and experiment have clearly established that there exist two distinguishable $[H_4,C,O]^{\bullet+}$ ions, namely, the conventional form $CH_3OH^{\bullet+}$ and the ylide–ion $CH_2OH_2^{\bullet+}$. The latter is thermochemically the more stable isomer by 11 kcal/mol (theory)[30] or 7 kcal/mol (experiment).[22] These two isomers can be readily distinguished by their characteristic CA mass spectra. It was observed[22,31] that the $[H_4,C,O]^{\bullet+}$ ions generated from metastable $HCO_2CH_3^{\bullet+}$ (**1**) were $CH_3OH^{\bullet+}$ to the exclusion of $CH_2OH_2^{\bullet+}$ in agreement with our calculations. The appearance energy (AE) of this process, AE = 11.28 eV,[31] leads to a heat of formation ($\Delta H_f°$) for the daughter ion of 201.5 kcal/mol which corresponds to that of $CH_3OH^{\bullet+}$. Thus, the $CH_3OH^{\bullet+}$ ions are produced at threshold, as concluded previously.[1] From the threshold photoelectron–photoion coincidence (TPEPICO) study of Nishimura et al.,[1] it is clear that at rate constants of 5×10^4 s^{-1} the reaction takes place very close to threshold; we estimate an excess energy of smaller than 0.2 eV. From the average kinetic energy release $\langle T \rangle = 0.04$ eV associated with the reaction $\mathbf{1} \rightarrow CH_3OH^{\bullet+} + CO$, it follows that a significant part (20%) of the excess energy appears in the translational modes; this is consistent with previous theoretical considerations[32] and experimental findings,[33] which show that for reactions taking place close to threshold the fraction of energy released as translational energy can be quite large (ca. 20%).

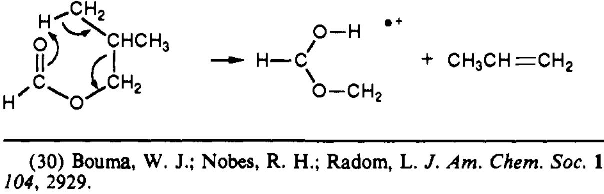
To elucidate the mechanism of CO loss, several specifically labeled compounds were investigated. For metastable ions we observed the following: (i) $H^{13}C(O)OCH_3$ exclusively loses ^{13}CO; (ii) $HC(O)^{18}OCH_3$ specifically loses $C^{16}O$; (iii) $DC(O)OCH_3$ produces $CH_3OD^{\bullet+}$ to the exclusion of $CH_2DOH^{\bullet+}$. Hence, the following change in atom connectivity is established (eq 7).



(7)

This scheme is consistent with a picture drawn previously[2b] that the reaction involves transfer of the formyl hydrogen to the methoxy oxygen. The above D-labeling experiment also shows that prior to dissociation there are no H/D exchange reactions in agreement with theory. From ab initio calculations, however, it is well known that the energy barrier for the hydrogen 1,2-shift is in general quite large indeed.[6,7] As discussed above, there is a low-energy path for the loss of CO: stretching of the $C–O(CH_3)$ bond does not immediately result in dissociation, but leads to a situation where the incipient formyl cation interacts electrostatically with the methoxy dipole. As the CO bond is stretched, simultaneous transfer of the "formyl hydrogen" to the "methoxy oxygen" occurs (see TS **1/5** in Scheme I and Chart I). Our calculations show that there should be a barrier (3.3 kcal/mol) for the reverse reaction, but TPEPICO experiments show that there is no such barrier. We propose that the hydrogen atom can tunnel through the barrier as is the case, e.g., in the loss of CH_4 from ionized acetone.[9] In this respect we note that the TPEPICO experiments show that loss of CO from $DC(O)OCH_3^{\bullet+}$ is much slower (by a factor of 10) than the loss of CO from the unlabeled parent ion.[1]

According to our calculations ionized methyl formate, **1**, can also rearrange to the distonic isomer **2** below the energy required for dissociation (Scheme I). We attempted to generate **2** independently according to eq 8.



(8)

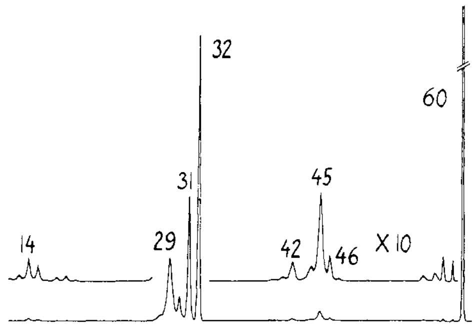


Figure 1. Collisional activation mass spectrum of $HC(O)OCH_3^{\bullet+}$.

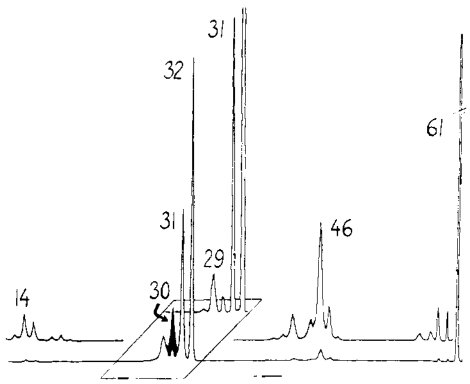


Figure 2. Collisional activation mass spectrum of $H^{13}C(O)OCH_3^{\bullet+}$. Collisional activation mass spectrum of $CH_3OH^{\bullet+}$ is given in rear.

m/z 60, $[C_2,H_4,O_2]^+$ is an intense peak in the mass spectrum of isobutyl formate, but it was not possible to assign the above structure to this ion since its CA mass spectrum was found to be closely similar to that of $HC(O)OCH_3^{\bullet+}$. It was proposed by Nishimura et al.[1] that the failure of RRKM/QET to predict the slow minimum rate may be the result of nonstatistical behavior and/or a fragmentation mechanism involving an isomerization into a thermochemically more stable form. Isomer **2** would appear a likely candidate. However, the calculated activation energy of 1.4 eV for loss of CO from **2** is still too small to account for the slow rate.[34] Rather, we explain the slow rate along the lines developed by Shao et al.,[8] namely, in terms of the extremely anharmonic potential well associated with ion/dipole complexes (i.e., ion **5**), which can accommodate a large number of states.

Ions **2** could in principle rearrange to ionized hydroxymethoxycarbene, $HOCOCH_3^{\bullet+}$, **8**. The latter ion has been generated in the gas phase and its $\Delta H_f°$ has been measured[35] (ΔH_f = 157 kcal/mol); for **1**, $\Delta H_f°$ amounts to 166 kcal/mol, so that **8** is, provided no significant barriers exist, in principle, accessible from **1**. However, its dissociation characteristics are totally different from those of ions **1** (and **2**), in that ions **8** abundantly (and exclusively) lose $^\bullet CH_3$. Only for collisional activation of **1**, isomer **8** is involved as a transient species, as discussed below.

Collision-Induced Dissociations. The CA mass spectrum of methyl formate is given in Figure 1. It can be seen that the low-energy process (formation of *m/z* 32) is still very abundant, but other intense signals are now found at *m/z* 31 $[CH_2OH]^+$, *m/z* 30 $[H_2,C,O]^{\bullet+}$, and *m/z* 29 $[H,C,O]^+$. Minor peaks are observed at *m/z* 15 $[CH_3]^+$, *m/z* 14 $[CH_2]^{\bullet+}$, *m/z* 45 (loss of $^\bullet CH_3$), *m/z* 46 (loss of CH_2), and surprisingly also *m/z* 42 (loss of H_2O). The formation of *m/z* 29 is accompanied by a large kinetic energy release resulting in peak broadening. The intensity distribution in the region *m/z* 28–32 resembles that of ionized methanol itself, and so it appears attractive to rationalize (part of) the CA mass spectrum in terms of excited $[CH_3OH]^{\bullet+}$ which

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Table II. Calculated Energies (kcal/mol) of Intermediates for Formation of $^{+}CH_2OH$ and $^{\bullet}CH_2OH$ from Ionized Methyl Formate and Methyl Acetate, Respectively

ion	**1**	TS **1/2**	**2**	TS **2/6**	**6**	product	level of theory
$HC(O)OCH_3^{\bullet+}$	0	15.5	−13.5	23.5	−1	19.1	MP3/6-31G**//6-31G*+ZPVE
$CH_3C(O)OCH_3^{\bullet+}$	0	11.2	−12.2	17.0	−0.5	14.4	MP2/6-31G*//3-21G+ZPVE

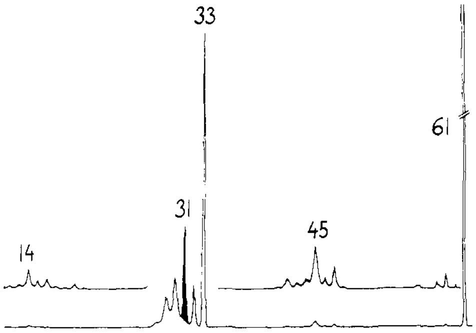


Figure 3. Collisional activation mass spectrum of $DC(O)OCH_3^{\bullet+}$.

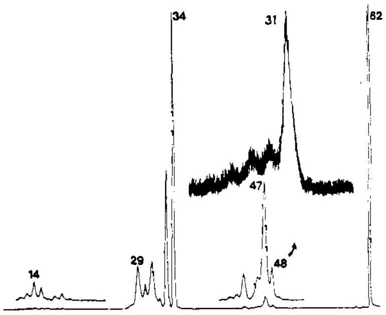


Figure 4. Collisional activation mass spectrum of $HC(O)^{18}OCH_3^{\bullet+}$. Inset: double-collision experiment (see text for discussion).

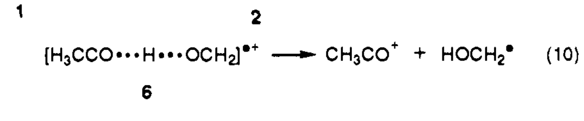
dissociates further by loss of $H^{\bullet}$, followed by loss of H_2. Indeed it has long been known[36] that loss of H_2 from CH_2OH^+ is characterized by a large kinetic energy release, and this would elegantly explain the broad peak at *m/z* 29. Following these lines of arguments, then $H^{13}C(O)OCH_3$ is predicted to produce $CH_3OH^{\bullet+}$, and so no mass shifts are expected for the peaks at *m/z* 28–32. The CA mass spectrum of $H^{13}C(O)OCH_3$ is given in Figure 2. It can be seen that *m/z* 29 is partially shifted to *m/z* 30, $H^{13}C{=}O^+$. Thus, in agreement with earlier work[37] we conclude that about 65% of $HC{=}O^+$ ions formed from the unlabeled compound are generated directly from the molecular ion (giving rise to *m/z* 30) and 35% by loss of H_2 from CH_2OH^+, thus generating *m/z* 29. Interestingly, the direct cleavage is accompanied by a large kinetic energy release as well, indicating that the collison-induced fission takes place well above the dissociation limit. If the contribution for the direct process (shaded signal) leading to $H^{13}CO^+ + {}^{\bullet}OCH_3$ is subtracted from the CA mass spectrum, then the resulting CA mass spectrum is closely similar to that of $CH_3OH^{\bullet+}$ (spectrum in rear of Figure 2). Now $CH_3OD^{\bullet+}$ ions, upon collisional activation, exclusively lose $H^{\bullet}$ to produce CH_2OD^+; no loss of $D^{\bullet}$ is observed. Hence, $CH_3OD^{\bullet+}$ ions generated by collisional activation of $DC(O)OCH_3^{\bullet+}$ are expected to lose $H^{\bullet}$ only. This is not what is observed experimentally. In Figure 3 the CA mass spectrum of $DC(O)OCH_3^{\bullet+}$ is shown. As expected, *m/z* 29 is partially shifted to *m/z* 30, DCO^+ (see above). However, there is also an intense peak at *m/z* 31 which, see above, cannot have arisen by $D^{\bullet}$ loss from *m/z* 33, $CH_3OD^{\bullet+}$. Rather this signal must correspond to a fragmentation of the molecular ion, without the intermediacy of methanol ions. CA data clearly show that *m/z* 31 is CH_2OH^+, not CH_3O^+ (see later). Similar observations are obtained for $HC(O)OCD_3^{\bullet+}$: in its CA mass spectrum *m/z* 34 is twice as intense as *m/z* 33, whereas $CD_3OH^{\bullet+}$ exclusively loses $D^{\bullet}$ to form *m/z* 33, CD_2OH^+. Thus, we conclude that for unlabeled methyl formate most of the CH_2OH^+ ions are generated directly from the molecular ion by loss of $HCO^{\bullet}$. Our ab initio calculations provide a rational mechanism for this process (see Scheme I) in terms of the transformation **1** → **2** → **6** → $CH_2OH^+ + HCO^{\bullet}$.

Upon activation of ions **2** the incipient formaldehyde molecule migrates in the electrostatic field of the hydroxycarbene ions well below the energy of $HCOH^{\bullet+} + CH_2{=}O$ (198 kcal/mol). The formaldehyde molecule drifts toward the hydroxyl group, thereby pulling the hydroxyl hydrogen toward itself to form the complex $HCO{\cdots}HOCH_2^{\bullet+}$ which then decomposes via a continuously endothermic process. We note that the spin and charge distribution in the complex already reflects decomposition products of lowest energy, i.e., $HCO^{\bullet}/CH_2OH^+$. The ions at *m/z* 32 (see Figure 3) could have been formed via a hydrogen "1,5"-shift in **6** leading to a degenerate isomerization followed by cleavage (eq 9).

$$[DCO{\cdots}HOCH_2]^{\bullet+} \rightarrow [DHCOH{\cdots}OCH]^{\bullet+} \rightarrow DHCOH^+/HCO^+ \quad (9)$$

If this is so, then the CA mass spectrum of specifically labeled $HC(O)^{18}OCH_3^{\bullet+}$ should contain an *intense* signal at *m/z* 31, $CH_2{}^{16}OH^+$ (see Figure 4). However, only a *small* peak is observed at *m/z* 31 (Figure 4), which according to a peak shape analysis corresponds to $HC^{18}O^+$, formed from $H_2C^{18}OH^+$, *m/z* 33; hence, $HC(O)^{18}OCH_3^{\bullet+}$ specifically generates $H_2C^{18}OH^+$. Thus, ions **6** do *not* undergo a degenerate isomerization via a hydrogen "1,5"-shift, and we propose that *m/z* 32 in the CA mass spectrum of $DC(O)OCH_3^{\bullet+}$ (Figure 3) results from another process, for example, subsequent dissociation of $CH_3OD^{\bullet+}$; see below.

From TPEPICO experiments, Nishimura et al.[1] concluded that the kinetic energy release for formation of *m/z* 31 from $DC(O)OCH_3^{\bullet+}$ is about twice that calculated using QET. They concluded that "This is one possible case of failure of the quasi-equilibrium hypothesis, which is at the centre of the statistical theory of mass spectra". We offer here an alternative interpretation. Nishimura et al.[1] assumed that the daughter ion is CH_3O^+ which would be formed at threshold. However, we have shown here that the daughter ions are CH_2OH^+, and our ab initio calculations indicate (and also the experiments of Nishimura et al.; see later) that there may well be a reverse activation energy (4.4 kcal/mol) for this process, and therein lies, we propose, the origin of the large energy release. The similarity of the mechanism for formation of CH_2OH^+ from ionized methyl formate and that for the dissociation of the higher homologue methyl acetate[2c] is striking. Methyl acetate ions dissociate to $CH_3C{=}O^+ + {}^{\bullet}OCH_3$ and to $CH_3C{=}O^+ + {}^{\bullet}CH_2OH$.[38] In complete agreement with the experiment, the formation of $^{\bullet}CH_2OH$ was calculated[2c] to proceed as follows (eq 10).



1 **2** **6**

$$[H_3CCO{\cdots}H{\cdots}OCH_2]^{\bullet+} \longrightarrow CH_3CO^+ + HOCH_2^{\bullet} \quad (10)$$

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[36] See, e.g., Wijenberg, J. H. O. J.; Van Lenthe, J. H.; Ruttink, P. J. A.; Holmes, J. L.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Processes* **1987**, *77*, 141.

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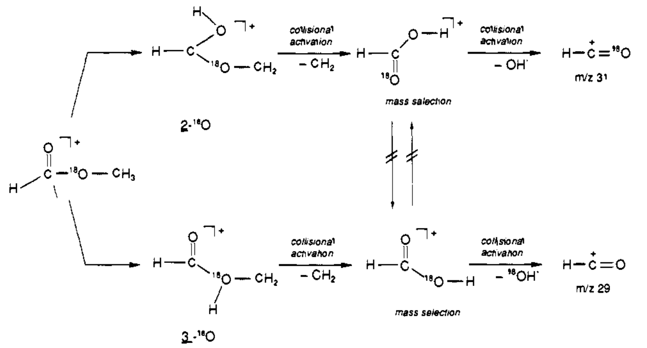
[38] a) Holmes, J. L.; Hop, C. E. C. A.; Terlouw, J. K. *Org. Mass Spectrom.* **1986**, *21*, 777. b) Burgers, P. C.; Holmes, J. L.; Hop, C. E. C. A.; Terlouw, J. K.; *Org. Mass Spectrom.* **1986**, *21*, 549. c) Mercer, R. S.; Harrison, A. G. *Org. Mass Spectrom.* **1987**, *22*, 710. d) Wesdemiotis, C.; Feng, R.; Williams, E. R.; McLafferty, F. W. *Org. Mass Spectrom.* **1986**, *21*, 689.

Scheme III. MS/MS/MS Experiment on $HC(O)^{18}OCH_3^{\bullet+}$ (See Text for Details)



The calculated energies of the respective intermediates and transition structures are quite similar for the two homologues (see Table II). As mentioned above, the observation that the charge appears on the acetyl moiety rather than on the CH_2OH part can be explained in terms of thermochemistry, i.e., in terms of Stevenson's and Audier's rule.[39]

Do we have any evidence in the case of methyl formate for the participation of **2**? The CA mass spectrum of **1** contains a weak but highly structure-indicative signal for loss of CH_2 and also for the formation of $CH_2^{\bullet+}$. Both ions **2** and **3** can directly lose CH_2, but theory indicates that **3** should not be energetically accessible. To see whether this prediction holds true, the following experiment was conceived and performed (see Scheme III). Ion **2** generated from labeled ion $HC(O)^{18}OCH_3^{\bullet+}$ will have the structure $HC(OH)^{18}OCH_2^{\bullet+}$, whereas **3** will correspond to $HC(O)^{18}O(H)CH_2^{\bullet+}$. Loss of CH_2 from **2**-^{18}O will yield $HC(^{18}O)OH^{\bullet+}$, whereas **3**-^{18}O will produce $HC(O)^{18}OH^{\bullet+}$. These latter two isotopomers, which are prevented by large barriers to interconvert,[26a] could be distinguished by a double-collision experiment,[40] using the ZAB-R instrument of BEE geometry, i.e., an instrument in which the magnet (B) precedes two consecutive electric sectors (E). $HC(O)^{18}OCH_3^{\bullet+}$ is introduced into the ion source, and upon acceleration (8 kV) and mass selection by the magnet the beam of *m/z* 62 molecular ions is fired into a collision gas chamber (pressurized with helium) located between the magnet and the first sector. The CA mass spectrum resulting from the collision-induced dissociations in this cell is recorded by scanning the first sector, and the result is shown in Figure 4. Next, the first sector is set to a value such that the *m/z* 48 ions generated by collision in this cell are selectively transmitted to a second collision chamber (also pressurized with helium) located between the first and the second sector. The CA mass spectrum of these *m/z* 48 ions was obtained by scanning the second sector, and its *m/z* 25–32 mass region is shown as the inset of Figure 4. It is seen that the major process which occurs is the formation of *m/z* 31 $HC{=}^{18}O^+$ ions, in agreement with the above prediction.

Our results indicate that there is only one possible rearrangement route below the threshold for dissociation, namely, **1** → **2**. These results are in agreement with a recent 4 K matrix ESR study[41] on the methyl formate cation radical, from which it was concluded that upon warming to 77 K the radical cation **2** and not **3** was formed by a hydrogen 1,4-shift in **1**.

The CA mass spectrum of the unlabeled methyl formate also contains a relatively intense peak for loss of $^{\bullet}CH_3$ (Figure 1). In the CA mass spectrum of $DC(O)OCH_3$ this peak remains at *m/z* 45, and thus $^{\bullet}CH_2D$ and not $^{\bullet}CH_3$ is lost (see Figure 3). Ions **2** can elegantly account for this result in terms of a hydrogen 1,3-shift to produce $HOCOCH_3^{\bullet+}$ followed by loss of $^{\bullet}CH_3$ to produce $HOCO^+$; the latter is thermochemically more stable than HCO_2^+.[42]

Table III. Partial 70-eV EI Mass Spectra of Methyl Formate and Methanol

m/z	$HC(O)OCH_3$	CH_3OH	$DC(O)OCH_3$	$H^{13}C(O)OCH_3$
33			41	
32	45	60	100	44
31	100	100	16	100
30	6	6	32	32
29	50	50	16	18
28	5	5	5	3

Mass Spectrum of Methyl Formate. Apart from the peak at *m/z* 60, the mass spectrum of methyl formate resembles very much that of methanol (see Table III). It is known that methanol ions generated by electron impact of methanol lose $H^{\bullet}$ to produce CH_2OH^+. The CH_2OH^+ ions lose H_2 to produce HCO^+, together with a little HOC^+. The mass spectrum of $DC(O)OCH_3$ is also shown in Table III, and it is clear from the intense peak at *m/z* 30 that direct dissociation to $DCO^+ + {}^{\bullet}OCH_3$ is an important process. *m/z* 29 arises by loss of HD from $CH_2OD^{\bullet+}$, *m/z* 32, as $CH_2OD^{\bullet+}$ generated from $CH_3OD^{\bullet+}$ specifically eliminates HD. Note that the sum of the intensities of *m/z* 30 and *m/z* 29 is equal to the intensity of *m/z* 29 in the unlabeled compound. It is observed that the mass spectrum of $DC(O)OCH_3$ contains a reasonably intense peak at *m/z* 31; CA experiments show that these ions are CH_2OH^+, not CH_3O^+ as assumed previously.[1] These CH_2OH^+ ions arise, as we propose, via the sequence **1** → **2** → **6** → $CH_2OH^+ + {}^{\bullet}DCO$ as discussed above. That *m/z* 31 for the labeled ions is more intense than expected had been observed previously[2b] but was not commented upon.

In summary methyl formate radical cations fragment as follows: (1) at low internal energies by loss of CO, $HC(O)OCH_3^{\bullet+} \rightarrow [CH_3OH{\cdots}CO]^{\bullet+} \rightarrow CH_3OH^{\bullet+} + CO$ (a); (2) at slightly higher energies another reaction comes into play, namely, $HC(O)OCH_3^{\bullet+} \rightarrow [HC(OH)OCH_2]^{\bullet+} \rightarrow [HCO{\cdots}HO{=}CH_2]^{\bullet+} \rightarrow CH_2OH^+ + HCO^{\bullet}$ (b); and (3) at higher energies still, in addition to reactions a and b, the direct dissociation to $HCO^+ + {}^{\bullet}OCH_3$ occurs; also at the elevated energies the $CH_3OH^{\bullet+}$ and CH_2OH^+ ions formed in reactions a and b fragment further.

Qualitatively the agreement between theory and experiment is very good. Indeed, the intriguing transformation **1** → **2** → **6** → $CH_2OH^+ + HCO^{\bullet}$ had lain unsuspected until now. Also an explanation can be given for the slow rate for formation of $CH_3OH^{\bullet+}$ in terms of intermediate ion/dipole complexes.[8] In addition, the large kinetic energy release associated with the formation of CH_2OH^+ from $DC(O)OCH_3^{\bullet+}$ is no longer anomalous. As stated above, the calculations provide a detailed insight into the central aspects of the unimolecular chemistry of solitary methyl formate ions.

Note Added in Proof. A very recent investigation[43] reports on the successful formation of ion **2** by unimolecular dissociation of ionized isobutyl formate (see eq 8). Charge-stripping mass spectrometry and neutralization–reionization experiments led to a clear distinction of ionized methyl formate and ion **2**.[44]

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Registry No. **1**, 82188-89-4; **2a**, 91024-59-8; **7**, 140201-49-6.

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[44] For very recent ab initio MO calculations on ionized methyl formate **1** and its distonic isomer **2**, see: ref 18.