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Loss of HF from $C_2H_4FO^+$ produced from 2-hydroxy-2-trifluoromethylpropanoic acid upon electron ionization

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Abstract

Metastable $C_2H_4FO^+$ ions (*m/z* 63) produced by electron ionization of 2-hydroxy-2-trifluoromethylpropanoic acid CH_3-$C(CF_3)(OH)COOH$ (**1**) decompose into CH_3CO^+ (*m/z* 43) and HF. The corresponding peak in the MIKE spectrum is composite with translational energy release values of 0.83 eV and <1 meV. The origin of this composite peak was investigated on the basis of quantum chemical calculations. We propose that the *m/z* 63 ion from $\mathbf{1}^{\bullet +}$ consists of two isomers, i.e., CH_3C^+FOH and $CH_3CO^+\cdots FH$, with the former (latter) being responsible for the broad (narrow) component of the peak. The decomposition processes of the precursor ion $CH_3C^+(CF_3)OH$ are also explored in some detail. (Int J Mass Spectrom 222 (2003) 1–9)

Keywords: Fragmentation; MIKE; Potential energy surface; Fluorine compound; Ion–dipole complex

1. Introduction

Fluorinated organic compounds are important industrial and biomedical materials. Due to the high electronegativity of fluorine and the strong carbon–fluorine bond, the chemistry of fluorinated organic compounds is considerably different from that of their fluorine-free analogs [1,2]. Fluorine chemistry is also important in connection with environmental chemistry of the stratosphere [3].

In the field of mass spectrometry, fluorine-containing organic ions show some characteristic decomposition processes. For example, the loss of difluorocarbene, CF_2, is a frequently observed process in compounds containing the CF_3 group [4,5], whereas the loss of CH_2 is a very rare process in hydrocarbons. The loss of HF is also a prevailing process for fluorine-containing organic ions. In some cases, a composite metastable peak due to the loss of HF is observed, indicating two or more distinct mechanisms. This has been seen during decomposition of $C_2H_2F_3O^+$ ion produced by electron ionization of some fluorinated alcohols, and the mechanisms were investigated both experimentally [6–8] and theoretically [8,9]. Hrusak et al. reported composite peaks due to the loss of HF from protonated fluorobenzene produced by chemical ionization [10] and elucidated the detailed mechanisms.

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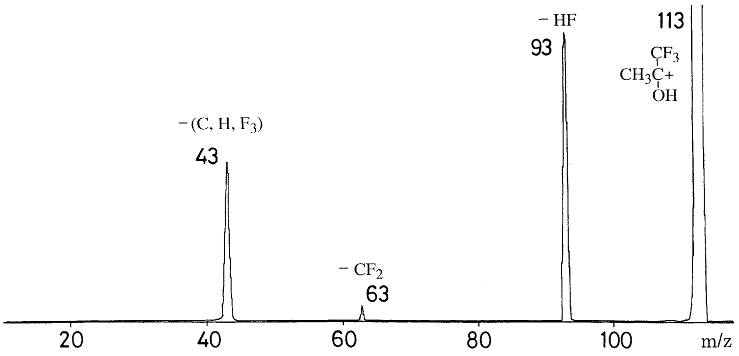


Fig. 1. The MIKE spectrum of ions with *m/z* 113 from $\mathbf{1}^{\bullet +}$.

Recently, we observed a composite metastable peak due to the loss of HF from the $C_2H_4FO^+$ (*m/z* 63) ion produced from 2-hydroxy-2-trifluoromethylpropanoic acid upon electron ionization [11]. In the present paper, this observation will be discussed in the light of results from quantum chemical calculations.

2. Experimental and calculation methods

The mass and the mass-analyzed ion kinetic energy (MIKE) spectra were recorded on a JEOL JMS HX-100 tandem (EBE) mass spectrometer. The electron energy for ionization was 70 eV and the ion acceleration voltage was 5 kV. The translational energy release was estimated from the full width of the metastable peak at half maximum ($T_{0.5}$) after correction for the width of the main beam [12].

2-Hydroxy-2-trifluoromethylpropanoic acid CH_3-$C(CF_3)(OH)COOH$ (**1**) was obtained from Oakwood Products Inc., and was used as received. The deuterated isotopomer, $CH_3C(CF_3)(OD)COOD$ (**1-d**$_2$), in which the hydroxyl hydrogens are substituted by deuterium was prepared by repeated exchange with D_2O.

Quantum chemical calculations were performed with the Gaussian 98 suite of programs [13]. The methods used were Hartree–Fock and Mϕller–Plesset perturbation theory to the second order (MP2) with 6-31G(d,p) or 6-311+G(d,p) basis sets. All stationary points found on the potential energy surface were characterized by complete optimization of the molecular geometry at each level, unless otherwise stated. The zero point vibrational energy calculated from the obtained harmonic frequencies were scaled [14] by a factor of 0.9181 (HF/6-31G(d,p)) and 0.9607 (MP2/6-31G(d,p)), and included in the relative energies.

3. Results and discussion

The most intense peaks in the mass spectrum of 2-hydroxy-2-trifluoromethylpropanoic acid (**1**, MW =

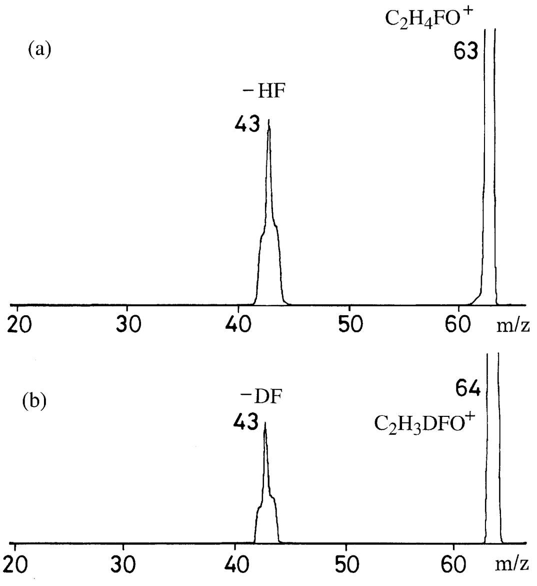
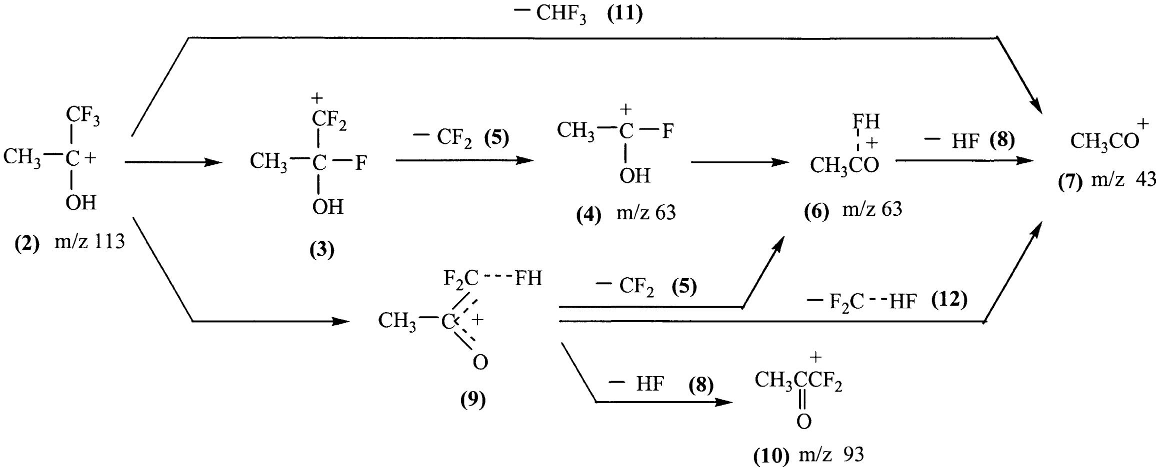


Fig. 2. The MIKE spectrum of (a) ions with *m/z* 63 from $\mathbf{1}^{\bullet +}$ and (b) *m/z* 64 from $\mathbf{1\text{-}d_2}^{\bullet +}$.



Scheme 1.

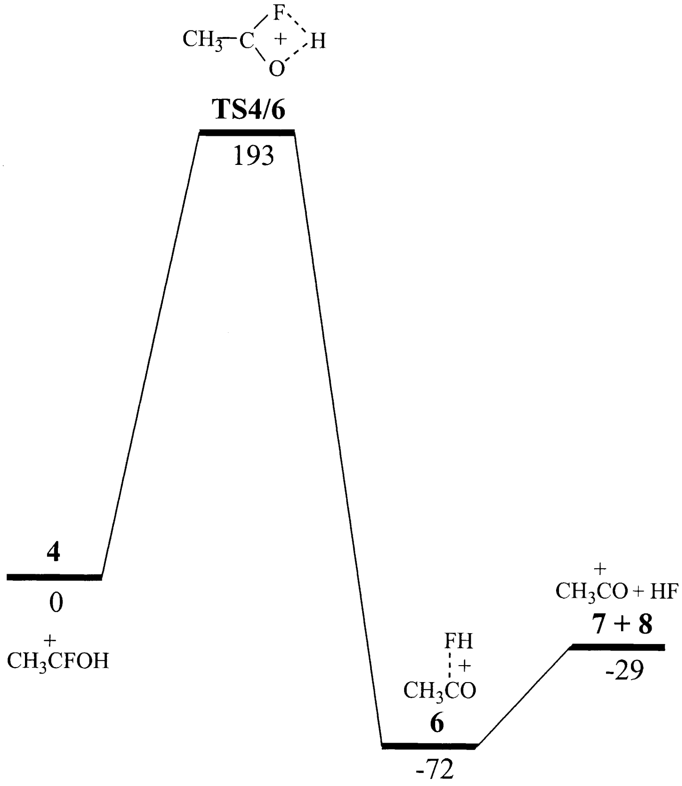


Fig. 3. Potential energy diagram for the loss of HF from CH_3C^+FOH (*m/z* 61) calculated at the MP2/6-311+G(d,p) level of theory.

158 Da) are *m/z* 43 (base peak), *m/z* 113 (83%), and *m/z* 63 (31%). The ion with *m/z* 43 is CH_3CO^+, and may be produced by various mechanisms [11]. The ion with *m/z* 113 is most likely $CH_3C^+(CF_3)OH$ produced from the molecular ion by loss of $COOH^{\bullet}$. Fig. 1 shows the MIKE spectrum of the ion with *m/z* 113. This ion decomposes into ions with *m/z* 93, *m/z* 63, and *m/z* 43.

At first, we would like to concentrate on the formation and the fragmentation of the ion with *m/z* 63. The most likely candidate for loss of 50 Da from the precursor (*m/z* 113) is difluorocarbene, CF_2. This quite stable carbene has a singlet ground state ($^1A_1$). The lowest triplet state ($^3B_1$) is ca. 240 kJ mol^{-1} higher in energy [15–18]. The putative molecular formula of the ion, $C_2H_4FO^+$, was confirmed by accurate mass determination under high resolution conditions, thereby excluding the alternative neutral losses of CH_3FO (or $HF + H_2CO$).

Fig. 2(a) shows the MIKE spectrum of the *m/z* 63 ion. This ion decomposes exclusively by loss of HF, and the corresponding peak is composite. The translational energy release values ($T_{0.5}$) for the broad and narrow components are estimated to be 0.83 eV and <1 meV, respectively. This indicates that two distinct mechanisms for the loss of HF with completely different $T_{0.5}$ values participate in this decomposition [19]. In the mass spectrum, the peak at *m/z* 63 shifts to *m/z* 64 upon substituting the hydroxy hydrogen atom with deuterium. Fig. 2(b) shows the MIKE spectrum of the ion with *m/z* 64 from **1-$\mathbf{d_2}$**. In this case, a composite peak due to the loss of DF is observed. Thus, the hydrogen (deuterium) atom contained in the leaving HF (DF) molecule originates from the incipient hydroxyl group. The $T_{0.5}$ values, as well as the intensity ratio of the broad and the narrow components are identical within experimental uncertainty in the two cases (Fig. 2).

The first mechanism for CF_2 loss we will consider is the route (**2**) → (**3**) → (**4**) of Scheme 1, where all the reaction paths concerned in this paper are summarized. The CH_3C^+FOH (**4**, *m/z* 63) ion so formed

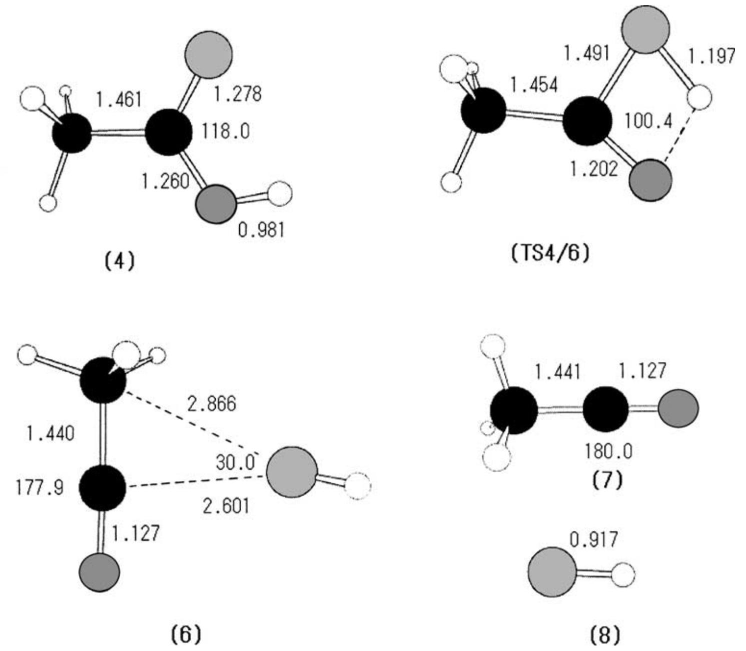


Fig. 4. Optimized (MP2/6-311+(d,p)) structure of species involved in the reactions of Fig. 3. Bond distances and angles are in angstrom (Å) and degree (°) units, respectively.

may then loose HF according to (**4**) → (**6**) → (**7**). The quantum chemical calculations of the latter part of the process came out with quite interesting results. The schematic potential energy diagram obtained by MP2/6-311+G(d,p) is shown in Fig. 3. The energy data and structures are presented in Table 1 and Fig. 4, respectively.

The two isomeric ions, CH_3C^+FOH (**4**) and $CH_3CO^+\cdots FH$ (**6**), are formally the two possible forms of protonated acetyl fluoride. It is worth to notice that protonation on the "hard" fluorine gives the lowest energy isomer. This is in stark contrast to, for example, amides and acids where the most basic site is the carbonyl oxygen [20]. Obviously, formation of

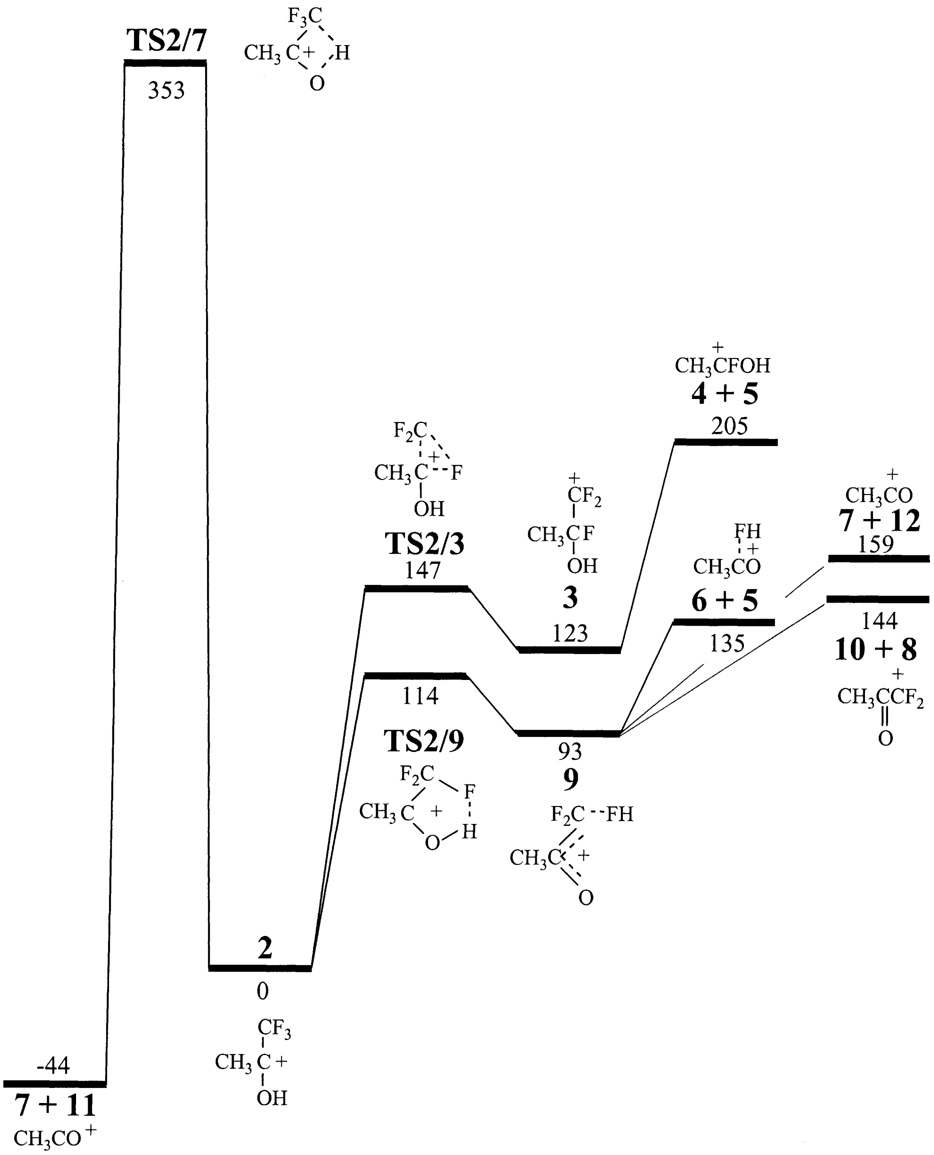


Fig. 5. Potential energy diagram for the decomposition of the *m*/*z* 113 ion calculated at the MP2/6-311+G(d,p)//MP2/6-31G(d,p) level of theory. Structures of the leaving neutrals are omitted from the figure. They are CF_2 (**5**), HF (**8**), CHF_3 (**11**), and $CF_2\cdots HF$ (**12**).

Table 1
Absolute and relative energies for decomposition of protonated acetyl fluoride (**4**)

	HF/6-31G(d,p)		MP2/6-31G(d,p)		MP2/6-311+G(d,p)	
	Total energy[a]	Relative energy[b]	Total energy[a]	Relative energy[b]	Total energy[a]	Relative energy[b]
CH_3C^+FOH (**4**)	−252.041519	0	−252.651014	0	−252.780001	0
$CH_3CO^+ \cdots FH$ (**6**)	−252.042023	−1	−252.662055	−29	−252.807439	−72
CH_3CO^+ (**7**)	−152.020966		−152.456032		−152.521312	
HF (**8**)	−100.002294		−100.185470		−100.269626	
7 + **8**	−252.023260	48	−252.641502	25	−252.790938	−29
TS4/6	−251.938569	270	−252.578068	191	−252.706514	193

[a] In Hartrees, scaled zero point vibrational energies included.
[b] In $kJ\,mol^{-1}$.

the strong H–F bond is the driving force. Upon this, the covalent C–F bond of the acid fluoride is substituted by an ion–dipolar interaction. According to the MP2/6-311+G(d,p) calculation, cleavage of the complex **6** requires 43 $kJ\,mol^{-1}$. This binding energy is rather independent of the wavefunction (Table 1).

The complex **6** bears considerable resemblances to fluorine protonated fluorobenzene [10]. This species is predicted to be even more poorly bounded, by 28 $kJ\,mol^{-1}$ (MP2/6-31G(d)//HF/6-31G(d)). The translational energy releases which accompany the direct dissociation of ion–dipole complexes are typically very small [21], whereas reactions with substantial barriers resulting from simultaneous bond making and bond breaking give high $T_{0.5}$ values [22]. Based upon this idea, we propose that the broad and the narrow

Table 2
Absolute and relative energies for decomposition of the ion with *m*/*z* 113 (**2**)

	HF/6-31G(d,p)		MP2/6-31G(d,p)		MP2/6-311+G(d,p)//MP2/6-1G(d,p)	
	Total energy[a]	Relative energy[b]	Total energy[a]	Relative energy[b]	Total energy[a]	Relative energy[b]
$(CH_3)(CF_3)C^+OH$ (**2**)	−488.763348	0	−489.840408	0	−490.110486	0
$(CH_3)(CF_2)C^+FOH$ (**3**)	−488.712077	135	−489.789367	134	−490.063684	123
CH_3C^+FOH (**4**)	−252.041519		−252.651014		−252.779779	
CF_2 (**5**)	−236.653604		−237.104745		−237.252720	
$CH_3CO^+ \cdots FH$ (**6**)	−252.042023		−252.662055		−252.806385	
CH_3CO^+ (**7**)	−152.020966		−152.456032		−152.520975	
HF (**8**)	−100.002294		−100.185470		−100.269599	
$CH_3COCF_2{}^+ \cdots FH$ (**9**)	−488.709839	140	−489.793799	122	−490.075228	93
$CH_3COCF_2{}^+$ (**10**)	−388.682989		−389.581120		−389.786159	
CHF_3 (**11**)	−336.747686		−337.389753		−337.606230	
$CF_2 \cdots FH$ (**12**)	−336.661910		−337.298269		−337.528805	
4 + **5**	−488.695123	179	−489.755760	222	−490.032499	205
6 + **5**	−488.695627	178	−489.766801	193	−490.059106	135
10 + **8**	−488.685283	205	−489.766590	194	−490.055758	144
7 + **11**	−488.768652	−14	−489.845784	−14	−490.127206	−44
7 + **12**	−488.682876	211	−489.754301	226	−490.049780	159
7 + **5** + **8**	−488.676864	227	−489.746247	247	−490.043295	176
TS2/3	−488.691544	188	−489.784163	148	−490.054417	147
TS2/9	−488.699007	169	−489.790401	131	−490.067019	114
TS2/7	−488.582636	474	−489.702514	362	−489.976030	353

[a] In Hartrees, scaled zero point vibrational energies included.
[b] In $kJ\,mol^{-1}$.

components of the peaks of Fig. 2 correspond to dissociation of CH_3C^+FOH (**4**) and $CH_3CO^+ \cdots FH$ (**6**), respectively.

In order to find out whether both **4** and **6** may be formed upon electron ionization of $CH_3C(CF_3)(OH)COOH$ (**1**), a new series of quantum chemical calculations were performed. Two different routes for CF_2 eliminations were investigated in detail, i.e., (**2**) → (**3**) → (**4**) and (**2**) → (**9**) → (**6**) in Scheme 1. The results with MP2/6-311+G(d,p)// MP2/6-31G(d,p) are presented in Fig. 5, together with the results for other decomposition processes. The energy data and structures are presented in Table 2 and Fig. 6, respectively. The first CF_2 elimination starts by a 1,2 F-shift to give isomer **3**, which then decomposes by loss of CF_2 to give CH_3C^+FOH (**4**). The second CF_2 elimination mechanism is initiated by a proton shift from oxygen to one of the three fluorines. The result is the complex $CH_3COCF_2{}^+ \cdots FH$ (**9**), which then may loose CF_2 to give $CH_3CO^+ \cdots FH$

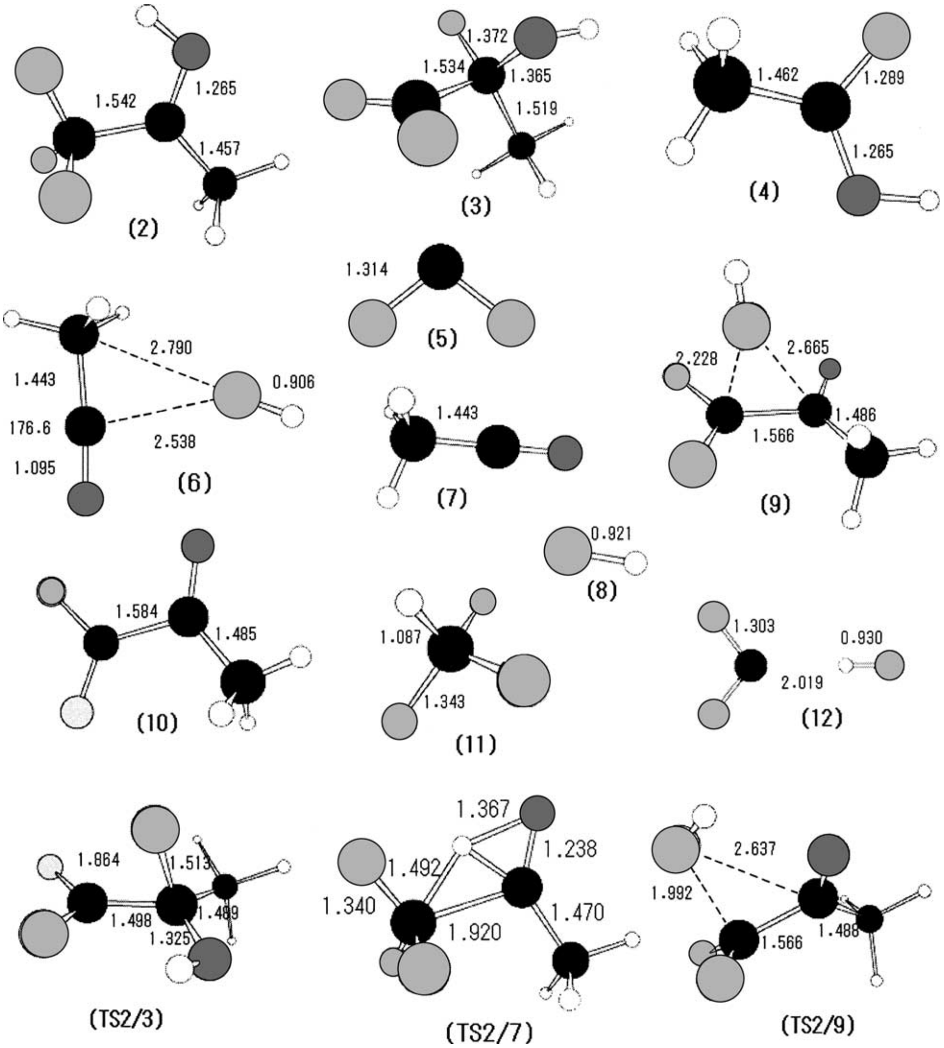


Fig. 6. Optimized (MP2/6-31G(d,p)) structure of species involved in the reactions of Fig. 5. Bond distances and angles are in angstrom (Å) and degree (°) units, respectively.

(**6**), HF to give $CH_3COCF_2{}^+$ (**10**, *m*/*z* 93) or (C, H, F_3) to give CH_3CO^+ (**7**, *m*/*z* 43). Fig. 5 shows that the energy needed for the production of CH_3C^+FOH (**4**) is higher than that of $CH_3CO^+\cdots FH$ (**6**) by about 70 kJ mol^{-1}. Thus, at least in the ion source, both isomers of the ions with *m*/*z* 63, **4** and **6**, are likely products.

As evident from Fig. 1, formation of the acetyl cation having *m*/*z* 43 is more favorable than any of the two isomers with *m*/*z* 63. Our first assumption was that CH_3CO^+ is formed by the loss of trifluoromethane (**11**) through route (**2**) → (**7**) in Scheme 1. However, elimination of this molecule is prevented by the barrier resulting from passage through **TS2/7** (Fig. 5). We, therefore, were led to the realization that formation of CH_3CO^+ is due to the pathway (**2**) → (**9**) → (**7**) with the loss of $CF_2\cdots HF$ [23], or alternatively $HF + CF_2$. Another possibility for the formation of CH_3CO^+ (**7**) from $CH_3COCF_2{}^+\cdots FH$ (**9**), where CHF_3 formed by the insertion of CF_2 into HF is expelled, was also considered, but the critical energy for this process is estimated to be higher than that for (**2**) → (**9**) → (**7**) in Scheme 1 by about 40 kJ mol^{-1}.

In Fig. 1, the peak at *m*/*z* 63 due to the loss of CF_2 is very weak, in spite of the lowest critical energy. Product distribution in the MIKE spectrum depends on several factors: (a) The exact form of the energy distribution function, which in this case is largely unknown. (b) The critical energy for formation of the particular product ions. (c) Entropical factors, i.e., tightness, of the key transition states. When CF_2 is expelled from the intermediate **9**, the HF moiety must be left behind. In order for this decomposition to occur, a highly congested configuration is needed. Thus, the loss of CF_2 is an entropically unfavorable process. Furthermore, $CH_3CO^+\cdots FH$ (**6**) is liable to decompose into CH_3CO^+ and HF, with the barrier being 43 kJ mol^{-1} (MP2/6-311G+(d,p)) or 41 kJ mol^{-1} (MP2/6-311G+(d,p)//MP2/6-31G(d,p)). Thus, a certain portion of $CH_3CO^+\cdots FH$ (**6**) formed from **2** would decompose further into CH_3CO^+. These are probably the reasons why the peak due to the loss of CF_2 is weak in spite of having the lowest critical energy.

In Fig. 2, the yields of the broad and narrow components of *m*/*z* 43 seem to be roughly equal, although the isomer **6** is far more favorably formed than the isomer **4**. This would also be concerned with the fragility of the isomer **6**. The MIKE experiment samples the decomposition in the third field-free region (3rd FFR) of the EBE instrument, and a large portion of **6** would decompose before entering the 3rd FFR because of its fragility.

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