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# Fluorofluoroxydioxirane and Other $CF_2O_3$ Isomers

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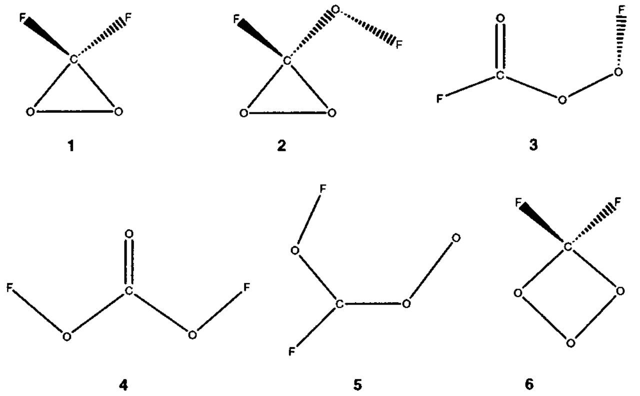
Seven structural isomers, and relevant transition states, on the lowest-energy spin-singlet potential energy surface of $CF_2O_3$ are characterized using correlated ab initio electronic structure methods. On the basis of preliminary comparative calculations, second-order Møller−Plesset perturbation theory with a correlation-consistent polarized valence double-$\zeta$ one-electron basis set (MP2/cc-pVDZ) was chosen with which to describe equilibrium structures and harmonic vibrational frequencies of all relevant rotamers. Accurate energy differences were determined using the coupled cluster method, with perturbative inclusion of triple excitations, and a valence triple-$\zeta$ basis (CCSD(T)/cc-pVTZ). The lowest energy isomer is predicted to be the molozonide of difluorocarbene, whose adiabatic decay is prevented by a sizable barrier. Plausible mechanisms for the isomerization of the titled compound to the low-energy fluoroformyl peroxyhypofluorite and nearly isenergetic carbonyl hypofluorite are suggested. An analogous reaction path may be of importance to the isomerization of difluorodioxirane ($CF_2O_2$) and is included in the study.

## 1. Introduction

Although dioxiranes are well-known powerful oxidants, which have actively been used for regio- and stereoselective epoxidations (see refs 1−7 and references therein), their isolation and experimental investigation prove to be quite difficult due to their low thermal stability and high reactivity.[8,9] For example, the parent dioxirane, $CH_2O_2$, has only been observed as an intermediate in the low-temperature gas-phase ozonolysis of ethylene.[10,11] Subsequent experimental[1,12,13] and, in particular, theoretical[14−21] studies have characterized this compound as a rather labile cyclic peroxide, which decomposes exothermically into $CO_2$ and $H_2$ with release of a large amount of heat (124.2 kcal/mol).[20] This observation motivated the search for and study of new substituted dioxiranes (e.g., bicyclic $CO_4$ and $CO_2N_2$[22−24]) as potentially interesting high-energy-density materials.

Previous theoretical investigations[16,19] (also see ref 25) showed that the parent dioxirane could be stabilized by appropriate substitution and, in particular, that difluorodioxirane $CF_2O_2$ (**1**) (Scheme 1) should be relatively stable thermodynamically (although much earlier this compound was proposed as an unstable intermediate in the decomposition of $CF_3OOCF_3$[26]). In 1993, Russo and DesMarteau[27] succeeded in synthesizing **1** by the reaction of its isomer FC(=O)OF with ClF, $Cl_2$, or $F_2$ in the presence of CsF and showed that **1**, in contrast to all known dioxiranes, could be isolated as a pure substance, which is thermally stable in the gas phase at room temperature. The O−O bond length in **1** [1.578(1) Å] is the largest among all known compounds.[30] The properties of this unusual molecule and its isomers have received much attention and have been studied both experimentally[27−32] and theoretically.[33,34] The most accurate IR and electron-diffraction measurements of **1** were performed by Casper et al.,[30] while $^{13}C$ and $^{17}O$ NMR spectra, heat of formation ($\Delta H_f^0(298) = -102 \pm 1.5$ kcal/mol), dipole moment (0.60 D), and relative energies of its isomers were determined by Kraka, Cremer, Schaefer, and co-workers[33] on the basis of extended ab initio calculations. In our recent work,[34] also the low-lying excited triplet states and the lowest energy electronic state of the cation of **1** were studied theoretically.

**SCHEME 1**



A number of substituted dioxiranes were considered in ref 34 and it was shown that the energetic stability of dioxiranes substituted by strongly electronegative atoms (such as O and F) is greater than that of the unsubstituted or N-substituted species. Fluorofluoroxydioxirane, $FC(OF)O_2$ (**2**), was predicted to be the most stable species studied, after difluorodioxirane, and to have a comparatively low exothermicity (26.8 kcal/mol) for decomposition into $CO_2 + F_2O$. It was also pointed out[34] that geometrical and vibrational characteristics of **2** are similar to those of **1** and that this compound might also be of interest as a powerful oxidizer. To the best of our knowledge, only two of its isomers, fluoroformyl peroxyhypofluorite, FC(=O)OOF (**3**), and carbonyl hypofluorite, FOC(=O)OF (**4**), have been studied earlier. The experimental investigations of Argüello et al.[32] showed that isomer **3** is formed during the synthesis of FC(=O)OF (the starting material for the synthesis of **1**) and decomposes rapidly into FC(=O)F and $O_2$; it was pointed out that the IR spectra of **3** and FC(=O)OF are very similar. McKee and Webb[35,36] have studied theoretically rotamers of both **3** and **4**, using the B3LYP variant of density functional theory. Isomer **3,** as a possible precursor of $FC(=O)O^\bullet$ radicals, may be of relevance in atmospheric chemistry and may also be of synthetic

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interest (see refs 35−38 and references therein). Two more isomers of **2**, namely fluorofluoroxycarbonyl oxide, FC(OF)OO (**5**), and an unusual cyclic structure containing a four-membered $CO_3$ ring (**6**), are plausible. Structure **5** is sure to be too reactive to be detected directly (as are $H_2COO$[20] and $F_2COO$[33]) but, as will be shown below, proves to be an important intermediate in isomerization processes of **2**. Finally, in analogy with $CO_4$, which was investigated theoretically,[22,24] it can be expected that **6** is one of the most energetically stable isomers of **2**.

In the present work, ab initio calculations are used to study all isomers of **2** at a uniform, correlated level to determine their structural and vibrational spectroscopic characteristics and to estimate their relative energetic stability using a more highly correlated method. Special attention will be paid to estimating potential barriers to interconversions of rotamers and to studying isomerization mechanisms between the isomers. Such processes, however, will be shown to be hardly possible without catalysts due to high potential barriers. Our analysis of mechanisms of isomerization in $CF_2O_3$ stimulated our studying such processes in difluorodioxirane and suggested that rearrangement of **1** into its isomer FC(═O)OF seems to be a more complex multistage process than previously hypothesized.[33] Moreover, such rearrangement is prevented by high potential barriers so that noncatalytic rearrangement is extremely difficult.

Calculations were carried out using the Gaussian94 package of programs (E-2 version).[39] The search for stationary points on the potential energy surface (PES) and determination of equilibrium structural parameters as well as the calculation of harmonic vibrational frequencies of the species were performed mainly at the MP2/cc-pVDZ level[40−42] of theory, while the single-point energy calculations were performed at the CCSD(T)/cc-pVTZ level.[43] Transition states were connected to neighboring stationary points by construction of minimum energy paths, if there was question as to their topological relevance. Additional calculations were carried out using different combinations of atomic basis sets and theoretical methods, including the QCISD method[44] in order to validate the outlined protocol for this molecular system. Absolute energies, zero-point corrections, and relative energies of the $CF_2O_3$ structures and of reference species of interest, calculated at different levels of theory, are presented in Table 1. The remainder of the paper is organized into nine additional sections. The first five of these focus on structural features of the various isomers and relative stabilities of rotamers. Section 7 considers the energetics in more detail, while section 8 suggests a mechanism for unimolecular rearrangement. In analogy with the processes discussed in section 8, section 9 considers the rearrangement of difluorodioxirane. A final section presents conclusions.

## 2. Fluorofluoroxydioxirane, $FC(OF)O_2$ (2)

It was previously shown that the MP2 method, with cc-pVDZ basis, describes semiquantitatively the structures, harmonic vibrational frequencies, and electronic properties of substituted dioxiranes.[30,33,34] This conclusion can be corroborated by examination of Tables 2 and 3, where structural parameters and vibrational frequencies of difluorodioxirane (**1**), obtained in the present work at the MP2/cc-pVDZ level, are compared with both experimental data[24] and the unscaled CCSD(T)/cc-VTZ2P+f values obtained by Kraka et al.[33] This comparison shows that bond lengths of **1** at the MP2/cc-pVDZ method are generally within 0.01 Å of CCSD(T) values and harmonic vibrational frequencies within ca. 3%. Moreover, the reaction energy of $CO_2 + F_2 \rightarrow CO_2F_2$ (−9.5 kcal/mol) and the dipole moment (0.69 D) of **1** at the MP2 level are reasonably close to their most accurate values (−8.0 kcal/mol and 0.60 D) from ref 33. Although the agreement between MP2/cc-pVDZ and CCSD(T)/cc-VTZ2P+f for dioxiranes must be considered fortuitous, it proves useful indeed. A more detailed analysis performed in ref 34 shows that the MP2 level of theory also proves to be sufficiently accurate to be useful in assessing relative stabilities of substituted dioxiranes.

As was pointed out earlier,[30,33] fluorination of $H_2CO_2$ shortens the C−O bond by 0.04 Å (1.388 vs 1.348 Å) and increases the O−O bond length from 1.516 to 1.578 Å; such lengthening is opposite to the effect of fluorination of noncyclic peroxides, where the O−O bond distance shortens from $CH_3OOCH_3$ (1.457 Å)[45] to $CF_3OOCF_3$ (1.419 Å).[46] Our previous calculations[34] showed that geometrical and vibrational characteristics of **2** should be quite similar to those of **1**.

In the present work, we identified two rotamers of **2**, **2a**, and **2b**, whose geometries and vibrational frequencies are presented in Figure 1 and Table 4. The rotamers differ by the relative positions of the fluorine atoms (above the $CO_2$ ring for **2a** and away for **2b**, respectively). The fluorines in **2a** have trans orientation whereas in **2b** the dihedral angle FCOF is equal to 54°. At the MP2/cc-pVDZ level, the $C_s$ symmetry rotamer **2a** is more stable than the asymmetrical structure **2b** by only 1.5 kcal/mol (1.3 kcal/mol at the CCSD(T)/cc-pVTZ level). Comparison of Figure 1 and Table 2 shows that substitution of a fluorine atom in **1** by the highly electronegative O−F group does not change the structural parameters of the dioxirane ring and that the asymmetry of the ring in **2b** is not remarkable. The structural parameters of the planar FCOF fragment in **2a** coincide, in fact, with those in *trans*-FC(═O)OF (Table 2); the largest deviation is in the C−O bond length, which is longer in **2a** by 0.013 Å. In contrast to **2a**, the FCOF fragment in **2b** is nonplanar and its ∠FCO angle is 9.2° larger than in **2a**. Presumably, this difference results from the need to compensate for the Coulomb repulsion between the fluorine atoms when they are positioned cis. The calculated dipole moment of **2a** (0.77 D) is close to that of **1** (0.66 D) but is larger than the dipole moment of **2b** (0.41 D). As can be seen from Table 4 and as should be expected on the basis of the similarity of structural parameters of **1**, **2a**, and **2b**, these species have quite similar vibrational frequencies for the dioxirane ring.

The harmonic frequency corresponding to $CO_2$ twisting is quite large (388 $cm^{-1}$ in **2a** and 407 $cm^{-1}$ in **2b**), and, hence, both rotamers can be expected to be quite rigid relative to rotations of the dioxirane ring plane. In the case of **2a**, rotation of the ring by 180° will lead to an equivalent minimum on the PES. Our calculations show, however, that the potential barrier to interconversion of such two equivalent minima of **2a** through a $C_s$ symmetry transition state **2aa** (see Figure S1, Supporting Information) is too large (70.3 kcal/mol) for such interconversions to occur.

The small values of the lowest vibrational frequencies of the rotamers (162 $cm^{-1}$ in **2a** and 109 $cm^{-1}$ in **2b**), corresponding to rotations of the fluorine atom of the O−F group, suggest that the PESs of these rotamers are quite flat near their minima and that the potential barriers preventing such rotations are not high. Indeed, our calculations show that the barrier to interconversion of two equivalent **2b** structures differing only in the position (i.e., right and left) of the fluorine atom relative to the FCO plane of the FC(═O)F fragment is only 2.8 kcal/mol. The structure of the $C_s$ symmetry transition state **2bb** connecting these two enantiomers of **2b** is shown in Figure S1. The rotation

**TABLE 1: Total, Zero-Point, and Relative Energies of $CF_2O_3$ Structures and Reference Species[a]**

| | MP2/cc-pVDZ | | | CCSD(T)/cc-pVTZ//MP2/cc-pVDZ | |
|---|---|---|---|---|---|
| | $E_{tot}$ | ZPE | $\Delta E$ | $E_{tot}$ | $\Delta E$ |
| | | $CO_2FOF$ | | | |
| **2a** ($C_s$) | −462.140 719 0 | 13.0 (0) | 25.0 | −462.645 524 5 | 27.8 |
| **2b** ($C_1$) | −462.138 082 9 | 12.8 (0) | 26.5 | −462.643 114 2 | 29.1 |
| **2aa** ($C_s$) | −462.025 986 7 | 11.3 (1) | 95.3 | | |
| **2bb** ($C_s$) | −462.133 379 4 | 12.6 (1) | 29.3 | | |
| **2ab** ($C_1$) | −462.131 013 6 | 12.5 (1) | 30.6 | | |
| **3a** ($C_1$) | −462.182 840 2 | 12.8 (0) | −1.6 | −462.686 230 9 | 2.1 |
| **3b** ($C_1$) | −462.179 726 6 | 12.7 (0) | 0.3 | −462.683 503 8 | 3.7 |
| **3aa** ($C_s$) | −462.174 320 2 | 12.6 (0) | 3.6 | | |
| **3aa′** ($C_s$) | −462.162 535 3 | 12.3 (1) | 10.7 | | |
| **3bb** ($C_s$) | −462.170 927 9 | 11.4 (1) | 4.5 | | |
| **3bb′** ($C_s$) | −462.157 557 8 | 12.1 (1) | 13.6 | | |
| **3ab** ($C_1$) | −462.166 730 0 | 12.2 (1) | 7.9 | −462.671 014 4 | 11.0 |
| **4a** ($C_s$) | −462.132 872 6 | 12.6 (0) | 29.6 | −462.636 793 2 | 32.9 |
| **4b** ($C_{2v}$) | −462.133 277 0 | 12.5 (0) | 29.2 | −462.636 371 6 | 33.0 |
| **4c** ($C_2$) | −462.123 135 5 | 12.4 (0) | 35.5 | | |
| **4ab** ($C_1$) | −462.122 309 5 | 12.3 (1) | 35.9 | | |
| **4ac** ($C_1$) | −462.116 210 4 | 12.1 (1) | 39.5 | | |
| **4 cm**$^3$ ($C_{2v}$) | −462.119 515 3 | 12.1 (1) | 37.4 | | |
| **5a** ($C_s$) | −462.058 409 9 | 12.3 (0) | 76.0 | −462.577 236 5 | 69.9 |
| **5b** ($C_s$) | −462.055 681 8 | 12.4 (0) | 77.8 | −462.573 332 0 | 72.5 |
| **5c** ($C_1$) | −462.052 952 6 | 12.1 (0) | 79.2 | | |
| **5d** ($C_s$) | −462.048 350 7 | 12.1 (0) | 82.1 | −462.565 559 2 | 77.1 |
| **6** ($C_{2v}$) | −462.181 267 3 | 13.4 (0) | 0.0 | −462.690 456 2 | 0.0 |
| **7** ($C_1$) | −462.187 792 9 | 12.7 (0) | −4.8 | −462.673 596 8 | 9.9 |
| **8a** ($C_1$) | −462.018 398 2 | 11.3 (0) | 100.1 | | |
| **8aa** ($C_s$) | −462.016 396 5 | 11.2 (1) | 101.3 | | |
| **8aa′** ($C_s$) | −462.016 570 0 | 11.2 (1) | 101.8 | | |
| **2b** → **5d** ($C_1$) | −462.039 729 4 | 12.0 (1) | 87.4 | −462.558 427 2 | 81.4 |
| **2b** → **5c** ($C_1$) | −462.043 332 5 | 11.9 (1) | 85.1 | | |
| **5d** → **3a** ($C_s$) | −462.005 434 6 | 11.5 (1) | 108.4 | −462.535 843 2 | 95.1 |
| **6** → **7** ($C_1$) | −462.137 148 4 | 12.4 (1) | 26.7 | −462.648 827 1 | 25.1 |
| **5b** → **8a** ($C_1$) | −462.010 164 8 | 10.9 (1) | 104.9 | −462.534 478 2 | 95.4 |
| **8a** → **4a** ($C_1$) | −462.014 74 5 | 11.0 (1) | 102.3 | −462.530 185 0 | 98.2 |
| | | Reference Species | | | |
| $CO_2$ | −188.133 552 7 | 7.2 | | −188.326 769 9 | |
| $O_3$ | −224.900 336 4 | 6.0 | | −225.132 447 1 | |
| $O_2$ | −149.973 182 5 | 2.0 | | −150.128 524 5 | |
| $O_2$ (singlet) | −149.922 895 9 | 1.7 | | −150.080 184 3 | |
| FOF | −274.045 247 8 | 3.2 | | −274.349 160 9 | |
| FCF | −237.157 189 2 | 4.4 | | −237.419 029 2 | |
| FC(=O)F | −312.310 326 7 | 8.9 | | −312.642 059 4 | |
| $CF_2O_2$ | −387.232 266 7 | 11.0 | | −387.650 832 6 | |
| $F_2COO$ | −387.144 231 4 | 10.5 | | −387.575 902 4 | |
| *cis*-FC(=O)OF | −387.221 170 3 | 10.7 | | | |
| *trans*-FC(=O)OF | −387.223 860 8 | 10.9 | | −387.641 540 0 | |
| FC(=O)FO | −387.105 133 6 | 9.4 | | | |
| **TS1** | −387.128 796 5 | 10.0 | | −387.5610531 | |
| **TS2** | −387.096 655 8 | 9.0 | | | |
| **TS3** | −387.102 951 6 | 9.2 | | | |
| **TS4** | −387.103 121 3 | 9.3 | | | |

[a] Total energies are given in atomic units, ZPE and $\Delta E$ are in kcal/mol. The number of imaginary frequencies of the stationary point is given in parentheses.

**TABLE 2: Comparison of Calculated Geometric Parameters (Å, deg) for $CF_2O_2$ (1), *trans*- and *cis*-FC(=O)OF, and $F_2COO$ with Other Theoretical and Experimental Data**

| $CF_2O_2$ | | | | *trans*-FC(=O)OF | | | | *cis*-FC(=O)OF | | | $F_2COO$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | present work | ref 33[a] | expt[30] | | present work | ref 35[b] | expt[32] | present work | ref 35[b] | expt[32] | | present work | ref 33[a] |
| C−O | 1.351 | 1.343 | 1.348(8) | C=O | 1.184 | 1.180 | 1.170(4) | 1.188 | 1.186 | 1.172 | C−O | 1.227 | 1.225 |
| O−O | 1.580 | 1.569 | 1.578(1) | C−F | 1.331 | 1.337 | 1.324(7) | 1.320 | 1.323 | 1.320 | O−O | 1.449 | 1.421 |
| C−F | 1.325 | 1.314 | 1.317(6) | C−O | 1.372 | 1.369 | 1.367(9) | 1.369 | 1.361 | 1.380 | $C-F_c$ | 1.282 | 1.276 |
| | | | | O−F | 1.430 | 1.425 | 1.418(5) | 1.439 | 1.441 | 1.425 | $C-F_t$ | 1.297 | 1.291 |
| OCO | 71.6 | 71.5 | 71.7(5) | O=C−F | 127.0 | | 126.5(6) | 126.9 | | 126.4 | COO | 114.2 | 117.1 |
| FCF | 108.6 | 108.8 | 108.8(7) | O=C−O | 130.3 | | 130.3(6) | 120.0 | | 120.9 | FCF | 113.5 | 114.4 |
| | | | | C−O−F | 106.5 | | 105.5(40 | 110.3 | | 109.6 | $OCF_c$ | 126.2 | 125.5 |

[a] Results of CCSD(T)/cc-VTZ2P+f,d calculations by Kraka et al.[33] [b] Results of B3LYP/6-31+G(d) calculations by McKee and Webb.[35]

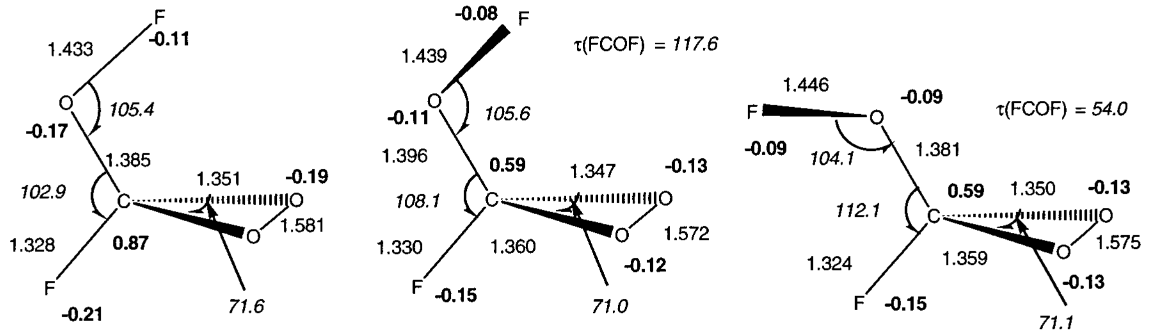
barrier between **2a** and **2b** through transition state **2ab** is 5.6 kcal/mol (cf. Figure 1).

On the basis of the CCSD(T) results, and assuming that the entropy differences are negligible, one can expect that if **2** can

**TABLE 3: Comparison of Calculated Harmonic Vibrational Frequencies (cm$^{-1}$) for $CF_2O_2$ (1), *trans*- and *cis*-FC(=O)OF with Experimental and Previous Theoretical Data. $F_2COO$ Results Included for Additional Comparison**

| $CF_2O_2$ | | | | | *trans*-FC(=O)OF | | | | | *cis*-FC(=O)OF | | | $F_2COO$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| sym | assign. | present work | ref 33[a] | expt[30] | sym | assign. | present work | ref 35[c] | expt[32] | present work | ref 35[c] | expt[32] | sym | present work |
| $a_2$ | $CF_2$ twist | 387 | 398 | 389[b] | a″ | bend | 191 | 187 | 186 | 141 | 145 | 150 | a″ | 236 |
| $a_1$ | $CF_2$ scissor | 523 | 524 | 511 | a′ | bend | 310 | 304 | 307 | 324 | 317 | 310 | a′ | 273 |
| $b_1$ | $CF_2$ rock | 567 | 572 | 557 | a′ | bend | 513 | 502 | 505 | 538 | 534 | 530 | a′ | 484 |
| $b_2$ | $CF_2$ wag | 626 | 631 | 621 | a′ | FC=O | 660 | 650 | 655 | 637 | 625 | 626 | a′ | 618 |
| $a_1$ | OCO def | 701 | 683 | 658 | a″ | C o−o-p | 753 | 729 | 743 | 749 | 726 | 737 | a″ | 704 |
| $a_1$ | CF sym str | 933 | 945 | 918 | a′ | O−F str | 925 | 945 | 910 | 888 | 899 | 861 | a′ | 751 |
| $b_2$ | CO asym str | 1148 | 1109 | 1062 | a′ | C−O str | 1017 | 1031 | 992 | 968 | 952 | 936 | a′ | 1004 |
| $b_1$ | CF asym str | 1301 | 1307 | 1260 | a′ | C−F str | 1233 | 1178 | 1191 | 1304 | 1261 | 1261 | a′ | 1477 |
| $a_1$ | CO sym str | 1528 | 1526 | 1467 | a′ | FC=O str | 1933 | 1970 | 1932 | 1960 | 1926 | 1906 | a′ | 1808 |

[a] Unscaled CCSD(T)/cc-VTZ2P+f values calculated by Kraka et al.[33] [b] Recommended value from ref 33. [c] Results of B3LYP/6-31+G(d) calculations by McKee and Webb.[35]



**2a:** $C_s$; 0.0 kcal/mol **2ab:** $C_1$; 5.6 kcal/mol **2b:** $C_1$; 1.5 kcal/mol

**Figure 1.** Geometries (in Å and deg), relative energies and Mulliken populations of FC(OF)$O_2$ (**2**) minima and transition states at the MP2/cc-pVDZ level.

**TABLE 4: Harmonic Vibrational Frequencies (cm$^{-1}$) and IR Intensities (km/mol) of $CF_2O_3$ Structures Calculated at the MP2/cc-pVDZ Level**

| | **2a** | **2b** | **3a** | **3b** | | **4a** | | **4b** | | **4c** |
|---|---|---|---|---|---|---|---|---|---|---|
| a′ | 162 (0) | 109 (0) | 102 (0) | 81 (1) | a″ | 131 (0) | $a_2$ | 34 (0) | b | 123 (0) |
| a″ | 278 (2) | 268 (2) | 131 (0) | 126 (1) | a″ | 181 (0) | $b_1$ | 126 (0) | a | 145 (1) |
| a″ | 388 (0) | 407 (0) | 334 (2) | 351 (2) | a″ | 258 (1) | $a_1$ | 251 (2) | a | 276 (0) |
| a′ | 477 (1) | 497 (3) | 434 (0) | 437 (2) | a′ | 340 (8) | $b_2$ | 350 (4) | b | 329 (9) |
| a″ | 603 (10) | 553 (10) | 572 (18) | 583 (16) | a′ | 521 (2) | $a_1$ | 460 (0) | b | 509 (5) |
| a′ | 633 (12) | 628 (11) | 687 (8) | 668 (7) | a′ | 626 (16) | $b_2$ | 700 (0) | a | 630 (10) |
| a′ | 685 (10)[a] | 723 (18)[a] | 765 (22) | 759 (27) | a″ | 722 (27) | $b_1$ | 730 (25) | b | 741 (41) |
| a′ | 909 (14) | 890 (15) | 814 (55) | 800 (53) | a′ | 867 (17) | $b_2$ | 910 (36) | a | 834 (24) |
| a′ | 992 (6) | 943 (7) | 921 (19) | 886 (16) | a′ | 953 (13) | $a_1$ | 947 (14) | b | 913 (6) |
| a″ | 1123 (89)[b] | 1139 (79)[b] | 977 (51) | 950 (69) | a′ | 991 (10) | $a_1$ | 1041 (7) | a | 961 (4) |
| a′ | 1252 (326) | 1282 (285) | 1228 (454) | 1260 (363) | a′ | 1259 (309) | $b_2$ | 1185 (369) | b | 1297 (263) |
| a′ | 1530 (338)[c] | 1494 (313)[c] | 1986 (329) | 1971 (378) | a′ | 1945 (296) | $a_1$ | 1975 (289) | a | 1884 (255) |

| | **5a** | | **5b** | **5c** | | **5d** | | **6** | **7** | **8a** |
|---|---|---|---|---|---|---|---|---|---|---|
| a″ | 173 (0) | a″ | 149 (3) | 26 (5) | a″ | 39 (2) | $b_1$ | 95 (0) | 195 (9) | 67 (1) |
| a′ | 209 (50) | a′ | 222 (8) | 187 (9) | a″ | 256 (4) | $a_2$ | 352 (0) | 282 (0) | 114 (1) |
| a″ | 258 (8) | a″ | 232 (4) | 252 (9) | a′ | 268 (6) | $a_1$ | 487 (3) | 320 (26) | 184 (4) |
| a′ | 341 (5) | a′ | 316 (1) | 341 (1) | a′ | 289 (1) | $b_2$ | 569 (6) | 440 (1) | 300 (22) |
| a′ | 500 (9) | a′ | 509 (0) | 464 (2) | a′ | 431 (0) | $b_1$ | 585 (4) | 500 (14) | 329 (71) |
| a′ | 558 (6) | a′ | 612 (3) | 640 (6) | a′ | 601 (0) | $a_1$ | 753 (0) | 581 (9) | 488 (2) |
| a″ | 698 (22) | a″ | 689 (22) | 667 (34) | a″ | 666 (22) | $a_1$ | 833 (20) | 594 (7) | 623 (12) |
| a′ | 780 (53) | a′ | 733 (7) | 732 (19) | a′ | 775 (24) | $b_2$ | 859 (5) | 686 (7) | 730 (49) |
| a′ | 807 (17) | a′ | 931 (17) | 908 (16) | a′ | 911 (41) | $a_1$ | 961 (4) | 908 (49) | 910 (42) |
| a′ | 999 (33) | a′ | 1038 (24) | 1000 (37) | a′ | 1046 (19) | $b_2$ | 1257 (130) | 1271 (349) | 966 (118) |
| a′ | 1475 (265) | a′ | 1424 (311) | 1446 (237) | a′ | 1392 (304) | $b_1$ | 1270 (386) | 1461 (454) | 1154 (345) |
| a′ | 1790 (303) | a′ | 1819 (352) | 1769 (233) | a′ | 1796 (347) | $a_1$ | 1328 (535) | 1612 (732) | 2024 (365) |

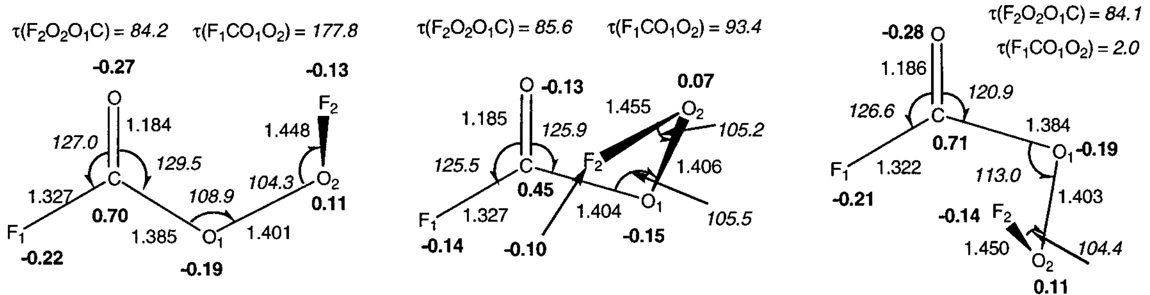
[a] OCO scissors. [b] CO asymmetric stretch. [c] CO symmetric stretch.

be produced then it will exist as a 18% **2b**: 82% **2a** mixture (at 298K) with **2b** existing as a racemic mixture.

## 3. Fluoroformyl Peroxyhypofluorite, FC(=O)OOF (3)

FC(=O)OOF has recently been identified by Argüello and co-workers[31,32] as an unstable byproduct (5% yield) of the synthesis of FC(=O)OF by the photochemical fluorination of FC(=O)OOC(=O)F. **3** is a little less volatile than FC(=O)OF and decomposes rapidly into FC(=O)F and $O_2$. Attempts to record characteristic IR absorptions of **3** failed because its spectrum is very similar to that of FC(=O)OF.[31] McKee and Webb[35] investigated geometrical, vibrational, and energetic properties of **3** theoretically at the B3LYB/6-31+G(d) level.

Tables 2 and 3 show that the MP2/cc-pVDZ method used in



**3a**: $C_1$; 0.0 kcal/mol **3ab**: $C_1$; 9.5 kcal/mol **3b**: $C_1$; 1.9 kcal/mol

**Figure 2.** Geometries (in Å and deg), relative energies and Mulliken populations of FC(=O)OOF (**3**) minima and transition states at the MP2/cc-pVDZ level.

the present work reproduces reasonably well the experimental geometries (≤0.01 Å bond length error) and vibrational frequencies (≤3% error) of both the trans- and *cis*-rotamers of the related FC(=O)OF molecule[32] and that these results are very close to the B3LYB/6-31+G(d) calculations.[35] Moreover, both methods lead to the same transition state for interconversion of rotamers and the calculated barrier heights (11.6 and 10.9 kcal/mol for MP2 and B3LYP, respectively) are acceptably close to the experimental value of 9.6 kcal/mol.[31] Both methods predict the trans conformer to be more stable, in agreement with experiment,[32] but the experimental value of their energy difference (1.3 ± 0.5 kcal/mol) is reproduced better by the MP2/cc-pVDZ method (1.5 kcal/mol) than by B3LYB/6-31+G(d) (0.3 kcal/mol).[35]

Figure 2 shows the results of our calculations for trans (**3a**) and cis (**3b**) rotamers of **3**. The structures of the FC(=O)O fragments in **3a** and **3b**, in fact, coincide with those in trans and cis rotamers of FC(=O)OF, respectively. Despite the (near) planarity of the FC(=O)O fragment, both **3a** and **3b** are predicted to be nonplanar on account of the terminal fluorine. Our calculations show that the dipole moments of **3a** and **3b** are 1.20 and 1.09 D, respectively, which are quite close to those of FC(=O)OF (1.10 and 0.93 D). Structural parameters of both isomers are in close agreement with the result of the previous calculations by McKee and Webb.[35] Both studies predict that the trans rotamer (**3a**) is the lowest-energy form, but, as in the case of FC(=O)OF, the difference in energies of **3a** and **3b** predicted in the present work (1.9 kcal/mol) is larger than that (0.8 kcal/mol) from ref 35. To obtain a more reliable prediction of the energy difference, we performed additional calculations at the CCSD(T)/cc-pVTZ level. The coupled cluster energy difference of 1.6 kcal/mol is in nice agreement with the MP2 result and further corroborates our use of the MP2 method in this study. These data confirm qualitatively the conclusion of McKee and Webb[35] that isomer **3** should exist as a mixture of rotamers. However, using our CCSD(T)/cc-pVTZ results, we expect only 7% cis and 93% trans at 298K, in comparison to a 24%: 76% mixture.

Our calculations identify five transition states on the PES of **3**: two transition states (**3aa** and **3aa′**) for the interconversion of **3a** enantiomers (see Figure S2, Supporting Information), two analogous transition states (**3bb** and **3bb′**) for **3b** (see Figure S2), and one transition state (**3ab**) for the interconversion of **3a** and **3b** (see Figure 2). The difference between transition states **3aa** and **3aa′** (**3bb** and **3bb′**) is the direction of rotation of the fluorine atom about the O−O bond. In the case of **3aa**, the fluorine atom is rotated downward to a trans position, while rotation of the atom upward leads to the cis structure **3aa′**. Structural parameters of **3aa** and **3ab** predicted in ref 35 are very close to those obtained in the present work. The smaller Coulomb repulsion between the fluorine atom and the oxygen atom of the C=O group in **3aa** leads to a lower barrier height of 5.2 kcal/mol (5.9 kcal/mol[35]) than the barrier of 12.3 kcal/mol in the case of **3aa′**. Analogously, the barrier height of **3bb** (6.1 kcal/mol) is significantly lower than that of **3bb′** (15.2 kcal/mol).

Transition state **3ab**, which interconverts **3a** and **3b** (and can be described as a rotation about the C-distal O axis), is characterized by a much longer O−O bond (by 0.07−0.08 Å) and shorter O−F bond (by 0.02−0.03 Å) than those in transition states between enantiomers. The calculated potential barrier of 9.5 kcal/mol (7.9 kcal/mol[35]) to conversion from **3a** into **3b** is predicted to be a little less than the rotational barrier in FC(=O)OF (where the calculated and experimental values of the barrier are 11.6 and 9.8 kcal/mol, respectively).

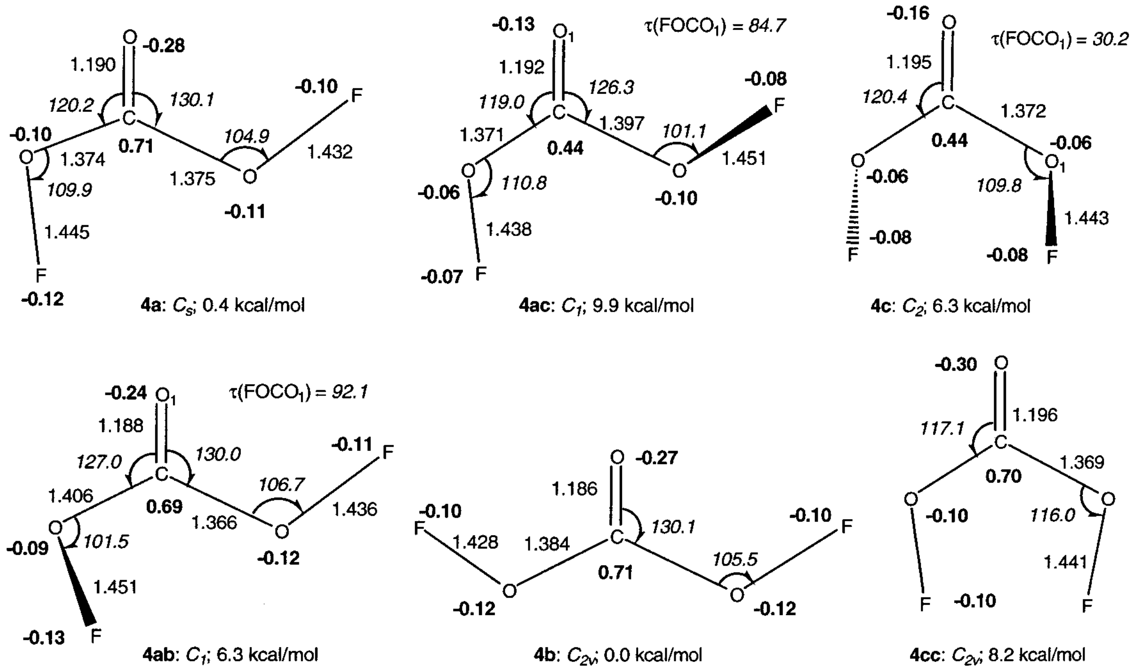
Vibrational frequencies and intensities of **3a** and **3b** calculated in the present work are given in Table 4; they agree nicely (≤4%) with the results of the calculations by McKee and Webb.[35] Thus, we confirm their conclusion that although the harmonic frequencies of **3** and of FC(=O)OF are very similar, the frequencies at 814 and 800 $cm^{-1}$ (824 and 801 $cm^{-1}$ [35]) for **3a** and **3b**, respectively, could be used to identify fluoroformyl peroxyhypofluorite.

## 4. Carbonyl Hypofluorite, FOC(O)OF (4)

While **4** has only been studied theoretically at the B3LYP/6-311+G(2df)//B3LYP/6-31+G(d) level,[36] Gobbato et al.[47] have recently reported the results of calculations of the related molecule $CF_2(OF)_2$ at several levels of theory and have shown that MP2/6-31G(d) disagrees with B3LYP/6-311+G(d) concerning the relative stability of the two lowest conformers. Moreover, these authors performed an electron diffraction study, which agrees with the MP2/6-31G(d) results. Consequently, there is a need to reexamine **4**.

Our MP2/cc-pVDZ calculations, in agreement with McKee and Webb,[36] identify three local minima on the PES of **4**: rotamers **4a**, **4b**, and **4c**. Their vibrational frequencies are presented in Table 4 and their geometries, relative energies, and Mulliken charges are shown in Figure 3. As seen from a comparison of the data of Figure 3 and Table 2, and as should be expected, substitution of the fluorine atom of the C−F group in FC(O)OF by the highly electronegative O−F group does not lead to any remarkable distortions of the C(O)OF fragment's structure.

As previously found using B3LYP,[36] the structures and vibrational frequencies of the **4a** and **4c** rotamers are quite close. Moreover, both studies predict that **4a** is more stable than **4c** (by 5.9 kcal/mol in the present work and 5.1 kcal/mol in ref 36). However, the results of B3LYP/6-31+G(d) optimization of the remaining structure, **4b**, are not in agreement with our MP2/cc-pVDZ calculations. In ref 36, it was predicted that **4b**



**4a**: $C_s$; 0.4 kcal/mol

**4ac**: $C_1$; 9.9 kcal/mol

**4c**: $C_2$; 6.3 kcal/mol

**4ab**: $C_1$; 6.3 kcal/mol

**4b**: $C_{2v}$; 0.0 kcal/mol

**4cc**: $C_{2v}$; 8.2 kcal/mol

**Figure 3.** Geometries (in Å and deg), relative energies and Mulliken populations of FOC(=O)OF (**4**) minima and transition states at the MP2/cc-pVDZ level.

is a nonplanar $C_2$ symmetry structure in which the O−F bonds are conrotated out of the $CO_3$ plane by 16.4°. In contrast, our calculations show that **4b** has planar $C_{2v}$ symmetry. In order to verify the correctness of these MP2/cc-pVDZ results, the geometry of **4b** was reoptimized at the QCISD/cc-pVDZ level, which confirmed the planar structure of this rotamer. It should be noted that the B3LYP calculations[36] predicted that the planar transition state separating the two equivalent **4b** minima has a barrier height of only 0.01 kcal/mol. As can be seen from Table 4, the lowest vibrational frequency of **4b** is predicted to be only 34 $cm^{-1}$ (39 $cm^{-1}$ at the QCISD/cc-pVDZ level), which confirms the conclusion of McKee and Webb[36] that the PES of **4b** is quite flat around the minimum. Although the B3LYP equilibrium structure is at odds with MP2 and QCISD results, vibrational averaging (even at $v = 0$) will bring the results into much closer agreement. Clearly, much higher level calculations, with respect to basis set, electron correlation, and nuclear wave function, are needed to decide definitively the structure of this stationary point.

At the MP2/cc-pVDZ level, **4b** is the lowest-energy rotamer, lying 0.4 kcal/mol below **4a**. However, CCSD(T)/cc-pVDZ predicts that **4a** and **4b** have the same stability (i.e., within 0.1 kcal/mol). On the basis of these results, we can only conclude that the energies of rotamers **4a** and **4b** are very close. In contrast, **4a** was predicted to be 1.2 kcal/mol more stable than **4b** in ref 36.

We have located three transition states, **4ab**, **4ac**, and **4 cc**[3], corresponding to the interconversions **4a** ↔ **4b**, **4a** ↔ **4c**, and to the racemization of **4c**, respectively (see Figure 3). The structural parameters of transition states **4ab** and **4ac**, predicted earlier by McKee and Webb,[36] are very close to those found in the present work. The MP2/cc-pVDZ barriers for the **4a** → **4b** isomerization (6.3 kcal/mol) and the **4a** → **4c** isomerization (9.9 kcal/mol) are close to the barriers predicted in ref 36 (6.0 and 9.2 kcal/mol, respectively). The barrier between **4c** enantiomers was estimated to be not higher than 0.7 kcal/mol; our MP2 value of the barrier height, 1.9 kcal/mol, is in reasonable agreement with this prediction.

The barrier heights discussed above are comparable with those measured for FC(O)OF,[31,32] and, together with the energetic data presented, support the expection that if carbonyl hypofluorite **4** can be produced, then a thermal sample will exist as a nearly equal mixture of **4a** and **4b** rotamers, and not predominately as the **4a** isomer predicted in ref 36. Our calculations confirm the conclusion of McKee and Webb that the vibrational spectra of **4a** and **4c** are quite similar, but show additionally that these spectra should differ significantly from that of **4b** not only in the region 1300−800 $cm^{-1}$ but also by their lowest frequencies (see Table 4). Moreover, while the dipole moments of the rotamers **4a** and **4c** are close (0.95 and 1.10 D, respectively), they are predicted to be larger than that of **4b** (0.63 D). These results could help in identifying rotamers of carbonyl hypofluorite **4**.

## 5. Fluorofluoroxycarbonyl Oxide, FC(OF)OO (5)

Although carbonyl oxides are involved in many oxidation reactions,[1,48] including the ozonolysis of olefins,[49] their high reactivity makes them difficult to study experimentally and their intermediacy can only be proven indirectly.[50] At the same time, accurate theoretical study of such species is also difficult and represents a rather complex correlation problem.[20,33] Cremer et al.[20] and Bach et al.[51] pointed out, however, that structural parameters of carbonyl oxides are predicted quite well at the MP2 level of theory with a polarized split valence basis, perhaps due to a cancellation of basis set and correlation errors. As can be seen from Table 2, our calculations of structural parameters of $F_2COO$ at the MP2/cc-pVDZ level are in reasonable agreement (with the exception of the O−O distance) with the B3LYP/6-311+G(3df, 3pd) values of Kraka, Schaefer et al.[33] In order to further verify the MP2/cc-pVDZ results, we performed QCISD/cc-pVDZ calculations with the following results: $R_{C-F(1)} = 1.297$ Å, $R_{C-F(2)} = 1.284$ Å, $R_{C-O} = 1.222$ Å, $R_{O-O} = 1.489$ Å, $\angle C-O-O = 114.2°$. Except for the O−O distance, the agreement is very good. And although QCISD/cc-pVDZ is hardly definitive, the close agreement suggests that the supposed fortuitous cancellation of errors is not overly

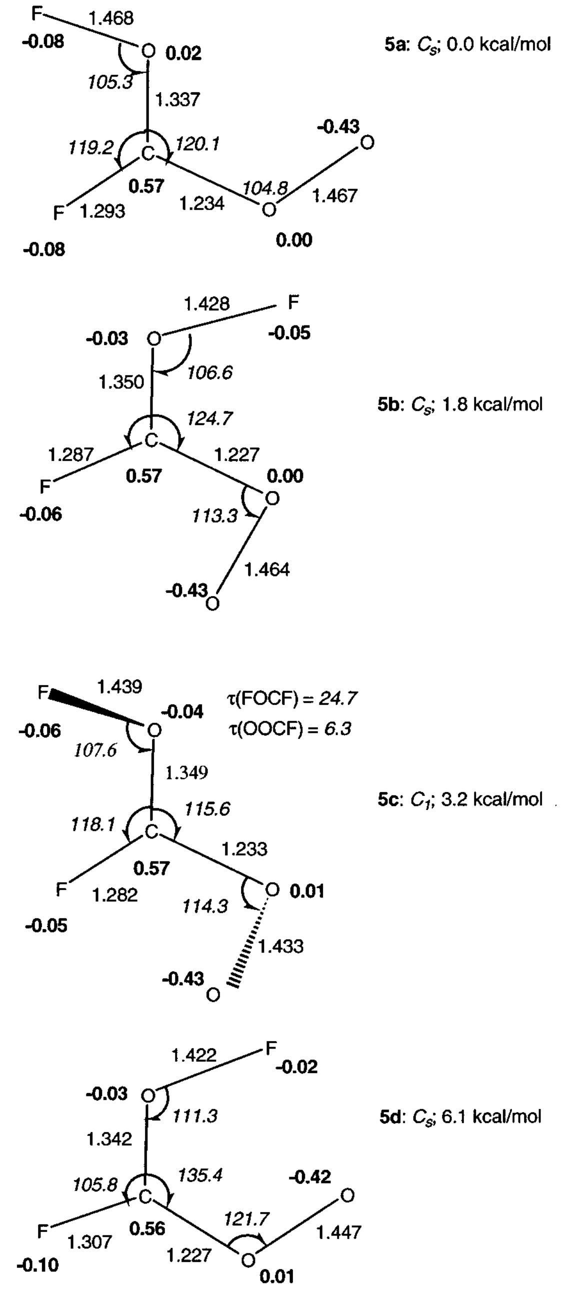


**Figure 4.** Geometries (in Å and deg), relative energies and Mulliken populations of FC(OF)OO (**5**) isomers at the MP2/cc-pVDZ level.

sensitive. Hence, continued use of MP2/cc-pVDZ for geometry optimizations was deemed appropriate. As in the case of **4**, one can expect that substitution of a fluorine atom in $F_2COO$ by an O−F group does not change the electron density drastically and that the MP2/cc-pVDZ level of theory will be satisfactory for a sufficiently reliable description of the structures of possible rotamers of **5**.

Four local minima of **5**, corresponding to rotamers **5a**, **5b**, **5c**, and **5d**, have been identified in our study. Their geometries, charge distributions, and relative energies are shown in Figure 4, and their vibrational frequencies are presented in Table 4. At the MP2/cc-pVDZ level, rotamer **5a** is predicted to be the most stable, while the relative energies of **5b**, **5c**, and **5d** are 1.8, 3.2, and 6.1 kcal/mol, respectively. Rotamers **5a**, **5b**, and **5d** have planar structures, while the structure of **5c** is expected to be nonplanar with a FOCF dihedral angle of 24.7°. Nonetheless, structural parameters of the FC(O)O moiety and charge distributions are quite similar in all of the rotamers; all four rotamers have very large and similar dipole moments (3.95, 4.28, 4.18, and 4.01 D for **5a**, **5b**, **5c**, and **5d**, respectively). The length of the C−O bond in the COF fragment (1.34−1.35 Å) is shorter (by 0.03−0.04 Å) than in **4** (1.37−1.38 Å), while the C−O bond length in the COO chain in **5** is the same as in **4** (1.23 Å) and close to that of a carbon−oxygen double bond (1.19 Å in **3**). Moreover, taking into account that the O−O bond length in the rotamers is 1.43−1.47 Å and thus close to typical values for a O−O single bond (1.45 Å), one can expect that **5** has zwitterionic character like $F_2COO$[33] and $H_2COO$.[20]

The very small values of the lowest vibrational frequencies in **5c** (26 $cm^{-1}$) and **5d** (39 $cm^{-1}$) suggest that potential barriers to rearrangements along the low-frequency modes will be very small. This observation will be used in section 7, where it will be shown that these rotamers prove to be of importance as intermediates in the unimolecular isomerizations **2** → **3** and **2** → **4**.

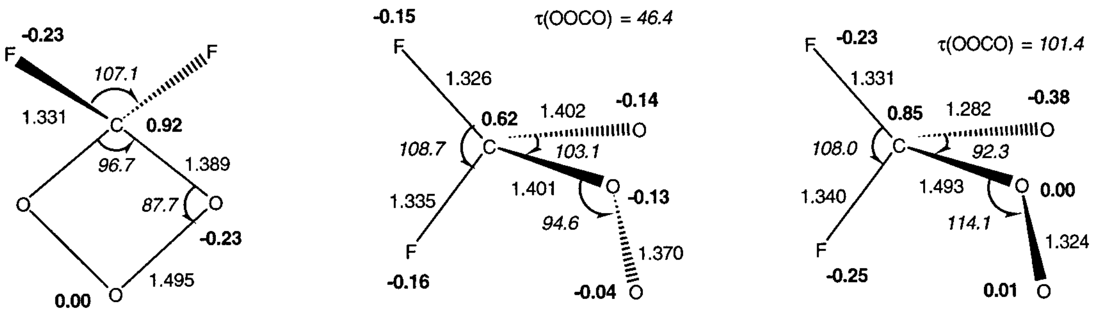
## 6. Molozonide of Difluorocarbene (6)

Although **6**, containing the planar four-membered $CO_3$ ring, has not yet been investigated, the closely related species $C(=O)O_3$ has been investigated earlier at the MP2 level in ref 22. In that work, it was pointed out that $C(=O)O_3$ is much more stable (by about 30 kcal/mol) than its bicyclic isomer $O_2CO_2$. Since the MP2 method is sufficiently reliable for describing difluorodioxirane **1** (see above) and $CO_2N_2$,[22,23] which in some aspects are similar to **6**, this method should also be adequate for studying structural parameters of this unusual species.

The $CF_2$ fragment is the same in **6** (see Figure 5) as it is in $CF_2O_2$ (see Table 2). The O−O bonds in **6** are the same as in the $C(=O)O_3$ isomer of $CO_4$, but the C−O bonds in **6** are longer (by about 0.05 Å) than in $C(=O)O_3$.[22] As a result, the lowest vibrational frequency in **6** (98 $cm^{-1}$), which corresponds to the normal mode dominated by the perpendicular motion of the apex oxygen atom, is smaller than the frequency (274 $cm^{-1}$) of the analogous mode in $C(=O)O_3$.[22] It is interesting that the charge on the aforementioned oxygen atom in **6** is close to zero and the dipole moment of **6** (0.17 D) is much smaller than that (1.1 D) of the $C(=O)O_3$ species.[22]

The planar $C_{2v}$ structure related to **6** has one imaginary frequency and corresponds to a transition state between enantiomers if the fluorine atoms would be distinguishable. But, as with **2a**, the potential barrier for such interconversion of equivalent **6** is far too high (72.8 kcal/mol at the MP2/cc-pVDZ level) to make this possible.

Using the experimental value of 22.5 kcal/mol for the $O_2(a^1\Delta_g)$ energy relative to its $X\ ^3\Sigma_g^-$ state,[52] **6** is estimated to be energetically metastable relative to its lowest adiabatic asymptote $F_2CO + O_2(a^1\Delta_g)$ by about 30 kcal/mol. However, according to our calculations, the adiabatic decomposition of **6** into $F_2CO$ and $O_2(a^1\Delta_g)$ does not proceed directly but rather through an intermediate, **7**. The structure of **7** is shown in Figure 5 and vibrational frequencies are given in Table 4. The $CF_2$ fragment in **7** is almost the same as it is in **6**, but one of the O−O bonds of the $CO_3$ moiety is broken in **7**. As a result, **7** contains not a ring but the C−O and C−O−O chains. The length of the C−O bond in the C−O chain (1.282 Å) is shorter than the C−O bond in **6** (1.389 Å), while the C−O bond in the C−O−O chain (1.493 Å) is longer than that in **6** by 0.1 Å. The O−O bond (1.324 Å) is shorter than it is in **6** by almost 0.2 Å and approaches the O−O bond length in $O_2(a^1\Delta_g)$ (1.259 Å). These structural features of **7** suggest that this structure is an intermediate minimum in the dissociation of **6** into $F_2CO$ and $O_2(a^1\Delta_g)$. At the MP2/cc-pVDZ level, **7** is predicted to be more



**6**: $C_{2v}$; 0.0 kcal/mol

**TS$_{6\text{-}7}$**: $C_1$; 26.7 kcal/mol

**7**: $C_1$; -4.8 kcal/mol

**Figure 5.** Geometries (in Å and deg), relative energies and Mulliken populations of **6** and **7** at the MP2/cc-pVDZ level.

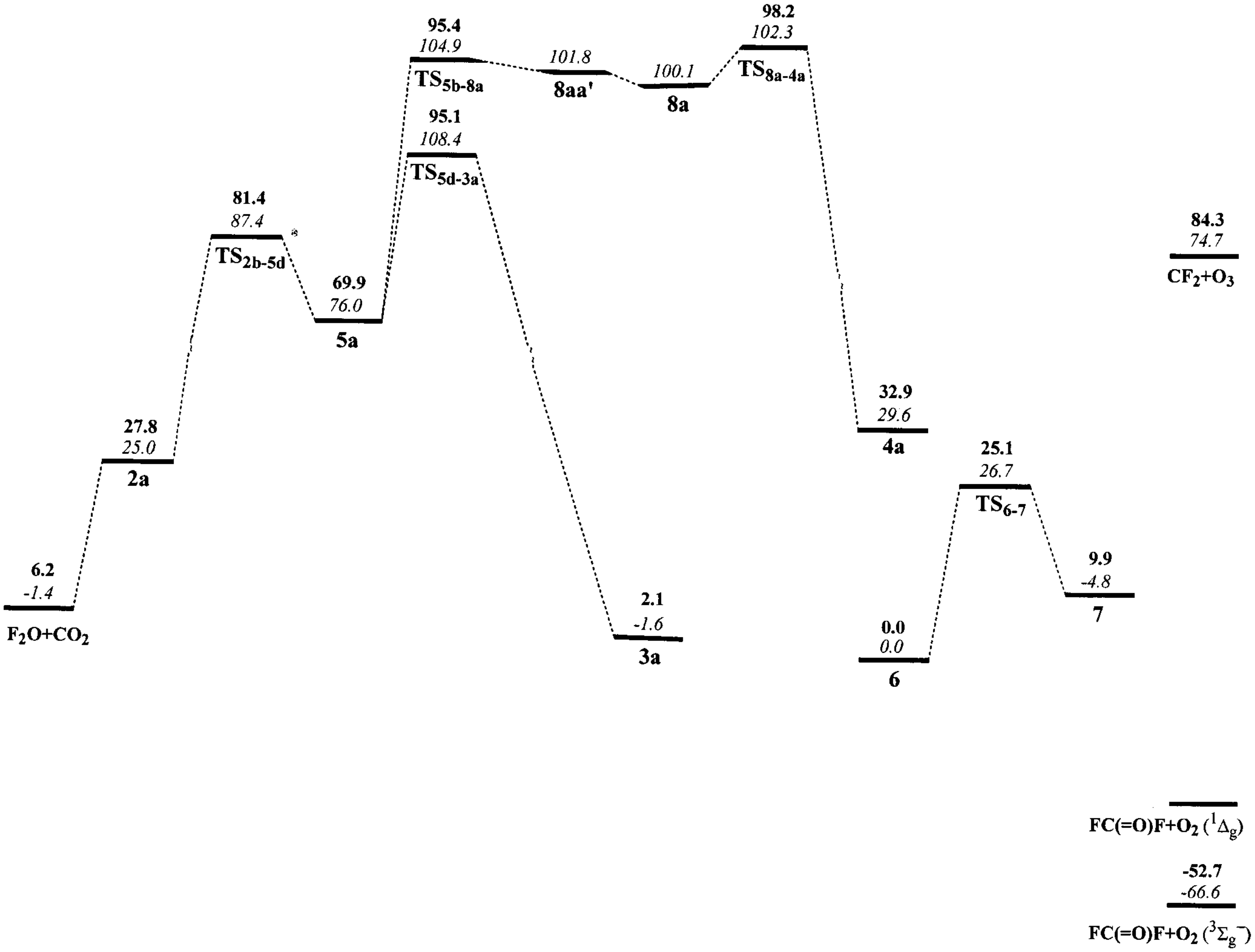


**Figure 6.** Schematic representation of the relative energies (kcal/mol) of $CF_2O_3$ stationary points and some possible dissociation limits (CCSD(T)/cc-pVTZ values in bold and MP2/cc-pVDZ values in italics).

stable than **6** by 4.8 kcal/mol, while the CCSD(T)/cc-pVTZ//MP2/cc-pVDZ calculations predict the inverse order: namely that **6** is 9.9 kcal/mol more stable than **7**.

According to our CCSD(T)/cc-pVTZ calculations, the potential barrier preventing the rearrangement of **6** into **7**, through transition state **TS$_{6-7}$**, is equal to 25.1 kcal/mol (26.7 kcal/mol at the MP2/cc-pVDZ level). This barrier should to be sufficiently high to permit observation of **6**. It is to be noted that besides the adiabatic rearrangement of **6** into **7**, the nonadiabatic transition from the $1^1A_1$ state of **6** into its $1^3B_1$ state is in principle possible. Indeed, at the equilibrium structure of **6** the $1^3B_1$ state is 95.9 kcal/mol higher in energy (at the MP2/cc-pVDZ level) than **6**, but the $F_2CO + O_2(X\ ^3\Sigma_g^-)$ asymptote correlating with this triplet state is 22.5 kcal/mol[52] lower than the $F_2CO + O_2(a^1\Delta_g)$ limit correlating with $1^1A_1$. As a result, the singlet and triplet potential surfaces cross. However, without a detailed investigation of the singlet−triplet seam, which is outside the scope of the present work, more cannot be said on the importance of the role of intersystem crossing here.

As can be seen from Figure 6, which shows the calculated relative energies of all the isomers of $CF_2O_3$ and related species, **6** could in principle be formed from the reaction of $CF_2(\tilde{X}^1A_1)$ with $O_3(\tilde{X}^1A_1)$. However, the exothermicity of this reaction is so high (84.3 kcal/mol at the CCSD(T)/cc-pVTZ level) that formation of **6** is likely to be followed by rearrangement into **7** or even decomposition into $F_2CO$ and $O_2$. It is possible,

**TABLE 5: Relative Energies (kcal/mol) of the Most Stable Rotamers of $CF_2O_3$ Calculated at Different Theory Levels**

| | 2a | 3a | 4a | 5a | 6 | 7 |
|---|---|---|---|---|---|---|
| MP2/cc-pVDZ | 25.0 | −1.6 | 29.6 | 76.0 | 0.00 | −4.8 |
| MP2/cc-pVTZ | 27.6 | 1.3 | 34.3 | 76.4 | 0.00 | −0.5 |
| MP2/aug-cc-pVTZ | 27.3 | 0.7 | 33.2 | 73.7 | 0.00 | −1.5 |
| QCISD/cc-pVDZ | 25.8 | −1.6 | 29.2 | 69.8 | 0.00 | 15.6 |
| QCISD(T)/cc-pVDZ | 25.1 | −1.8 | 28.4 | 68.7 | 0.00 | 4.9 |
| CCSD/cc-pVDZ | 26.0 | −1.0 | 29.8 | 71.4 | 0.00 | 17.4 |
| CCSD(T)/cc-pVDZ | 25.1 | −1.5 | 28.6 | 69.4 | 0.00 | 5.3 |
| CCSD(T)/cc-pVTZ | 27.8 | 2.1 | 32.9 | 69.9 | 0.00 | 9.9 |

however, that a controlled reaction of $CF_2(\tilde{X}^1A_1)$ with $O_3(\tilde{X}^1A_1)$ in the presence of a heat sink could lead to **6** as a product.

## 7. Relative Stability of Isomers

The relative energies of the most stable rotamers of the $CF_2O_3$ isomers, calculated in the present work at various levels of theory, are presented in Table 5. As seen from the table, isomers **3a**, **6**, and **7** are predicted to be most stable. However, their ordering is quite sensitive to both the level of theory and the basis set. In particular, for all combinations the relative energies of **3a** and **6** are very close; at the highest level, CCSD(T)/cc-pVTZ, **6** is predicted to be more stable than **3a** by 2.1 kcal/mol. The relative energies of the open structures **5a** and **7** are more sensitive to the level of calculation. In the case of **5a**, increasing the level of theory from MP2 to CCSD(T) decreases its relative energy by 6.5 kcal/mol, but increasing the size of the basis set is less essential. On the contrary, all three factors turn out to be quite important in the case of **7**: Inclusion of triple excitations decreases the relative energy of this isomer by 11−12 kcal/mol, while increasing the basis set and the level of treatment of singles and doubles increases this energy by 5 kcal/mol (from cc-pVDZ to cc-pVTZ) and 20−22 kcal/mol (from MP2 to CCSD or QCISD), respectively. These results demonstrate that isomers of $CF_2O_3$ (especially, open structures **5** and **7)** represent rather difficult correlation problems; and, considering the structural similarities to the well-known difficult compounds, $CH_2O_2$,[20] $CF_2O_2$,[33] and FOOF,[53] this conclusion should not be considered surprising.

Despite the challenges to describing accurately the electronic structure of some of the isomers, ancillary calculations support the theoretical level used, at least at the semiquantitative level: The CCSD(T)/cc-pVTZ energies of the dissociation limits $F_2O(\tilde{X}^1A_1) + CO_2(\tilde{X}\ ^1\Sigma_g^+)$ (58.9 kcal/mol) and $CF_2(\tilde{X}^1A_1) + O_3(\tilde{X}^1A_1)$ (137.0 kcal/mol) relative to the lowest triplet asymptote, $F_2CO + O_2(X\ ^3\Sigma_g^-)$, are in reasonable agreement with their experimental values[47] (64.4 and 143.1 kcal/mol, respectively). Similarly, even though singlet oxygen, $O_2(a^1\Delta_g)$, should be described by a multideterminant reference, (single reference) CCSD(T)/cc-pVTZ predicts an excitation energy of 30 kcal/mol, which is to be compared with the experimental result of 22.5 kcal/mol.[52]

The results of our calculations for relative energies can be compared with those obtained by McKee and Webb[36] for **3** and **4**. In ref 36 it was predicted at the B3LYP/6-311+G(2df)//B3LYP/6-31+G(d) level of theory that the isomerization reaction FOC(=O)OF (**4**) → FC(=O)OOF (**3**) and the decomposition reactions FOC(=O)OF → $F_2O + CO_2$ and FOC(=O)OF → FC(=O)F + $O_2$ are exothermic by 28.9, 28.4, and 86.1 kcal/mol, respectively. Our CCSD(T)/cc-pVTZ calculations predict that these reactions are exothermic by 30.8, 26.7, and 85.6 kcal/mol, respectively, and, thus our results are in agreement with those obtained by McKee and Webb.[36]

To conclude this section, let us note that, according to our calculations, isomer **3** is one of the most stable isomers of $CF_2O_3$ and, from this viewpoint, it is not surprising that this isomer has been observed experimentally.[31] As mentioned in ref 35, the large exothermicity, i.e., 54.8 kcal/mol in our work and 54.6 kcal/mol in ref 35, for the decomposition of this molecule to FC(O)F and triplet oxygen, without compelling evidence of a large barrier, suggests that such decomposition may proceed readily, in agreement with experimental observation.[31]

## 8. $CF_2O_3$ Unimolecular Processes

In the course of studying isomerizations of $CF_2O_3$, we found that these processes are often multistage and involve rotamers of the carbonyl oxide **5** as important intermediates. In particular, minimum energy path calculations show that the conversion of **2** into **3** is a two-stage process involving **5d** as an intermediate, while the isomerization **2** → **4** is an even more complex process that involves both **5d** and **5b** as intermediates. Both of these processes start from the asymmetrical rotamer, **2b**, of the dioxirane (**2**) and lead first to **5d**. The paths of these isomerization reactions, including selected stationary points, are shown schematically in Figure 6.

The structure of the $\mathbf{TS_{2b-5d}}$ transition state, optimized at the MP2/cc-pVDZ level, is shown in Figure 7. This structure is formed as a result of first breaking the longer C−O bond in the dioxirane ring in **2b** and then simultaneously rotating the O−O group and the O−F group toward their cis relative position. The structure of $\mathbf{TS_{2b-5d}}$ is easily seen, by comparing Figures 4 and 7, to be quite close to that of **5d** but, in contrast to **5d**, this structure is not planar. At the CCSD(T)/cc-pVTZ level, the barrier height to the conversion of **2b** to **5d** is predicted to be quite high (52.3 kcal/mol).

The second stage of the **2** → **3** isomerization involves the conversion of the intermediate, **5d**, into **3a** through the planar transition state $\mathbf{TS_{5d-3a}}$ which is also shown in Figure 7. The conversion of **5d** into **3a** involves the shift of the fluorine atom from the COF group to the terminal oxygen atom of the COO chain. This process is prevented by a potential barrier of about 18 kcal/mol, but, if successful, is followed by the release of about 93 kcal/mol of heat. Thus, although the whole two-stage isomerization **2b** → **3a** is predicted to be exothermic by 27.0 kcal/mol, it is prevented by a high potential barrier (of about 66 kcal/mol).

The mechanism of the conversion **5** → **4** (i.e., the second stage of the isomerization from **2** to **4**) is predicted to be essentially more complex. This conversion, leading to **4a**, starts not from **5d**, which is formed as a result of the **2** → **5** isomerization, but rather from the rotamer **5b**. Although we did not determine the barrier for the **5d** → **5b** rearrangement, this barrier is not expected to be large (see section 5). In contrast to the minor complication of the **5d** → **5b** rearrangement, our calculations show that the **5** → **4** conversion proceeds through a hitherto unexpected high-energy minimum, **8a**. This local minimum of $CF_2O_3$, shown in Figure 8, looks like **4a**, but includes the novel C−F−O chain (with a very weak F−O bond (1.77 Å)) instead of C−O−F. In the C−F−O chain, the C−O distance is 2.465 Å, which clearly demonstrates that in fact there is no C−O bond. **8a** lies 23.8 kcal/mol above **5b**. Two enantiomers of **8a** are connected through two transition states **8aa** and **8aa′** (shown in Figure S3), corresponding to the rotation of the F−O bond downward and upward, respectively, relative to the plane of the rest of the molecule. The potential barrier heights of the transition states **8aa** and **8aa′** are very low (1.2 and 1.7 kcal/mol at the MP2/cc-pVDZ level, respectively).

Conversion of **5b** into **8a** requires that a potential barrier of 22.9 kcal/mol be surmounted. The O−O bond is already broken

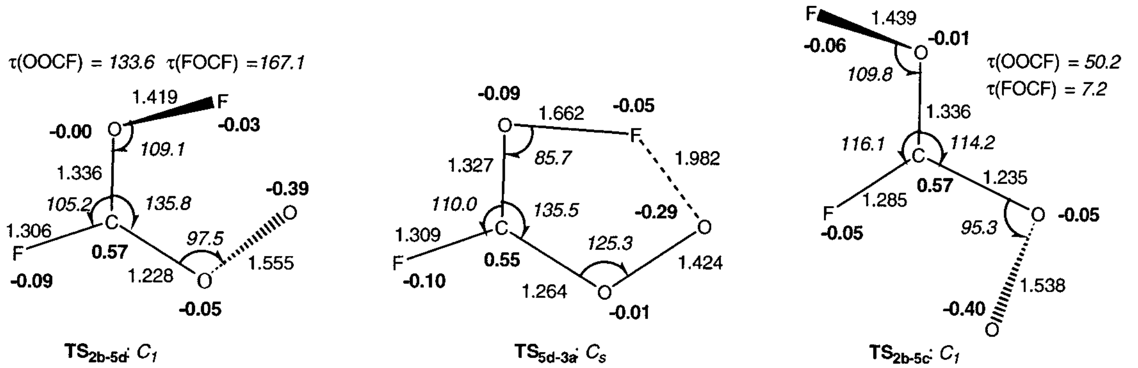


**Figure 7.** Geometries (in Å and deg) and Mulliken populations of transition states for **2** → **3** at the MP2/cc-pVDZ level.

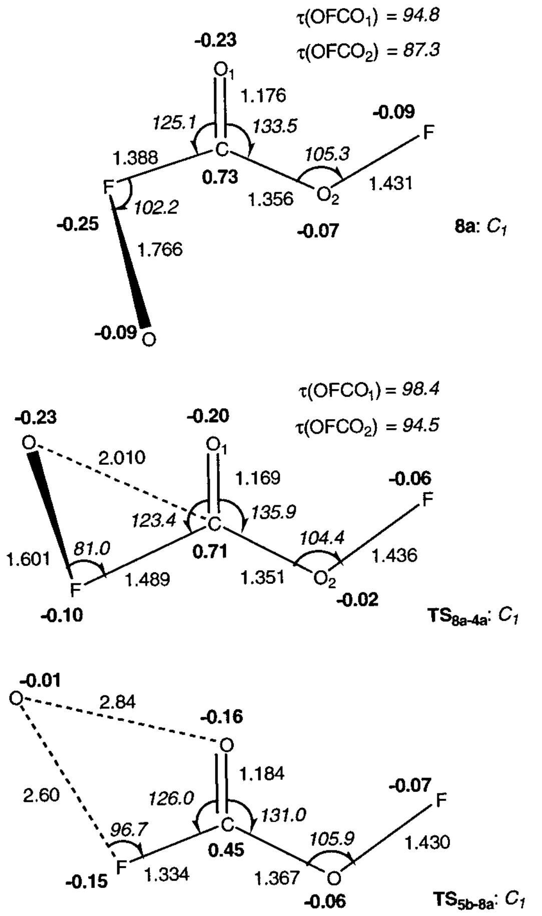


**Figure 8.** Geometries (in Å and deg) and Mulliken populations of transition states for **5** → **4** at the MP2/cc-pVDZ level.

($R_{O-O}$ = 2.84 Å) in the transition state $\mathbf{TS_{5b-8a}}$ (see Figure 8), but the O−F bond has not yet formed ($R_{O-F}$ = 2.60 Å). It is interesting that a displacement from the $\mathbf{TS_{5b-8a}}$ transition state along its imaginary mode (in-plane bending) leads to another transition state, **8aa′**, which lies 3.1 kcal/mol below $\mathbf{TS_{5b-8a}}$ (at MP2/cc-pVDZ level), and not directly to the minimum: **8a**.

The final step, i.e., conversion of **8a** into **4a**, involves overcoming a barrier of 1.9 kcal/mol, associated with the transition state $\mathbf{TS_{8a-4a}}$ (see Figure 8). This structure exhibits longer C−F (by 0.10 Å) and shorter O−F (by 0.16 Å) bonds than those in **8a**.

In summary, the isomerization of **2b** to **4a** involves four steps (**2b** → **5d**, **5d** → **5b**, **5b** → **8a** through **8aa′**, and, finally, **8a** → **4a**) and is prevented by a quite high potential barrier of about 69.1 kcal/mol, while the reverse process is prevented by a barrier of about 65.3 kcal/mol. It is clear that, as was the case for **2a** → **3a**, these barriers are too high for the isomerization processes **2a** ↔ **4a** and **2a** ↔ **3a** to proceed unimolecularly. The results of this section and those of section 5 lead one to the conclusion that although FC(OF)OO (**5**) is a high-energy isomer which is surely difficult to observe experimentally, it proves to be an important intermediate for isomerization processes in $CF_2O_3$.

## 9. $CF_2O_2$ Unimolecular Processes

Although this paper discusses the $CF_2O_3$ potential energy surface, the similarities between difluorodioxirane (**1**) and fluorofluoroxydioxirane (**2**), and the novel path suggested for the **2a** → **4a** isomerization, motivated us to address the analogous, and unsolved, problem for $CF_2O_2$. As mentioned above, difluorodioxirane (**1**) was synthesized by Russo and DesMarteau[27] through the reaction of its isomer FC(═O)OF with ClF, $Cl_2$, or $F_2$ in the presence of CsF.[27] On the basis of ab initio calculations of some of the stationary points on the $CF_2O_2$ PES, Kraka et al.[33] hypothesized that the major path of decomposition of $CF_2O_2$ "should be characterized by OO cleavage and a subsequent F shift leading to the somewhat more stable isomer FC(═O)OF" and that "rearrangement to FC(═O)OF is the most likely reaction of $CF_2O_2$ although it has not been observed experimentally". Our calculations corroborate their hypothesis, but show that the conversion from **1** into FC(═O)OF proves to be a rather complex multistage process, which is analogous to the **2a** → **4a** isomerization process in $CF_2O_3$.

The isomerization mechanism of $CF_2O_2$, suggested by our calculations, is shown schematically in Figure 9. The first step, which is completely analogous to the $CF_2O_3$ case (Figure 6), involves rearrangement of the dioxirane (**1**) into carbonyl oxide, $F_2COO$, through transition state **TS1**. As seen from Figure 10, the structural parameters of **TS1** predicted in the present work, at the MP2/cc-pVDZ level, and by Kraka et al.[33] are in good agreement. According to our CCSD(T)/cc-pVTZ calculations, $F_2COO$ is 46.5 kcal/mol less stable than **1** and the barrier for the $F_2COO$ → **1** isomerization is 8.8 kcal/mol; in ref 33, these values were predicted to equal to 42.3 and 11.2 kcal/mol, respectively. Note that the barrier to rearrangement of **1** into $F_2COO$, 55.3 kcal/mol, is very close to the barrier of 53.6 kcal/mol predicted for the analogous process, **2** → **5**, in $CF_2O_3$ (Figure 6).

The conversion from $F_2COO$ into FC(═O)OF, which is the analogous to the **5** → **4** step in $CF_2O_3$, proves to be a multistage process. The first step involves overcoming a potential barrier of 28.4 kcal/mol (at the MP2/cc-pVDZ level) through transition state **TS2** (Figure 9). Note that the analogous barrier in $CF_2O_3$ is predicted to have similar height (25.7 kcal/mol). It is at this stage that the supposition of Kraka et al.[33] concerning OO

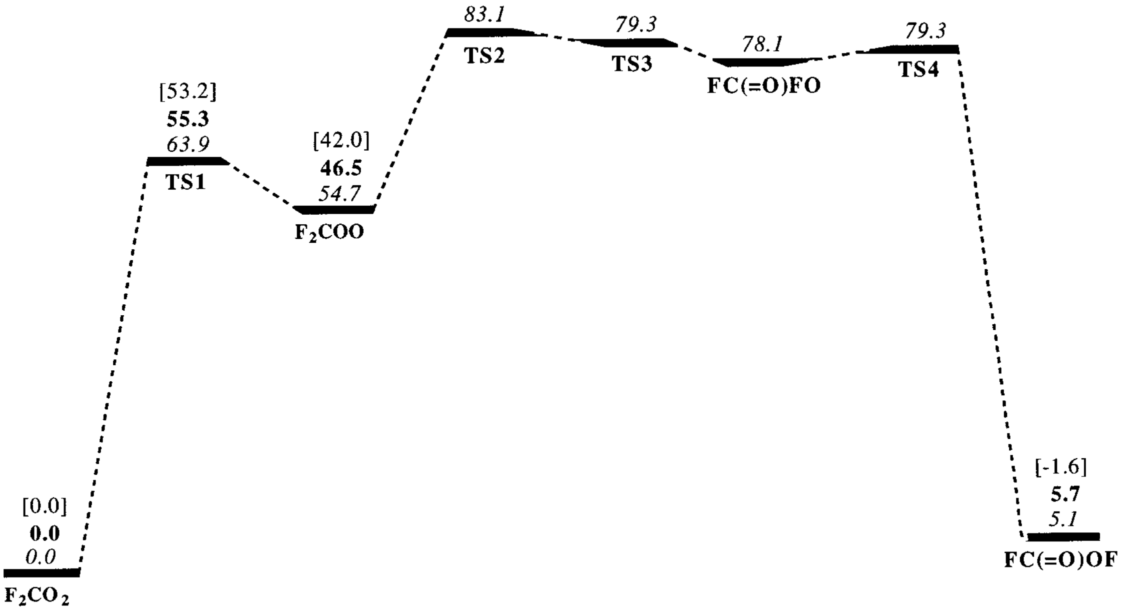
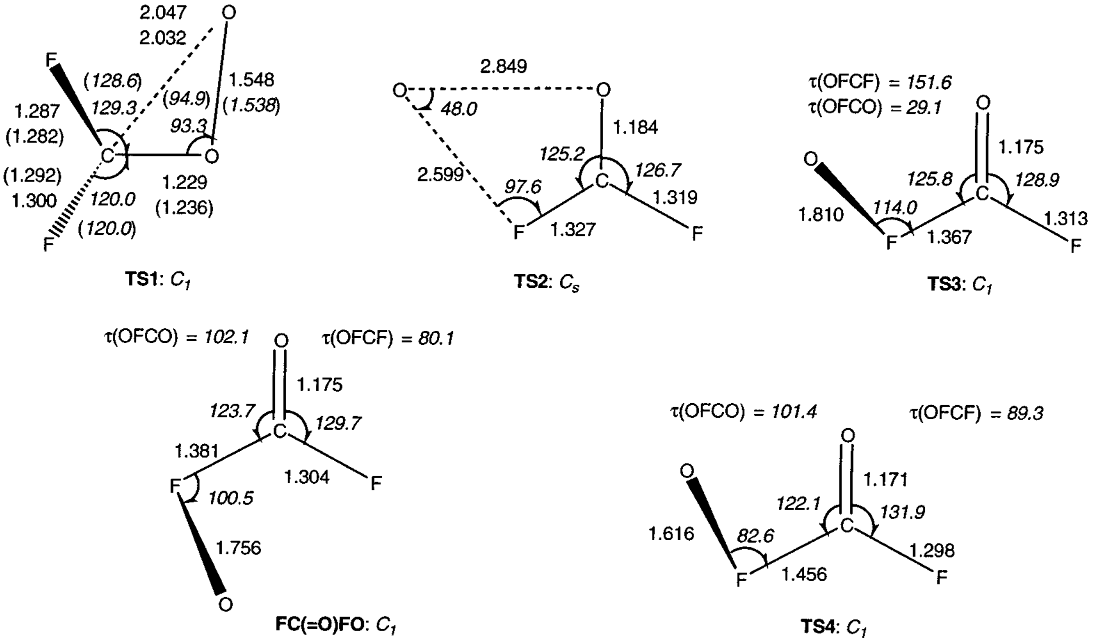


**Figure 9.** Schematic representation of the relative energies (kcal/mol) 504of $F_2CO_2$ and other stationary points of interest (CCSD(T)/cc-pVTZ values in bold, MP2/cc-pVDZ values in italics, and values from ref 33 in brackets).



TS1: $C_1$ TS2: $C_s$ TS3: $C_1$ FC(=O)FO: $C_1$ TS4: $C_1$

**Figure 10.** Geometries of transition states (in Å and deg) for $F_2COO \rightarrow FC(=O)OF$ at the MP2/cc-pVDZ level.

cleavage is realized. As should be expected, the structures of the transition states **TS2** in $CF_2O_2$ and **TS$_{5b-8a}$** in $CF_2O_3$ (Figure 6) are quite similar. Subsequent displacement along the imaginary mode of **TS2** leads (through intermediate transition state **TS3**) to the high-lying local minimum FC(=O)FO (which can be seen from Figure 10 to be similar to **8a**). FC(=O)FO converts to FC(=O)OF by surmounting a small potential barrier (of only 1.2 kcal/mol) corresponding to transition state **TS4**.

In summary, the results of our calculations show that rearrangement of difluorodioxirane (**1**) into its isomer FC(=O)OF proves to be a quite complex multistage process prevented by a high potential barrier (about 83 kcal/mol). With this understanding, it is hardly surprising that the synthetic preparation[27] made use of catalysts.

## 10. Conclusions

This paper considered the meagerly explored lowest singlet potential energy surface of $CF_2O_3$ using generally reliable ab initio electronic structure methods. Searching basins chosen using chemical intuition, five structural isomers were located and their equilibrium geometries and vibrational frequencies were calculated at the MP2/cc-pVDZ level. The adequacy of MP2/cc-pVDZ for geometrical data was assessed by comparisons with the few theoretical structures previously published and with QCISD calculations on one of the isomers (**4**) and on a related compound, $F_2COO$, that have particularly challenging electronic structures. In the course of investigating rearrangement pathways, two additional structural isomers (i.e., **7** and **8**) became known to us. Two open structures, i.e., not containing a ring, were found to be quite stable, lying at 2.1 kcal/mol (**3a**) and 9.9 kcal/mol (**7**) (at CCSD(T)/cc-pVTZ level) relative to the global minimum corresponding to the molozonide (**6**). The dioxirane (**2a**) and the carbonyl hypofluorite (**4a**) are less stable, lying at 27.8 and 32.9 kcal/mol, respectively. The two highest-energy isomers, fluorofluoroxycarbonyl oxide (**5**) and a novel compound, exhibiting divalent fluorine, **8**, while unlikely synthetic targets, seem to be critical to unimolecular rearrangments.

Whereas comparisons of CCSD(T)/cc-pVTZ calculations and experimental data on asymptotic limits showed that our calculations are likely to be semiquantitatively correct, say within ca. 7 kcal/mol, there is need for additional high-level calculations. Moreover, the differences between MP2 and CCSD(T) relative energies, and, to lesser extent, between QCISD(T) and CCSD(T), suggest significant multireference character in at least some of the wave functions. Subsequent stability checks on the isomers listed in Table 5 demonstrated that all have RHF−UHF instabilities, corroborating significant nondynamical correlation.

All rotamers of the structural isomers were calculated, as were most transition states between rotamers. Our results on molecular geometries and vibrational frequencies corroborate in general the B3LYP studies of McKee and Webb on isomers **3**[35] and **4**.[36] However, we find that if carbonyl hypofluorite (**4**) can be produced then it will exist as a mixture of its nearly isenergetic rotamer **4a** and **4b**, and we predict that **3** should exist in predominantly one form.

Our characterization of high-energy intermediates and transition states between structural isomers suggested a plausible mechanism for the isomerization of fluorofluoroxydioxirane to more stable isomers. In particular, we find that such isomerization is quite complex and proceeds through multiple steps involving carbonyl oxide structures as quite important intermediates. Drawing on the analogy between fluorofluoroxydioxirane and difluorodioxirane, we also suggest a mechanism for the isomerization of the latter that appears to explain the necessity of catalysts in the experimental synthesis. Our mechanism subsumes the earlier suggestion of Kraka et al.[33]

This study extends essentially knowledge of the $CF_2O_3$ lowest singlet PES. In our opinion, several isomers of $CF_2O_3$ may be observable experimentally, albeit at low temperature. While metastable, the adiabatic decay of the lowest-energy isomer (the molozonide, **6**) is prevented by a sizable barrier.

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**Supporting Information Available:** Figures of transition states between stereoisomers of **2**, **3**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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