

Theoretical study on potential energy surface of the C₂HF₂O and C₂F₃O radicals

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Abstract

The potential energy surface of the C₂HF₂O and C₂F₃O radicals were computed at the B3LYP density functional and the CCSD(T) ab initio levels of theory. For C₂HF₂O radical, the resonance dominating methyl radical (HFC'–CF=O) is found to be the most stable isomer, followed by the difluoro acetyl ([F₂HCC=O]) isomer by 9.9 kcal/mol. However, the most stable C₂F₃O radical isomer is trifluoro acetyl radical ([F₃CC=O]), followed by the methyl isomer (F₂C'–CF=O) by 1.8 kcal/mol. Both acetyl radicals are relatively stable towards dissociation of being endothermic with low barriers, while other transformations (cyclization, hydrogen, and fluorine arrangements) are endothermic and have very high barriers.

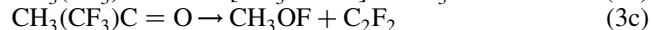
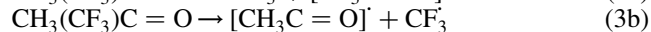
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Keywords: Theoretical calculations; Isomerization; Potential energy surface; C₂HF₂O and C₂F₃O radicals

1. Introduction

Hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) are being used as substitutes for chlorofluorocarbons (CFC) and halogens (chlorofluorobromocarbons) in air condition and refrigeration applications because of the depletion of ozone layer. The short lifetimes of the HCFC make them much less damaging to the ozone layer than the CFC. In contrast to chlorine and bromine, fluorine has been known to be benign toward the ozone layer [1]. However, many of the substitutes HCFC and HFC contain trifluoromethyl groups formed from decomposition of fluorocarbons such as HFC-134a (tetrafluoroethane-CF₃CFH₂), which would mimic chlorine to deplete ozone [2]. Trifluoroacetic acid (TFA, CF₃COOH), formed by atmospheric oxidation of HFC-134a [3,4], is widespread in the aqueous environment, such as in fog, rain, rivers, lakes, groundwater and most significantly, in seawater [5,6]. Because fluorocarbons are particularly good absorbers of

infrared radiation, TFA accumulation will promote warming of the earth surface, and can have profound effects on climate. Therefore, in order to reduce undesirable impact from fluorocarbons, it is necessary to understand the stability and degradation of HFC and HCFC decomposition products. Difluorovinoxy ([CHF=CFO]'), the resonance structure will be discussed later) and trifluoroacetyl ([CF₃C=O]') radicals are such intermediates in the atmospheric degradation of several HFCs and HCFCs [7], and are generated from the following reactions, respectively [8,9].



Previous investigations analyzed the potential energy surface of [C₂H₂FO] and identified eight isomers to have considerably kinetics stability [10], and the existence of [C₂H₂FO] has been observed by laser-induced fluorescence spectroscopy (LIF) [11,12]. Recently, *trans*- and *cis*-CHF=CFO radicals were observed by LIF spectroscopy, and their structures were

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calculated at the CASSCF/6-31G(d) level [12]. But no theoretical studies on their isomerization and dissociation stability were done so far.

For C_2F_3O radical, trifluoroacetyl radical $F_3CC=O^{\cdot}$ was found in the IR multiphoton dissociation of CF_3COCl and the reaction of $CF_3 + CO$ [13], in the intense laser excitation of trifluoroacetone [9], and in the photodissociation of TFA. Moreover, $F_3CC=O^{\cdot}$ can be degraded as $CF_3C(O)O^{\cdot}$ [14] and the kinetics of the reaction of $F_3CC=O^{\cdot}$ with O_2 indicated 99.5% of the loss of $F_3CC=O$ radical in the atmosphere reacted with O_2 and produced $CF_3C(O)O_2$, and 0.5% of that dissociated to CF_3 and CO . Furthermore, the product $CF_3C(O)O_2$ can react with NO and produce $CF_3C(O)O^{\cdot}$ and NO_2 [15]. These experimental and theoretical studies suggest the importance of trifluoroacetyl radical for the studies of the degradation of HFC and HCFC. However, no theoretical work has been done on electron states and kinetic stability of various isomers of C_2F_3O radical to our best knowledge. Therefore, we focus on a detailed study for electron states and the potential energy surface of C_2HF_2O and C_2F_3O radicals, and analyze their spin density and kinetic stability to aid future identification.

2. Computational methods

All calculations were carried out using the GAUSSIAN 98 program package [16]. The optimized structures and harmonic frequencies of the local minima, transition state structures and dissociated products are obtained at the (U)B3LYP/6-311G(d,p) level. Frequency calculations identify minimum structures with all real frequencies, while transition states with only one imaginary frequency, and also provide zero-point vibration energies (ZPVE). To confirm whether the obtained transition states connect the right isomers, the intrinsic reaction coordinate (IRC) calculations are performed at the (U)B3LYP/6-311G(d,p) level. The final relative energies are calculated at the (U)CCSD(T)/6-311G(d,p) level using the (U)B3LYP/6-311G(d,p) geometries with ZPVE corrections. The calculated total harmonic vibrational frequencies, infrared intensities, dipole moments, and rotational constants are shown in the Supporting Information.

3. Results and discussions

C_2HF_2O radicals. For the C_2HF_2O radicals, 10 minimum isomers and 11 transition states are obtained at the (U)B3LYP/6-311G(d,p) level. The computed total electronic and relative energies are summarized in Table 1. As shown in Fig. 1, structures **1** and **1'** are *cis* and *trans* isomers of $[(HFC=CHO)^{\cdot}]$, and their energy difference is negligible (0.1 kcal/mol). Both isomers can be considered as the resonance structures of the vinoxy and methyl radicals (as indicated by the calculated spin density

Table 1

Total (E_{tot} , a.u.) and relative (E_{rel} , kcal/mol) of the isomers, dissociation products and transition states of C_2HF_2O radical

Species	E_{tot}^a	E_{tot}^b	E_{rel}^c
1	−351.76490	−350.99204	0.0
1'	−351.76435	−350.99169	0.1
2	−351.74692	−350.97202	12.5
3	−351.74135	−350.97632	9.9
4	−351.69697	−350.93038	38.6
5	−351.68920	−350.92131	44.8
5'	−351.69048	−350.92256	44.0
6	−351.69139	−350.91929	45.8
7	−351.67990	−350.90937	51.5
7'	−351.67961	−350.90859	52.2
P₁ ($CHF_2 + CO$)	−351.72988	−350.97337	8.8
P₂ ($FCCF + OH$)	−351.58122	−350.81577	106.0
P₃ ($CFH + CFO$)	−351.60686	−350.84492	87.1
P₄ ($CF_2 + CHO$)	−351.65163	−350.89016	58.3
TS(1/1')	−351.74094	−350.97227	11.8
TS(1/3)	−351.67917	−350.89262	60.8
TS(1/5)	−351.66270	−350.88618	65.4
TS(1/7')	−351.65242	−350.87763	69.1
TS(1/5')	−351.66285	−350.88754	64.3
TS(2/2)	−351.71876	−350.95209	24.6
TS(2/3)	−351.66310	−350.88581	63.7
TS(2/4)	−351.67155	−350.89604	60.0
TS(2/6)	−351.62361	−350.84709	87.2
TS(3/P₁)	−351.72519	−350.96105	17.4
TS(6/7)	−351.57997	−350.79704	120.3
Allyl radical/ C_{2v}	−117.29613	−116.95270	0.0
Allyl radical/ C_s (TS)	−117.26881	−116.92894	13.9

^a At (U)B3LYP/6-311G(d,p).

^b At (U)CCSD(T)/6-311G(d,p)/(U)B3LYP/6-311G(d,p).

^c At (U)CCSD(T)/6-311G(d,p)/(U)B3LYP/6-311G(d,p) + ZPVE ((U)B3LYP/6-311G(d,p)).

discussed below), and they can interchange via the rotation of the formal central C–C double bond. However, the central C–C bonds (1.432–1.434 Å) and the C–F bonds of the CFH group (1.321–1.319 Å) are longer and shorter than those (1.326 vs. 1.348/1.350 Å) of *cis*-1,2-difluorovinyl alcohol (**1'-H**, *cis*-HFC=CF(OH)), but the C–C bond in **1** is much shorter than that (1.535 Å) in the related acetyl aldehyde (**3-H**). These geometric differences indicate the delocalization of the single electron over the whole molecule. As a consequence, the rotational barrier should be smaller than those of substituted ethylenes. Indeed, the rotation transition state of the central C–C bond with an imaginary frequency of $196 i \text{ cm}^{-1}$ is located and the corresponding barrier is only 11.8 kcal/mol. This indicates a small, but still significant delocalization effect in **1** or **1'**. On the basis of the C–C bond length and the related rotation barrier, one might conclude that corresponding methyl radical ($HFC^{\cdot}-CF=O$) dominates the resonance structure, there isomer **1** or **1'** represents a methyl radical rather than a vinoxy isomer. Similarly, the experimental results of the rotational barrier for $[1\text{-}^2\text{H}]$ allyl radical is $15.7 \pm 1.0 \text{ kcal/mol}$ at 50–110 °C [17], and the corresponding calculated values is 13.9 kcal/mol at our CCSD(T) level,

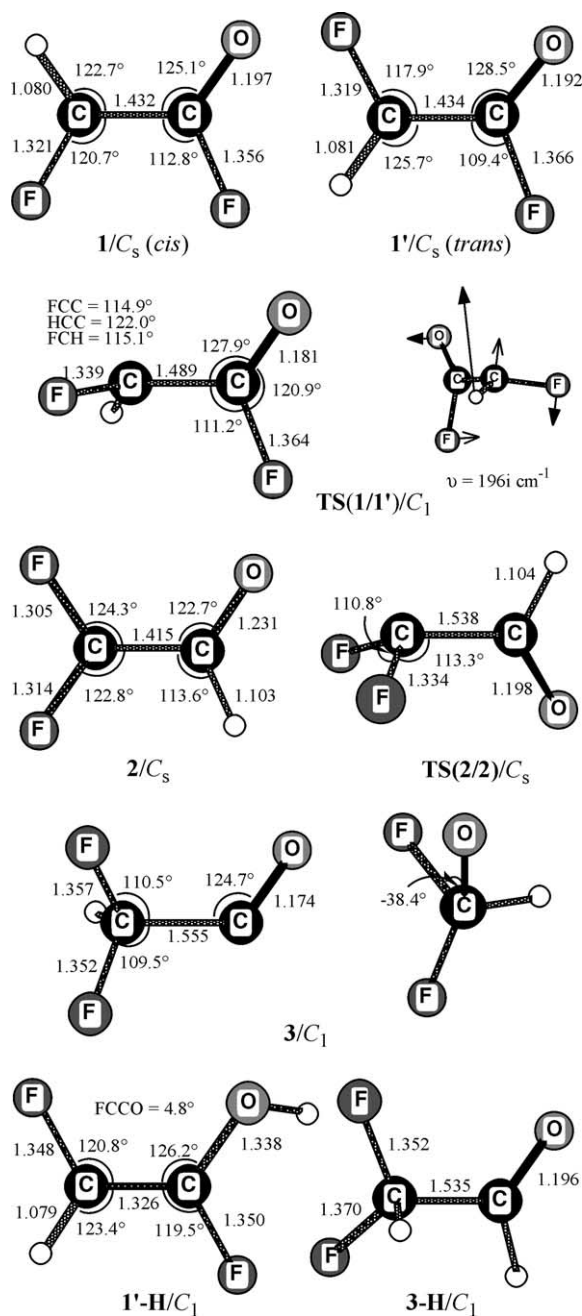


Fig. 1. (U)B3LYP/6-311G(d,p) optimized structures of C_2HF_2O isomers (in Å and degree).

and in agreement with the previous MP4/6-31G computation [18]. For comparison, we also calculated the rotational barrier of *trans*-difluoroethene to be 74.3 kcal/mol at the same level. Moreover, the experimentally determined rotational barrier of ethylene is 64 kcal/mol [19], and the calculated values of $H_2C=CH_2$, $F_2C=CH_2$, and $F_2C=CF_2$ are 65.4, 63.2, and 51.7 kcal/mol, respectively, at the GVB(6/12)/6-31G(d,p) level [20].

In the transition state (TS(1/1')), the carbon center at -CFO is nearly planar with a dihedral angle of 179.4°, and the dihedral angles of OCCF and FCCF are -98.6°, and 82.0°, indicating that the CFO group is rotated by

around 90° and also the turn off of delocalization. The second carbon center at -CFH is somewhat pyramidal rather than planar, and the sum of the three bond angles is 352.0°. This can be the result of the localization of the single electron at the -CFH group. This is also supported by the two different C-F bond lengths, e.g., C-F bond at -CFO of 1.364 Å is longer than at -CFH by 1.339 Å, and C=O bond of 1.181 Å is also shorter than those (1.197/1.192 Å) in the ground states (1/1'). In line with these bond parameters changes, the calculated atomic spin density of 0.930 at the carbon center of -CFH shows the localization of the single electron in the transition state. For comparison, we have also calculated the spin density in the ground state (1) with 0.766 at carbon (CFH) and 0.236 at oxygen. The spin densities for these isomers are also shown in Fig. 2. This corresponds the HOMO of allyl radical in which the orbital coefficients are on the two terminal carbons [21]. This spin density indicates the dominant resonance structure of the methyl over the corresponding vinoxy radical.

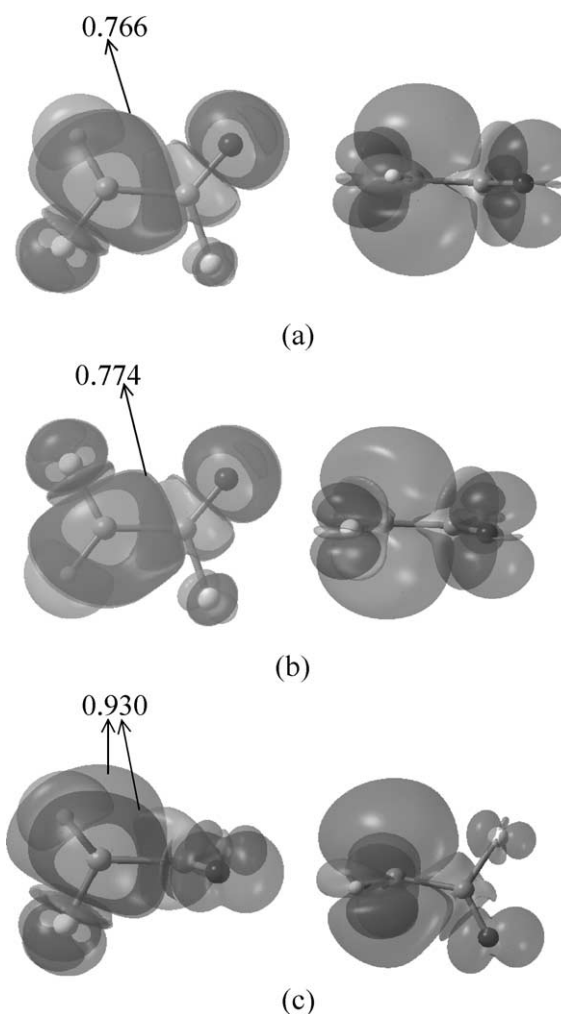


Fig. 2. Illustration of the spin density of C_2HF_2O isomers at (U)B3LYP/6-311G(d,p) level.

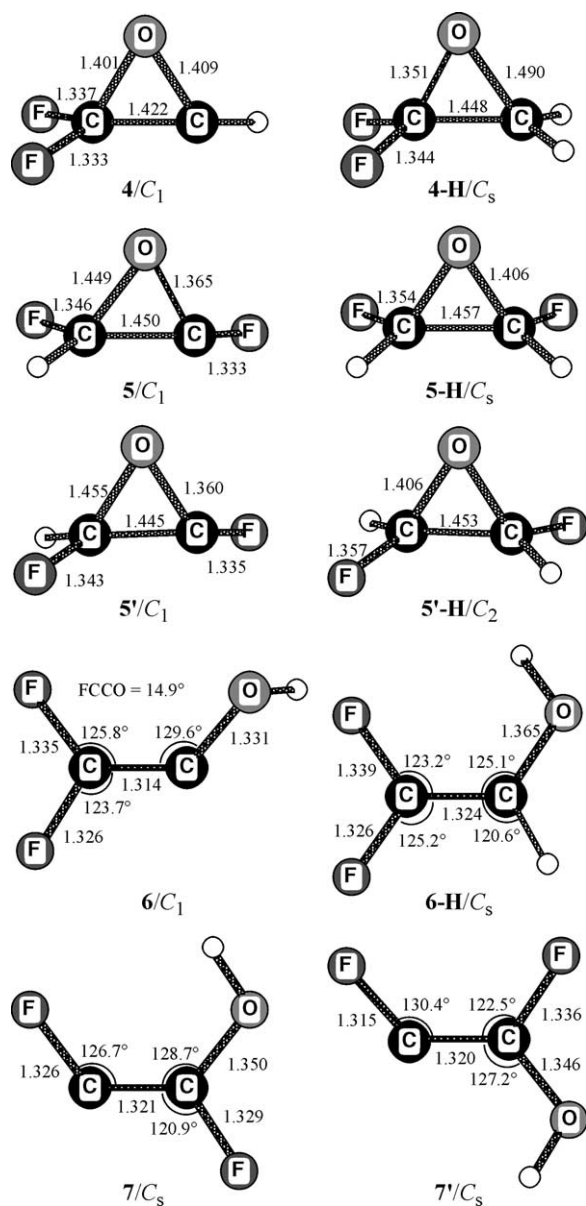


Fig. 3. (U)B3LYP/6-311G(d,p) optimized structures of C_2HF_2O isomers (in Å and degree).

In addition to **1**, which is considered as the global minimum on the potential energy surface, we also have computed other structural isomers **2–7**, which are shown in Fig. 3. As given in Table 1, **2** and **3** are the next stable isomers, but higher in energy than **1** by 12.5 and 9.9 kcal/mol.

As expected, the structural parameters of **2** are close those of **1** and **1'** and the single electron in **2** is also delocalized with the calculated spin density of 0.579 at the F_2C carbon center, and 0.381 at the oxygen center. The rotation barrier of formal $C=C$ center bond in **2** via the transition state **TS(2/2)** is 12.1 kcal/mol, comparable to the value of **1** (11.8 kcal/mol). Therefore, **2** is a substituted methyl radical ($F_2C-CH=O$). In **TS(2/2)** the formyl ($-CHO$) is planar, while F_2C- is pyramidal, indicating

the localization at the F_2C- carbon center with the calculated spin density of 0.825.

In the acetyl radical **3**, the $C-C$ (1.555 Å) and $C-O$ (1.174 Å) bond lengths are longer and shorter than those (1.535 vs. 1.196 Å) in of the corresponding aldehyde (**3-H**, F_2HCCHO). This also shows that the single electron delocalizes, e.g. 0.118 at the F_2CH carbon center, 0.271 at the oxygen center, and 0.577 at the CO carbon center, and **3** is indeed an acetyl radical ($[F_2HCC=O]$).

Isomers **4** and **5** have radicals from the corresponding oxiranes, and their radical centers are substituted by hydrogen or fluorine. The optimized structures including their saturated counterparts are shown in Fig. 3 for comparison. As structural isomers, they are much higher in energy than **1** and **1'**. The single electron in **4** is mostly located at the carbon center, as indicated by the calculated spin density (0.825) and only slightly at the oxygen center (0.191), therefore, **4** is a type of σ -radical, and the same is also for **5** (0.756 vs. 0.130) and **5'** (0.761 vs. 0.125), respectively.

As shown in Fig. 3, it is clear to see that the bonds of oxygen to radical carbon is shorter than those of oxygen to saturated carbon, and they are shorter and longer than the corresponding $C-O$ bonds of their saturated counterparts (**5-H** and **5'-H**). The $C-C$ and $C-F$ bonds of the radical species are shorter than those of their saturated counterparts.

Isomers **6–7** are vinyl radicals from the corresponding alkenes (**6-H** and **1/1'-H**). Radical **6** has somewhat delocalized character with spin density of 0.824 at the carbon center and 0.170 at the oxygen center, while **7** and **7'** are localized σ -radical with spin density mainly at the carbon centers (0.979 and 0.942). Compared to their saturated counterparts, the bond lengths of the radical species change only slightly.

To inspect the kinetic stability of C_2HF_2O radical, the entire potential energy surface was constructed according to the relative energy of the isomers, dissociation products, and transition states as shown in Fig. 4 and the relative energetic relations are shown in Fig. 5. Apart from the internal rotation between **1** \rightarrow **1'** with a lower barrier of 11.8 kcal/mol, there are ring closure processes **1** \rightarrow **TS(1/5)** \rightarrow **5**; **1'** \rightarrow (**TS(1'/5')**) \rightarrow **5'** and **2** \rightarrow (**TS(2/4)**) \rightarrow **4**, and the energy barriers are 65.4, 64.2; 47.5 kcal/mol, and the cyclization enthalpies are endothermic by 47.7, 46.5, and 31.0 kcal/mol, respectively. This indicates the high kinetic stability of isomers **1** and **2** towards cyclization.

The difluoroacetyl radical (**3**) can be considered as the product of fluorine or hydrogen shifts from **1** and **2** with high barriers (50.9 kcal/mol for **TS(1/3)** and 53.8 kcal/mol for **TS(2/3)**, respectively). However, **3** can dissociate easily with a small barrier of 7.5 kcal/mol through the transition state (**TS(3/P₁)**) into CHF_2 radical and CO , whereas the dissociation of **1** into singlet fluorocarbon (FHC) and fluoroformyl radical (FCO') or **2** into singlet difluorocarbon (F_2C) and formyl (HCO') radical has no barriers, but the corresponding reactions are endothermic

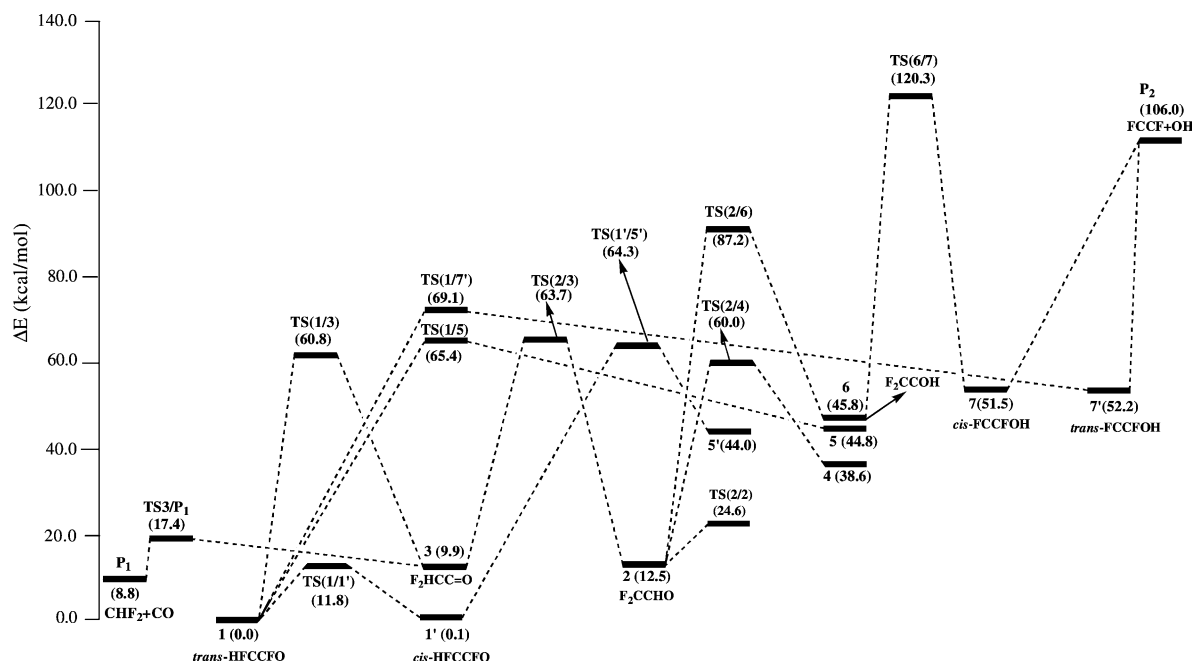


Fig. 4. Potential energy surface of C_2HF_2O at the (U)CCSD(T)/6-311G(d,p)//(U)B3LYP/6-311G(d,p) + ZPVE ((U)B3LYP/6-311G(d,p)) level.

by 95.4 and 55.6 kcal/mol, respectively. Therefore, the kinetic stability of isomer **3** is governed by its dissociation to $CHF_2 + CO$.

Vinyl radicals **6** and **7** can be considered as the products of 1,2-hydrogen shift from vinoxy radical **2**, and of 1,3-hydrogen shift from **1** with the barriers of 74.7 and 69.1 kcal/mol, respectively. The related transition states are **TS(2/6)** and **TS(1/7')**. **7** and **7'** are *cis* and *trans* isomers. Moreover, **6** can be considered as the product of 1,2-fluorine shift from **7**, through the transition state **TS(6/7)**, and the barrier is 74.5 kcal/mol.

C_2F_3O radicals. For the C_2F_3O radical, there are only three isomers as minimum structures, the trifluoroacetyl radical (**8**), the methyl radical (**9**, deduced from **1** and **2**) and the cyclic **10**. The structures and energies of these isomers and transition states as well as their saturated counterparts (**8-H**, **9-H** and **10-H**) are given in Fig. 6, and Table 2 as well as Fig. 7, respectively. The lowest energetically isomer is the trifluoroacetyl radical **8**, followed by **9** and **10** by 1.8 and 39.6 kcal/mol.

As shown in Fig. 6, we have computed both *syn* and *anti* isomers for trifluoroacetyl radical (**8**), and the *syn* isomer is found to be an energy minimum, while the *anti* isomer is a transition state for the internal C–C bond rotation. However, the rotation barrier is negligible (0.2 kcal/mol). The single electron in **8** is located mainly on the carbon (0.580) center of CO, followed by oxygen (0.269) and the second carbon center (0.125). While the corresponding spin density of **TS(8/8)** is 0.580, 0.267 and 0.124. In comparison with the saturated **8-H**, the bond of oxygen to radical carbon (1.171 Å) is shorter than that of

oxygen to saturated carbon (1.194 Å). So **8** has somewhat delocalized character.

The situation of radical **9** mimics that of the methyl radical **1**, and the formal C=C double bond (1.427 Å) is close to that of **1** (1.432 Å), but much longer than of **1** the saturated **9-H** (1.325 Å) and shorter than the C–C single bond in **8-H**. This indicates the single electron is strongly delocalized, as supported by the lower internal rotation barrier by 7.8 kcal/mol. The related transition state is C_s symmetrical, and the CFO carbon center is planar, while that of F_2C is pyramidal, and the sum of the bond angle is 337.1°. This reveals that the radical center is at F_2C and the calculated spin density is 0.831 at carbon and 0.136 on the two fluorine centers. Isomer **10** is the radical of the corresponding oxirane **10-H**. On the basis of radical **4** and **5**, one can expect that **10** is also a σ -type radical with spin densities of 0.765 at the carbon center and 0.131 at the oxygen center.

Trifluoroacetyl isomer **8** ($CF_3C=O$) needs low barrier (8.7 kcal/mol) to dissociate into $F_3C\cdot$ and CO. Isomer **9** (F_2CCFO) lies in relatively low potential well, and can be connected with four isomers such as isomer **8** and **9** through the transition states **TS(8/9)** and **TS(9/10)** with the barriers of 61.9 and 56.6 kcal/mol, respectively. The dissociation to difluoroketene ($F_2C=C=O$) and F radical via the transition state (**TS(9/P4)**) need 84.7 kcal/mol. So isomer **9** has considerably kinetic stability. Isomer **10** (F_2COCF) of the three membered CCO ring with exocyclic C–F bonding need to overcome 56.6 kcal/mol to convert to the isomer **9** through the transition state **TS(9/10)**, and the cyclization enthalpies is 42.4 kcal/mol.

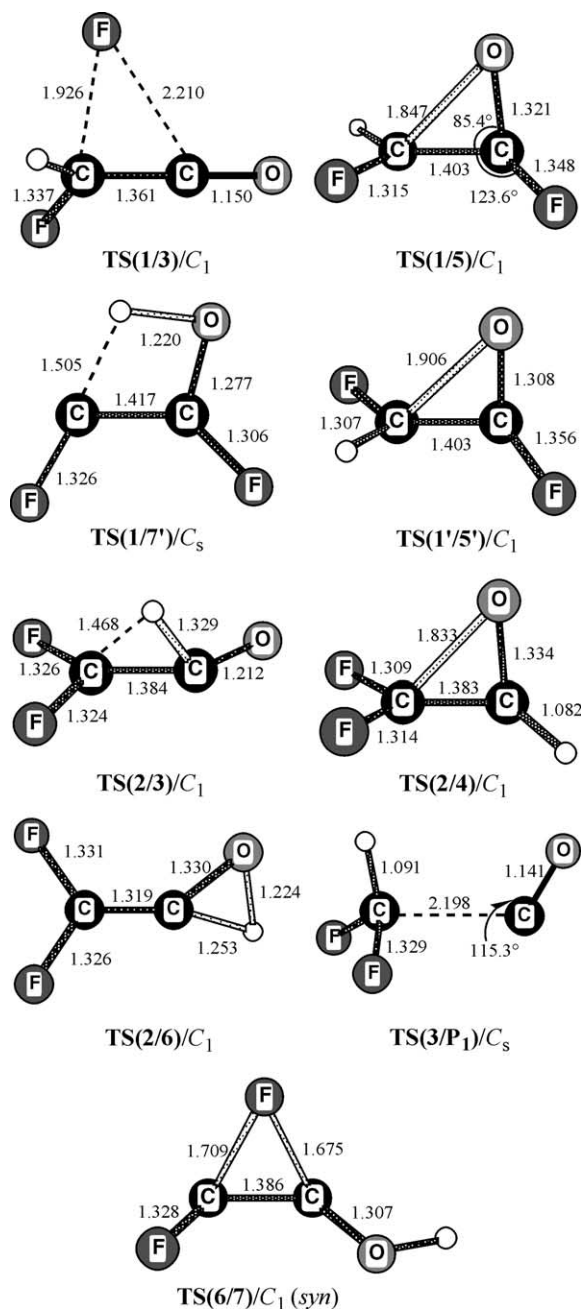


Fig. 5. B3LYP/6-311G(d,p) optimized structures of C_2HF_2O transition states (in Å and degree).

4. Conclusion

The potential energy surface of two fluororadicals, C_2HF_2O and C_2F_3O have been computed at the (U)B3LYP density functional and (U)CCSD(T) electron correlated ab initio levels of theory. For C_2HF_2O , the most stable isomer is the resonance dominating methyl radical ($FHC-CF=O$), followed by fluoroacetyl radical [$F_2HCC=O$] $^{\cdot}$ and ($F_2C-CH=O$) isomer by 9.9 and 12.5 kcal/mol, respectively. The cyclic isomers are much higher in energy. The rotation barriers of the methyl radical around the central C–C bond are much lower than those of

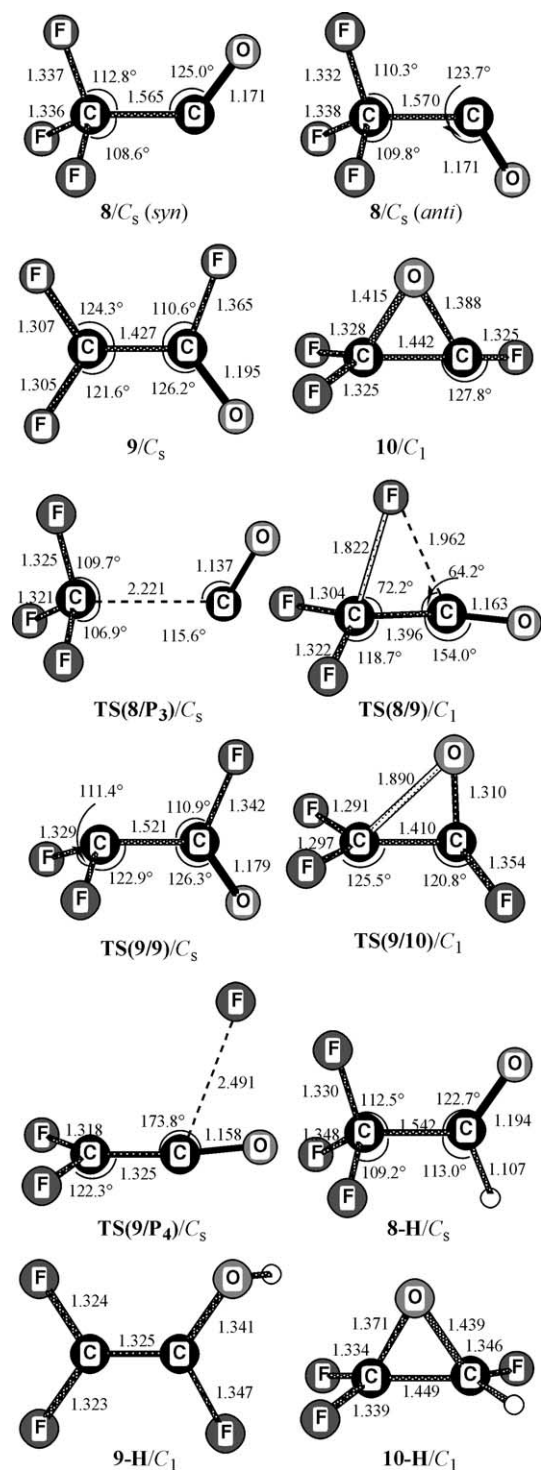


Fig. 6. (U)B3LYP/6-311G(d,p) optimized structures of C_2F_3O isomers and transition states (in Å and degree).

substituted ethylenes, indicating the delocalization of the single electron, as supported by the calculated spin densities. On the other hand, the most stable isomer of C_2F_3O is trifluoroacetyl radical [$F_3CC=O$] $^{\cdot}$, followed by the methyl radical ($F_2C-CF=O$), and the cyclic form is much higher in energy. It is found that both the acetyl radicals, [$F_2CHC=O$] $^{\cdot}$ and [$F_3CC=O$] $^{\cdot}$ are slightly stable

Table 2

Total (E_{tot} , a. u.) and relative (E_{rel} , kcal/mol) of the isomers, dissociation products and transition states of $\text{C}_2\text{F}_3\text{O}$ radical

Species	$E_{\text{tot}}^{\text{a}}$	$E_{\text{tot}}^{\text{b}}$	$E_{\text{rel}}^{\text{c}}$
8	−451.01736	−450.06448	0.0
9	−451.02655	−450.06267	1.8
10	−450.95859	−450.00195	39.6
P₅ ($\text{CF}_3 + \text{CO}$)	−451.00399	−450.05911	1.1
P₆ ($\text{F}_2\text{CCO} + \text{F}$)	−450.87994	−449.92658	84.6
P₇ ($\text{F}_2\text{COC} + \text{F}$)	−450.82309	−449.88196	112.3
TS(8/8)	−451.01637	−450.06381	0.2
TS(8/9)	−450.93540	−449.96060	63.7
TS(8/P₅)	−451.04363	−450.04787	8.7
TS(9/9)	−451.00746	−450.04974	9.6
TS(9/10)	−450.93553	−449.97042	58.4
TS(9/P₆)	−450.89464	−449.92406	86.5

^a At (U)B3LYP/6-311G(dp).

^b At (U)CCSD(T)/6-311G(d,p)/(U)B3LYP/6-311G(d,p).

^c At (U)CCSD(T)/6-311G(d,p)/(U)B3LYP/6-311G(d,p) + ZPVE ((U)B3LYP/6-311G(d,p)).

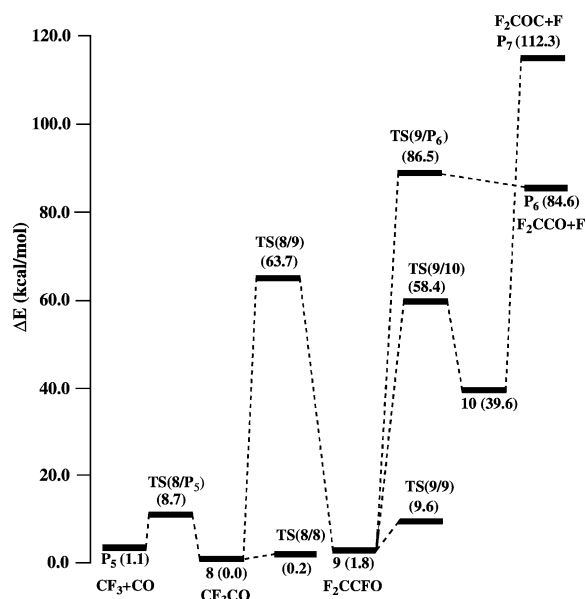


Fig. 7. Potential energy surface of $\text{C}_2\text{F}_3\text{O}$ at the (U)CCSD(T)/6-311G(d,p)/(U)B3LYP/6-311G(d,p) + ZPVE ((U)B3LYP/6-311G(d,p)) level.

towards dissociation into substituted methyl radical ($\text{F}_2\text{HC}^\bullet$ and $\text{F}_3\text{C}^\bullet$) with low barriers, while the cyclization, hydrogen and fluorine arrangements are very endothermic with high barriers.

5. Supplementary material

Tables of total harmonic vibrational frequencies, the infrared intensities, dipole moments as well as rotational constants for all systems are summarized. This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

Acknowledgements

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