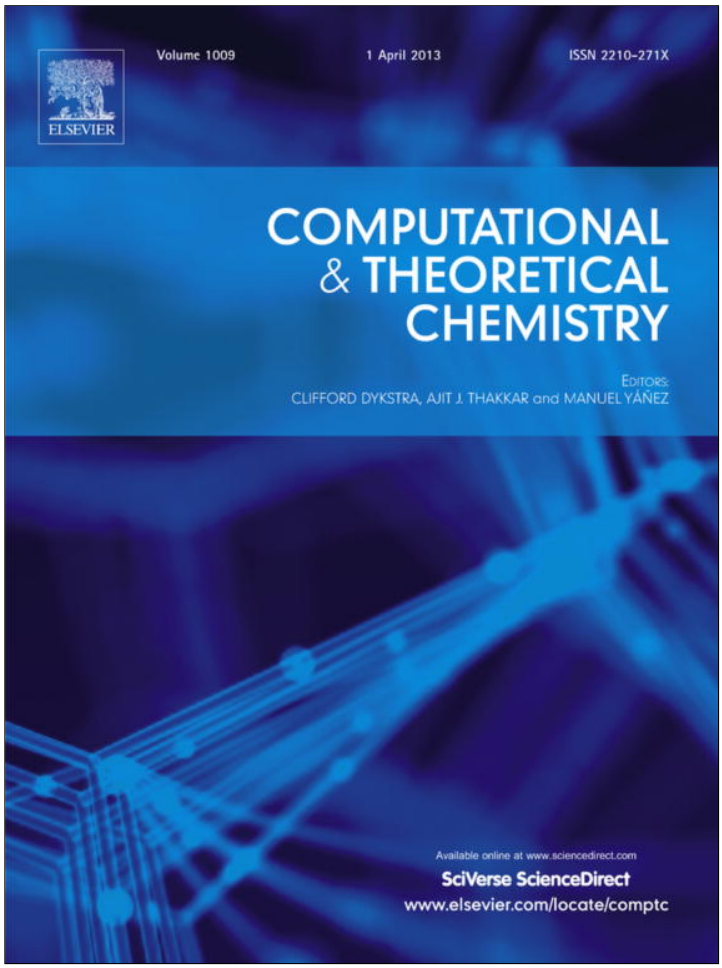

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Theoretical study of the molecular conformations, vibrational frequencies and thermochemistry of the FC(O)OOO(O)CF, FS(O_2)OOO(O_2)SF and FC(O)OOO(O_2)SF trioxides

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ABSTRACT

The molecular structures, conformational mobilities, harmonic vibrational frequencies and thermochemistry of the FC(O)OOO(O)CF, FS(O_2)OOO(O_2)SF and FC(O)OOO(O_2)SF trioxides were studied by *ab initio* and density functional methods. The potential energy curves for the internal rotations were calculated using the B3LYP hybrid functional with the 6-311+G(3df) basis set. The equilibrium conformations are characterized by skew structure with dihedral angles COOO and SOOO of about 90° and 95°, respectively. The most stable structures were also calculated using the G3(MP2)B3 and G4(MP2) *ab initio* methods and with the functional M06-2X/6-311+G(3df). Average standard enthalpies of formation at 298 K derived for FC(O)OOO(O)CF, FS(O_2)OOO(O_2)SF and FC(O)OOO(O_2)SF from isodesmic reactions energies calculated at the G3(MP2)//B3LYP/6-311++G(3df,3pd) and G4(MP2) levels of theory are predicted to be −195.4, −255.6, and −226.5 kcal mol^{-1}. From these values, O—O bond dissociation enthalpies of 25–33 kcal mol^{-1} were estimated.

1. Introduction

As alkyl peroxides, the alkyl trioxides and the corresponding radical decomposition products play a role in hydrocarbon oxidation in the atmosphere and in low-temperature combustion processes. To our knowledge, neither thermodynamic parameters relevant for the estimation of reaction pathways nor rate coefficients for these species are available. Due to the extensive calculation time, realistic *ab initio* calculations for polyatomic molecules were not feasible up to a few years ago. Before this, group additivity was the chosen method for the estimation of thermodynamic properties of large compounds. However, nowadays, with the increasing power of computers, the calculation time for large molecules is normally not a problem.

Because of the high thermal stability of CF_3OOOCF_3, ascribed to the presence of fluorine atoms, only this trioxide has been known for many years [1,2]. Previous kinetic studies have lead to a O—O bond dissociation energy of 30.3 ± 0.2 kcal mol^{-1} [3]. Other fluorinated open-chain trioxides more recently synthesized, isolated and characterized are $CF_3OC(O)OOO(O)COCF_3$ and $CF_3OC(O)OOO(O)CF$ [4,5]. The first was proved thermally stable up to 243 K and decomposes with a half-life of 1 min at room temperature. The latter is a thermally labile compound that decomposes at room temperature by rupture of either nonequivalent O—O bonds.

Only the first of the compounds here studied, FC(O)OOO(O)CF, has been described in the literature. Moreover, all members of the FC(O)O_x(O)CF series, with $x = 0$ [6,7], 1 [8], 2 [9,10] and 3 [11,12], have been isolated and characterized. In particular, the largest member of the series is formed as a secondary product in the FC(O)OO(O)CF synthesis (reaction of F_2 and CO in the presence of O_2 [12,13]). The trioxide was separated from the more volatile FC(O)OO(O)CF by sublimation at 178 K [12]. On the other hand, this trioxide is formed during the 248-nm photodissociation of $(FCO)_2$ in the presence of O_2 at room temperature [14]. Under these conditions, a high-pressure rate coefficient for the FC(O)O + FC(O)OO → FC(O)OOO(O)CF recombination reaction of 3.7×10^{-12} cm^3 molecule^{-1} s^{-1} was determined [14].

Regarding the other symmetric trioxide studied, FS(O_2)OOO(O_2)SF, a recent evaluation of the O—O bond dissociation energy at 298 K leads to a value comparable to the experimental O—O bond dissociation energy in the stable peroxide FS(O_2)OO(O_2)SF [15,16]. In that work, G3(MP2)B3 calculations suggest the formation of a stable FS(O_2)OOO(O_2)SF trioxide by association of FS(O_2)O and FS(O_2)OO radicals [15]. The first radical has been subject of a number of experimental and theoretical kinetic investigations [16–25], while the existence of the second one has been suggested to explain the pronounced influence of O_2 on the reaction mechanism of the photolysis of FS(O_2)OF in the presence of

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SO_2 and SO_3 [17] and on the reaction mechanism of the thermal $FS(O_2)OF/CO$ system [19]. More recently, additional experimental and theoretical evidences for the existence of the $FS(O_2)OO$ have been reported [15].

Finally, the stability of the asymmetrical trioxide $FC(O)OOO(O_2)SF$ has been also theoretically investigated in the present work. All mentioned trioxides possess stable related peroxides. It is well-known the increase in stability as the oxygen chain increases in perfluorinated and specially perfluoroalkylated compounds [26]. Besides, the presence of acyl groups in the three trioxides may confer additional stability. To our knowledge, no experimental or theoretical data about the structure, vibrational frequencies or bond dissociation energy of $FC(O)OOO(O_2)SF$ have been reported so far.

The main goal of this work is the theoretical characterization of the gas-phase conformational structures, harmonic vibrational frequencies and thermal stabilities of the trioxides $FC(O)OOO(O)CF$, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$ by using very well established quantum-chemical methods.

2. Computational details

The calculations were performed with the Gaussian 09 program package [27]. The popular hybrid B3LYP of the density functional theory, DFT, which employs Becke's three-parameter nonlocal exchange functional [28,29] together with the nonlocal correlation functional of Lee et al. [30], was used to calculate the potentials for the internal rotations of $FC(O)OOO(O)CF$, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$. The 6-311+G(3df) split-valence Pople's basis set was selected for this case [31]. The extended triple split-valence basis set confers remarkable flexibility to represent regions of high electron density among the bonded atoms and far from the nuclei. The optimized geometrical parameters and harmonic vibrational frequencies for the different conformers were obtained using analytical gradient and analytical second derivatives methods at the same level of theory. Unscaled vibrational frequencies were used to evaluate the zero-point energies (ZPE) and the vibrational contribution to the thermal correction at 298.15 K. Furthermore, the more recent M06-2X method was also employed [32]. This is a high nonlocal functional with double amount of nonlocal exchange (2X). It is recommended for applications that include the prediction of accurate structures, thermochemistry and electronic barriers for compounds containing main-group elements [32].

More accurate estimates of energy were carried out by using the G3(MP2)B3 [33,34] and G4(MP2) [35] model chemistries. In the G3(MP2)B3 method, the optimized molecular structure and harmonic vibrational frequencies (scaled by a factor 0.96) are calculated at the B3LYP/6-31G(d) level. Based on the optimized structure, the energy at 0 K is obtained from a set of single-point energy evaluations at the levels MP2/6-31G(d), QCISD(T)/6-31G(d) and MP2(full)/GTMP2Large. Spin-orbit, higher-level and zero-point vibrational energy corrections used to calculate the total electronic energy at 0 K were performed *a posteriori* [33,34]. However, a slightly modified method, G3(MP2)//B3LYP/6-311+G(3df), was employed in this work. Here, optimized molecular structures and harmonic vibrational frequencies (unscaled) at B3LYP/6-311+G(3df) instead of B3LYP/6-31G(d) are used. Also the bond additivity correction (BAC) procedure for the G3(MP2)B3 quantum chemistry method has been employed [36]. This empirical model applies atomic, molecular and pair wise bond corrections to theoretical enthalpies of formation improving the predictive capability of the G3(MP2)B3 method.

Finally, we employed the G4(MP2) model which is a modification of the more accurate G4 method in which second-order perturbation theory is used instead of fourth-order perturbation theory [35]. It uses B3LYP/6-31G(2df,p) optimized geometries and harmonic vibrational frequencies (scaled by 0.9854) followed by a series of single point energy calculations at higher levels of theory. The first single point energy calculation is performed at the triples-augmented coupled cluster level of theory, CCSD(T), with the 6-31G(d) basis set. This energy is then modified by a series of energy corrections. In this way, the average absolute deviation of the G4(MP2) estimations from well-known experimental enthalpies of formation values is close to the typically chemical accuracy of about 1 kcal mol^{-1} [35].

3. Results and discussion

3.1. Torsional barriers

To determine the accurate thermochemistry of the trioxides, the characterization of their more stable conformers is required. Therefore, a detailed rotational analysis was carried out. Symmetrical $FC(O)OOO(O)CF$ and $FS(O_2)OOO(O_2)SF$ trioxides present four internal rotations around the two O—O bonds and two C—O or S—O bonds, respectively. However, by symmetrical restrictions, only two internal rotations must be calculated for each trioxide. In the case of $FC(O)OOO(O_2)SF$, the number of internal rotations is also four, around C—O, S—O and the two not equivalent O—O bonds. As a result, the rotational conformers shown in Fig. 1 were derived. It can be noted that the number of conformers increases with the complexity of the trioxide, being four for $FC(O)OOO(O)CF$, five for $FS(O_2)OOO(O_2)SF$ and six for $FC(O)OOO(O_2)SF$.

To compute the different torsional barriers, we have performed a potential energy scan by varying the corresponding torsional angle in steps of 15°, and allowing the optimization of the remaining geometrical parameters at each step. The local and global minima corresponding to different conformers and the maxima corresponding to transition states were fully optimized. To derive an analytic potential function $V(\Phi)$ for each internal rotation, the truncated Fourier expansion (1)

$$V(\Phi) = a_0 + \sum a_i \cos(i\Phi) + \sum b_i \sin(i\Phi), \quad (1)$$

was fitted to the potential values computed at the B3LYP/6-311+G(3df) level of theory. The resulting values for the a_i and b_i coefficients ($i = 1–4$) are listed in Table A (Supporting Information). The calculated electronic potentials for all internal rotations are shown in Figs. 2–5. As can be seen, excellent fits with squared correlation coefficients r^2 better than 0.996 were obtained for all cases.

Fig. 2A shows the calculated rotational barriers around the S—O bond for $FS(O_2)OOO(O_2)SF$. The resulting three conformers exhibit different O=SOO dihedral angles, being of about 317° for the most stable conformer (conformer 1) and about 173° and 69° for the conformers 2 and 3, respectively. The last conformers are 0.2 and 2.9 kcal mol^{-1} less stable than conformer 1. These conformers are separated by two small barriers of 3.2 and 3.3 kcal mol^{-1} and one higher of 5.7 kcal mol^{-1} (imaginary vibrational frequencies of $\nu = 41i$, $31i$ and $75i$ cm^{-1}, respectively). Fig. 2B shows the calculated rotational potential for the S—O bond of the trioxide $FC(O)OOO(O_2)SF$. As can be seen, both potentials exhibit quite similar characteristics and present analogous rotational barriers.

Fig. 3 shows the rotations about the O—O bonds next to the S atom, SO—OO. Again the calculated potentials for $FS(O_2)OOO(O_2)SF$ (Fig. 3A) and $FC(O)OOO(O_2)SF$ (Fig. 3B) are very similar. For $FC(O)OOO(O_2)SF$, the computed electronic potential leads to two minima (conformers 1 and 4) and two maxima. However, in the case of the $FS(O_2)OOO(O_2)SF$ trioxide, a third minimum is observed (conformer 5). The SOOO dihedral angles of the most stable conformations are both of about 95°. Conformers 4 and 5 are about 2.5 kcal mol^{-1} less stable than conformer 1, and present potential

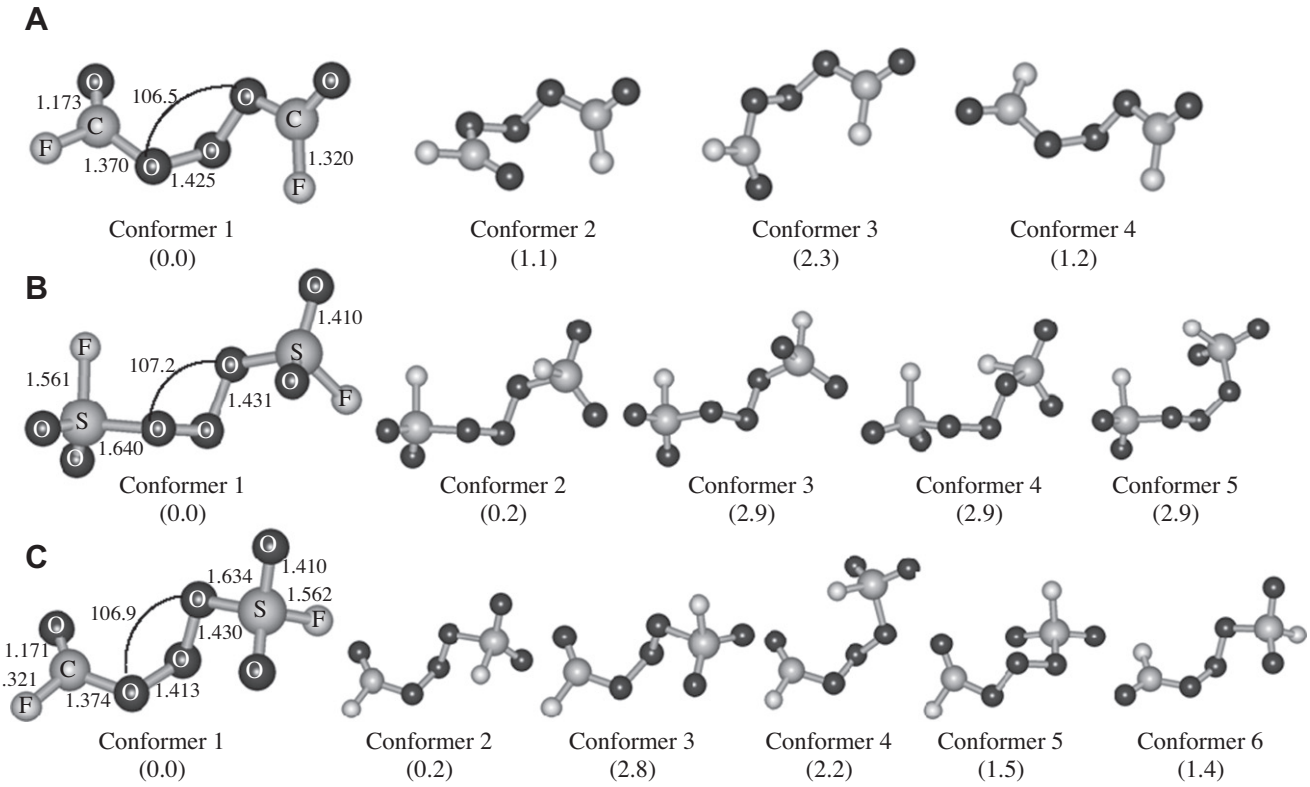

Fig. 1. Molecular geometries of different conformers obtained for (A) FC(O)OOO(O)CF, (B) $FS(O_2)OOO(O_2)SF$ and (C) $FC(O)OOO(O_2)SF$ at the B3LYP/6-311+G(3df) level of theory. The relative energies of the rotational conformers are indicated in brackets (in kcal mol^{-1}).

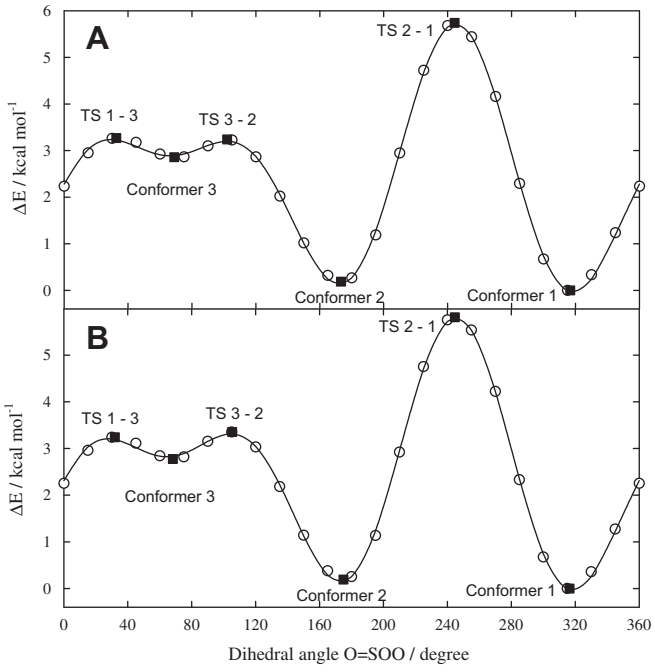

Fig. 2. Potential energy barriers for internal rotation around O═SOO bond for (A) $FS(O_2)OOO(O_2)SF$ and (B) $FC(O)OOO(O_2)SF$. (○) Calculated at the B3LYP/6-311+G(3df) level. (■) Full optimized at the same level. (—) Fourier analysis with the coefficient of Table A.

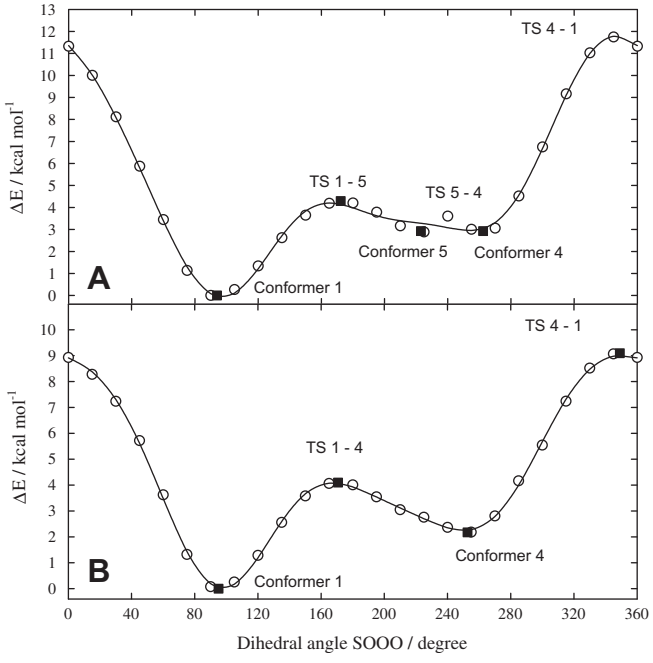

Fig. 3. Potential energy barriers for internal rotation around SO—OO bond for (A) $FS(O_2)OOO(O_2)SF$ and (B) $FC(O)OOO(O_2)SF$. (○) Calculated at the B3LYP/6-311+G(3df) level. (■) Full optimized at the same level. (—) Fourier analysis with the coefficient of Table A.

energy barriers of about 4.2 and 9.1 kcal mol^{-1}, with molecular structures characterized by imaginary vibrational frequencies of 36*i* and 93*i* cm^{-1} respectively for both mentioned trioxides.

The computed potential for the O—O bonds next to C atom in FC(O)OOO(O)CF and $FC(O)OOO(O_2)SF$ molecules, CO—OO, are shown in Fig. 4. This rotation leads to two minima (conformers 1 and 5) and two maxima for $FC(O)OOO(O_2)SF$, and the calculated

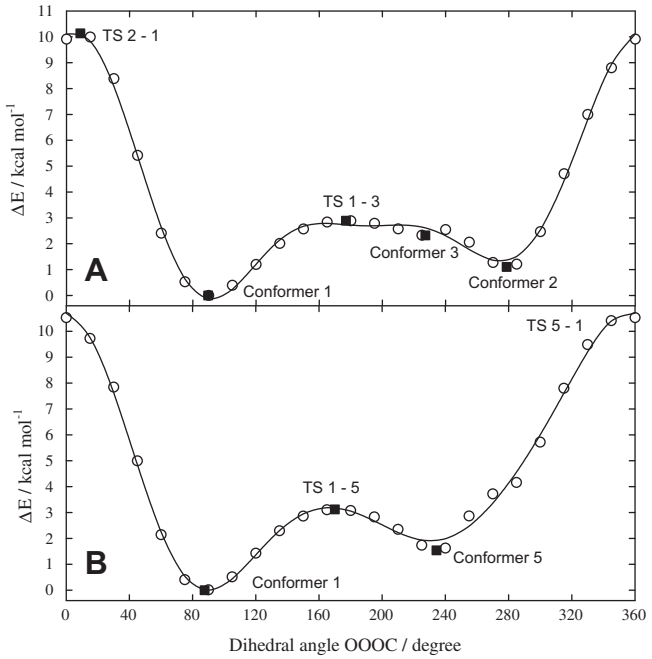

Fig. 4. Potential energy barriers for internal rotation around OO—OC bond for (A) FC(O)OOO(O)CF and (B) FC(O)OOO(O_2)SF. (○) Calculated at the B3LYP/6-311+G(3df) level. (■) Full optimized at the same level. (—) Fourier analysis with the coefficient of Table A.

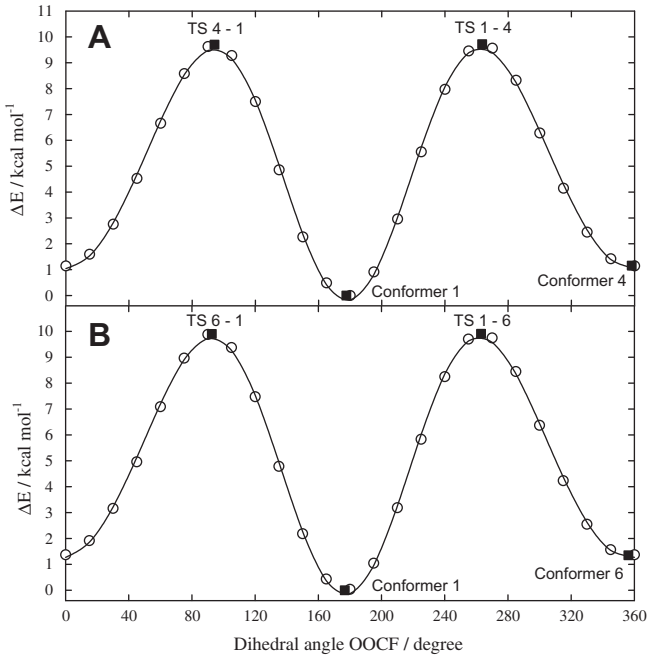

Fig. 5. Potential energy barriers for internal rotation around OO—CF bond for (A) FC(O)OOO(O)CF and (B) FC(O)OOO(O_2)SF. (○) Calculated at the B3LYP/6-311+G(3df) level. (■) Full optimized at the same level. (—) Fourier analysis with the coefficient of Table A.

potential presents some differences compared to the corresponding to the symmetrical trioxide. In FC(O)OOO(O)CF, conformer 2 appears at dihedral angle of about 280°, larger than conformer 5 in FC(O)OOO(O_2)SF, at 234°. Besides, in the symmetrical trioxide another minimum is observed at about 227° (conformer 3). The conformers 2 and 3 of FC(O)OOO(O)CF are 1.1 and 2.3 kcal mol^{-1} less stable than the corresponding conformer 1, and the conformer 5 of FC(O)OOO(O_2)SF is 1.5 kcal mol^{-1} less stable than the most stable conformer for this trioxide. In the case of FC(O)OOO(O)CF, minima are separated by a high electronic barrier of 10.1 kcal mol^{-1} (ν = 107i cm^{-1}) at dihedral angle of about 9° and a smaller barrier of 2.9 kcal mol^{-1} (ν = 27i cm^{-1}) at about 177°. FC(O)OOO(O_2)SF trioxide exhibits electronic barrier slightly higher of 10.6 and 3.1 kcal mol^{-1} at about 350° and 170°, respectively (ν = 99i and 32i cm^{-1}).

Finally, Fig. 5 shows the potential curves calculated for the C—O bond in FC(O)OOO(O)CF and FC(O)OOO(O_2)SF trioxides. Both rotational potentials present two minima and two maxima. The two minima differ in 1.2 kcal mol^{-1} for FC(O)OOO(O)CF and in 1.4 kcal mol^{-1} for FC(O)OOO(O_2)SF. The barriers located at about 93 and 263° possess both the same height with values of 9.7 (98i cm^{-1}) and 9.9 kcal mol^{-1} (98i cm^{-1}) for FC(O)OOO(O)CF and FC(O)OOO(O_2)SF, respectively.

3.2. Molecular structures and harmonic vibrational frequencies

The geometrical parameters and harmonic vibrational frequencies for the global minimum structures of FC(O)OOO(O)CF, FS(O_2)-OOO(O_2)SF and FC(O)OOO(O_2)SF were obtained from B3LYP/6-311+G(3df) and M06-2X/6-311+G(3df) calculations. Under these conditions, the frequency scaling factor is expected to be close to unity [37].

3.2.1. FC(O)OOO(O)CF

The calculated structural parameters for FC(O)OOO(O)CF are presented in Table 1. The most stable conformation of this trioxide (see Fig. 1A) exhibits the C—O bonds *trans* and both C=O bonds *syn* respect to the OOO plane, that is, the most stable rotamer is *trans-syn-syn* bis(fluoroformyl)trioxide, like have been found by X-ray diffraction in the crystal structure [12]. The calculated geometry is in very good agreement with the experimentally determined. In fact, small mean absolute deviations (MAD) of 0.0095 and 0.014 Å were obtained for the bond lengths at the B3LYP/6-311+G(3df) and M06-2X/6-311+G(3df) levels, respectively. A comparison between computed and experimental data also leads to small MAD values of 3.0° and 1.2° for the bond angles. The main structural characteristics of trioxides are the COOO dihedral angle and the O—O bond lengths. In the case of FC(O)OOO(O)CF the calculated values for the mentioned dihedral angle are next to 90° and the mean O—O bond length is of 1.425 and 1.393 Å at B3LYP/6-311+G(3df) and M06-2X/6-311+G(3df) levels, respectively. To compare, CF_3OOOCF_3 trioxide also present a skew structure with COOO dihedral angle of 96° and slightly longer O—O bond lengths of 1.452 Å in the gas phase and of 1.437 Å in the crystal [38].

The harmonic vibrational frequencies and infrared intensities computed for the most stable conformer of FC(O)OOO(O)CF are listed in Table B of the Supporting Information. In addition, mode assignments, obtained from the animation of the normal modes and by comparison with species with similar groups, are included. However, the great majority of the modes are strongly coupled with each other and therefore only approximate assignments are expected. An inspection of Table B shows the very good correlation found between experimental and calculated frequencies. In fact, MAD values of 12.4 and 69.3 cm^{-1} were respectively obtained using the B3LYP/6-311+G(3df) and M06-2X/6-311+G(3df) levels. The symmetrical and asymmetrical carbonyl stretching modes are located at 1956 and 1935 cm^{-1} respectively. The first agree very well with the experimental value of 1921.7 cm^{-1} [12]. The computed C—F and C—O stretching modes of 1218 and 941 cm^{-1} also agree reasonably well with the respective experimental values of 1162 and 903 cm^{-1} [12].

Table 1
Calculated and experimental geometrical parameters of FC(O)OOO(O)CF (bond lengths in Angstroms and angles in degrees).

Parameter	Experimental [12]	B3LYP/6-311+G(3df)	M06-2X/6-311+G(3df)
$r(C—F)_m$	1.314	1.320	1.309
$r(C=O)_m$	1.162	1.173	1.167
$r(C—O)_m$	1.364	1.370	1.364
$r(O—O)_m$	1.440	1.425	1.393
$\angle(F—C=O)_m$	125.8	126.3	126.5
$\angle(O—C=O)_m$	130.1	121.1	128.8
$\angle(F—C—O)_m$	104.1	104.0	104.7
DIH(O=C—O—O)	−2.1	2.3	−2.2
DIH(C—O—O—O)	99.0	90.1	86.1
∠(O—O—O)	104.0	106.5	106.2

3.2.2. $FS(O_2)OOO(O_2)SF$

The obtained geometrical parameters for $FS(O_2)OOO(O_2)SF$ are shown in Table 2. In this trioxide, the most stable rotamer possesses a skew structure with *trans* orientation of the two $FS(O_2)$ groups and a SOOO dihedral angle of about 95°. The two S—F bonds are *syn* with respect to the OOO plane and the O—O bond lengths are of 1.431 and 1.402 Å at the B3LYP/6-311+G(3df) and M06-2X/6-311+G(3df) levels, respectively. As in the case of FC(O)OOO(O)CF, the last functional predicts slightly smaller bond lengths. No experimental structural data are available for $FS(O_2)OOO(O_2)SF$ to comparison. However, the calculated geometrical parameters agree very well with some compounds containing the $FS(O_2)O$ group. For example, the S=O bond length of 1.410 Å compares very well with the measured bond length in the hypofluorite $FS(O_2)OF$ of 1.409 Å [39].

Calculated harmonic vibrational frequencies, approximate mode assignments and infrared intensities for $FS(O_2)OOO(O_2)SF$ are given in Table C (Supporting Information). The average values derived for the symmetrical S=O stretching at the B3YP/6-311+G(3df) and M06-2X/6-311+G(3df) levels are 1499 and 1555 cm^{-1}. These values are close to the experimental value corresponding to gaseous $FS(O_2)OF$ of 1502 cm^{-1} [39]. Similarly, the B3LYP/6-311+G(3df) asymmetrical S=O stretching of about 1250 cm^{-1} is in nice agreement with the experimental of $FS(O_2)OF$, 1252 cm^{-1} [39], while the obtained for the S-F stretching of about 823 cm^{-1} is somewhat larger than reported for the $FS(O_2)OF$ of 787 cm^{-1} [39].

3.2.3. $FC(O)OOO(O_2)SF$

The computed geometrical parameters for $FC(O)OOO(O_2)SF$ are listed in Table 3. Also this trioxide presents a twisted skeleton with COOO and SOOO dihedral angles next to 90° and 95° respectively. In addition, two C—F bonds *syn* respect to the OOO plane and a $FC(O)OO—O(O_2)SF$ bond slightly longer than the $FC(O)O—OO(O_2)SF$ bond are predicted.

Table 2
Calculated geometrical parameters of $FS(O_2)OOO(O_2)SF$ (bond lengths in Angstroms and angles in degrees).

Parameter	B3LYP/6-311+G(3df)	M06-2X/6-311+G(3df)
$r(S—F)_m$	1.561	1.539
$r(S=O)_m$	1.410	1.400
$r(S—O)_m$	1.640	1.618
$r(O—O)_m$	1.431	1.402
$\angle(F—S=O)_m$	107.1	107.2
$\angle(O—S=O)_m$	111.2	110.5
$\angle(F—S—O)_m$	98.5	98.0
DIH(S—O—O—O)	95.2	95.5
∠(O—O—O)	107.2	106.2

Table 3
Calculated geometrical parameters of $FC(O)OOO(O_2)SF$ (bond lengths in Angstroms and angles in degrees).

Parameter	B3LYP/6-311+G(3df)	M06-2X/6-311+G(3df)
r(S—F)	1.562	1.539
$r(S=O)_m$	1.410	1.401
r(S—O)	1.634	1.613
$r(O—O)_{next\ to\ S}$	1.437	1.406
$r(O—O)_{next\ to\ C}$	1.413	1.386
r(C—O)	1.374	1.367
r(C—F)	1.321	1.307
r(C=O)	1.171	1.167
$\angle(F—S=O)_m$	107.0	107.1
$\angle(O—S=O)_m$	111.5	110.8
∠(S—O—O)	110.8	109.9
∠(F—C=O)	126.5	126.7
∠(O—C=O)	129.5	128.5
∠(F—C—O)	104.0	104.7
∠(C—O—O)	109.5	109.2
DIH(S—O—O—O)	95.0	93.2
DIH(C—O—O—O)	87.7	83.4
∠(O—O—O)	106.9	106.5

Computed vibrational properties are presented in Table D (Supporting Information). In this case, the characteristic movements of $FS(O_2)O$ and FC(O)O moieties are observed at wave numbers similar to those observed for the symmetrical trioxides.

3.3. Thermochemistry

Enthalpies of formation of FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$ trioxides were computed from both total atomization energies and isodesmic reactions. The first approach was used to calculate the enthalpies of formation at 0 K, $\Delta_f H_0$, by subtracting the computed total atomization energies, ΣD_0, with explicit consideration of atomic spin-orbit effects, from the experimental enthalpies of formation of the carbon (169.98 ± 0.1 kcal mol^{-1}), fluorine (18.47 ± 0.07 kcal mol^{-1}), sulfur (65.66 ± 0.06 kcal mol^{-1}) and oxygen atoms (58.99 ± 0.02 kcal mol^{-1}) [40]. The spin-orbit corrections were obtained from the atomic energy levels from Moore [41] and the spin-orbit splittings from Huber and Herzberg [42]. They correspond to a weighted average of the splittings of the lowest energy state. Estimated thermal contributions and $H°_{298.15}–H°_0$ values for carbon, fluorine, sulfur and oxygen atoms of 0.25, 1.05, 1.05 and 1.04 kcal mol^{-1} were employed afterwards to transform the $\Delta_f H_0$ values to 298 K, $\Delta_f H_{298}$ [43]. The computed ΣD_0, $\Delta_f H_0$ and $\Delta_f H_{298}$ for FC(O)OOO(O)CF, $FS(O_2)$-$OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$ are listed in Table 4. As expected, due to the fact that this method requires an accurate determination of the energetics of the molecule and its constituent atoms, large basis set effects were observed. In fact, we find a reduction of calculated enthalpies of formation values of about of

Table 4
Calculated atomization energies and enthalpies of formation for FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$ (in kcal mol^{-1}).

Level of theory	FC(O)OOO(O)CF			$FS(O_2)OOO(O_2)SF$			$FC(O)OOO(O_2)SF$		
	ΣD_0	$\Delta_f H_0$	$\Delta_f H_{298}$	ΣD_0	$\Delta_f H_0$	$\Delta_f H_{298}$	ΣD_0	$\Delta_f H_0$	$\Delta_f H_{298}$
B3LYP/6-311+G(3df)	855.1	−185.3	−187.5	796.2	−218.5	−222.7	826.4	−202.7	−205.9
M06-2X/6-311+G(3df)	868.7	−198.9	−201.2	815.4	−237.7	−242.3	843.3	−219.6	−223.0
G3(MP2)//B3LYP/6-311+G(3df)	857.6	−185.8	−187.9	817.0	−235.8	−240.1	838.5	−212.0	−215.2
BAC-G3(MP2)//B3LYP/6-311+G(3df)[a]	857.6	−185.8	−187.9	832.8	−251.6	−255.9	846.4	−219.9	−223.1
G4(MP2)	856.5	−184.7	−186.8	825.7	−244.5	−248.7	842.4	−215.9	−219.0

[a] Bond additivity corrections at G3(MP2)//B3LYP/6-311+G(3df) level are listed in Table E (Supporting Information).

Table 5
Isodesmic reactions, calculated enthalpy changes and enthalpies of formation (in kcal mol^{-1}) for FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$.

Isodesmic reactions	
(1)	$2CH_3OH + 2F_2CO + 2H_2O_2 \rightarrow FC(O)OOO(O)CF + 2CH_3F + 3H_2O$
(2)	$2CH_3OH + 2F_2CO + HOOOH \rightarrow FC(O)OOO(O)CF + 2CH_3F + 2H_2O$
(3)	$2HFSO_3 + 2H_2O_2 \rightarrow FS(O_2)OOO(O_2)SF + 3H_2O$
(4)	$2HFSO_3 + HOOOH \rightarrow FS(O_2)OOO(O_2)SF + 2H_2O$
(5)	$HFSO_3 + CH_3OH + F_2CO + 2H_2O_2 \rightarrow FC(O)OOO(O_2)SF + CH_3F + 3H_2O$
(6)	$HFSO_3 + CH_3OH + F_2CO + HOOOH \rightarrow FC(O)OOO(O_2)SF + CH_3F + 2H_2O$

Isodesmic reactions	B3LYP/6-311++G(3df,3pd)		M06-2X/6-311++G(3df,3pd)		G3(MP2)//B3LYP 6-311++G(3df,3pd)		G4(MP2)	
	ΔH_r	$\Delta_f H_{298}$	ΔH_r	$\Delta_f H_{298}$	ΔH_r	$\Delta_f H_{298}$	ΔH_r	$\Delta_f H_{298}$
1	−23.1	−194.8	−22.2	−193.9	−24.6	−196.3	−23.6	−195.3
2	−7.9	−193.9	−7.5	−193.3	−9.4	−195.4	−8.7	−194.6
3	−1.6	−253.1	0.1	−251.5	−5.0	−256.6	−3.8	−255.4
4	13.7	−252.2	14.8	−251.1	10.2	−255.7	11.2	−254.7
5	−13.1	−224.8	−12.3	−224.0	−16.0	−227.7	−15.0	−226.6
6	2.1	−223.9	2.4	−223.6	−0.8	−225.8	−0.1	−226.0

60 kcal mol^{-1} in average, with the addition of 2d functions and one f function to the 6-311+G(d) basis set. The importance of including high *d*- and *f*-polarization functions in sulfur and fluorine containing compounds is well documented [44]. By comparing B3LYP with M06-2X results it is evident that the Becke's three parameter exchange functional in conjunction with the LYP correlated functional predicts a smaller stability for all trioxides studied. To assess the performance of the B3LYP calculations, they have been compared against more accurate results provided by the G3(MP2)//B3LYP/6-311+G(3df) and G4(MP2) models. The derived values are smaller than those obtained with B3LYP hybrid functional and compare reasonably well with those calculated with the M06-2X functional.

As mentioned above, calculations were also performed using selected isodesmic and isogyric reaction schemes [45]. In this procedure, the enthalpy of formation for a given molecule is obtained by combining the computed isodesmic enthalpy change, ΔH_r, with well-established thermochemical data for the other species involved in the reaction. In these, normally hypothetical, reactions, the number of chemical bonds and the spin multiplicities are conserved. As a consequence, some systematic errors due to both incompleteness of the basis sets and deficiencies in the treatment of the electron correlation energy are mostly compensated, such that more accurate enthalpies of formation than those obtained from atomization energies are obtained [45,46]. The reactions employed in this study to estimate the enthalpies of formation of the trioxides are given in Table 5. The calculated isodesmic reaction enthalpies and the derived enthalpies of formation are also included in this table. In these calculations we have used the following well established enthalpies of formation (in kcal mol^{-1}): -180.0 ± 2 ($HFSO_3$) [40], -57.798 ± 0.010 (H_2O), -32.5 ± 0.05 (H_2O_2), −21.5 (HOOOH), -48.04 ± 0.14 (CH_3OH), -57.1 ± 0.2 (CH_3F) and -149.1 ± 1.4 (F_2CO) [47]. The largest error limit corresponds to $HFSO_3$. However, the recommended value [40] agrees very well with that calculated at the CCSD(T) level of theory with a basis set extrapolated to the CBS limit, of −179.5 kcal mol^{-1} [48]. On the other hand, the recommended NASA value for the enthalpy of formation of HOOOH is based on CCSD(T) total atomization energies computed with augmented correlation consistent basis sets (cc-pVnZ, *n* = *Q*, 5) extrapolated to the CBS limit, without an stated error limit [47]. However, due to the high level of theory employed, an error close to the chemical accuracy of ±1 kcal mol^{-1}, has been reported by the authors [49].

In this case, as expected, no large basis set effects are observed. In average, for the three trioxides, only a relatively small difference in the $\Delta_f H_{298}$ values of 1.0 kcal mol^{-1} is obtained as one passes from the B3LYP/6-311++G(d,p) to the B3LYP/6-311++G(3df,3pd) method. However, the enthalpies of formation calculated at the G3(MP2)//B3LYP/6-311++G(3df,3pd) and G4(MP2) levels of theory result in more negative values than those obtained with the B3LYP and M06-2X functionals. In addition, the values derived from atomization energies of Table 4 are, as usually, less negative than the values corresponding to the isodesmic method. At the best levels of theory employed here, G3(MP2)//B3LYP/6-311++G(3df,3pd) and G4(MP2), the average values of −195.4, −255.6 and −226.5 kcal mol^{-1} for enthalpies of formation of FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$ were derived. An error estimate, based on the experimental enthalpies, of ±2 kcal mol^{-1} is assigned to these values.

The main thermal decomposition products of the present trioxides are probably formed by breaking of one of its O—O bonds. Therefore, to investigate the thermal stability of FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$, we estimated the dissociation enthalpy for both O—O bonds of each trioxide and for C—O and S—O bonds, as applicable. To this end, we use the isodesmic enthalpies of formation derived for FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$ given in Table 5 in conjunction with the values of -41.6 ± 0.5, -86.7 ± 0.6, -76.6 ± 3, -94.0 ± 2, -120.9 ± 2,

Table 6
Calculated bond dissociation enthalpies at 298 K derived from isodesmic, atomization and direct methods (in kcal mol^{-1}).

Reaction	ΔH_{298}								
	B3LYP/6-311+G(3df)		M06-2X/6-311+G(3df)		G3(MP2)//B3LYP/6-311+G(3df)		BAC-G3(MP2)//B3LYP/6-311+G(3df)[a]	G4(MP2)	
	Isod.	Direct	Isod.	Direct	Isod.	Direct	Atom.	Isod.	Direct
FC(O)OOO(O)CF → FC(O)OO + FC(O)O	31.1	13.9	30.3	26.5	32.6	23.6	24.2	31.7	20.9
$FS(O_2)OOO(O_2)SF \rightarrow FS(O_2)O + FS(O_2)OO$	22.0	11.3	20.6	24.1	25.5	25.5	26.8	24.4	20.8
$FS(O_2)OOO(O_2)SF \rightarrow FS(O_2) + FS(O_2)OOO$	32.4	17.6	31.0	37.4	35.9	36.4	35.9	34.8	35.0
$FC(O)OOO(O_2)SF \rightarrow FCO + FS(O_2)OOO$	56.5	44.5	55.9	61.6	58.9	57.9	54.7	58.4	56.0
$FC(O)OOO(O_2)SF \rightarrow FC(O)O + FS(O_2)OO$	27.9	13.4	27.3	27.4	30.3	25.4	26.4	29.8	21.9
$FC(O)OOO(O_2)SF \rightarrow FC(O)OO + FS(O_2)O$	26.9	13.4	26.3	25.8	29.3	26.2	26.9	28.8	22.4

[a] Bond additivity corrections at G3(MP2)//B3LYP/6-311+G(3df) level are listed in Table E (Supporting Information).

-109.8 ± 2 and -126.3 ± 2 kcal mol^{-1} for the enthalpies of formation of FC(O) [47], FC(O)O [47,50], FC(O)OO [25], $FS(O_2)$ [51], $FS(O_2)O$ [51], $FS(O_2)OO$ [51] and $FS(O_2)OOO$ [51], respectively. The dissociation enthalpy was also calculated in a direct way using computed total energies corrected by thermal effects. The results of the both approaches are presented in Table 6. An examination of the resulting values shows the importance of using a high level of theory to estimate bond dissociation energies, especially when these calculations are performed in a direct way. This may be due to the fact bond dissociation reactions are not isodesmic and rarely isogyric (for instance the C_2F_4 dissociation to give two singlet biradicals CF_2). Moreover, they constitute a difficult calculation test that could reveal systematic errors in the methods employed. However, when we use the enthalpies of formation derived from isodesmic reactions, besides of from other well established thermodynamic data, such problem is largely minimized.

The obtained results suggest that the G3(MP2)//B3LYP/6-311++G(3df,3pd) and G4(MP2) methods improve the estimations. In fact, all employed methods indicate that the O—O bond fission is the more propitious dissociation channel, having both O—O bonds of asymmetrical trioxide $FC(O)OOO(O_2)SF$ approximately the same dissociation energy. Our best values for the O—O bond dissociation enthalpies in FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$ derived from the average values of isodesmic enthalpies of formation at G3(MP2)//B3LYP/6-311++G(3df,3pd) and G4(MP2) levels are 32.2, 25.0 and 29.6 (average of both O—O bonds) kcal mol^{-1}, respectively.

A comparison between the obtained O—OO bond dissociation enthalpies and available data for the O—O values for the related peroxides appear to be interesting. The resulting value for the $FS(O_2)OO—O(O_2)SF$ bond dissociation enthalpy of 25.0 kcal mol^{-1} is higher than the experimental value for the O—O bond in the stable related peroxide $FS(O_2)OO(O_2)SF$ of 22.1 kcal mol^{-1} [16]. The same is true for FC(O)OO—O(O)CF bond dissociation enthalpy of 32.2 kcal mol^{-1} when it is compared with the experimental value of 23.9 kcal mol^{-1} measured for FC(O)O—O(O)CF [52]. These results indicate that these trioxides present stability higher than its related peroxides. For $FC(O)OO(O_2)SF$ no experimental data for the O—O bond dissociation energy is available. For that reason, we calculate its enthalpy of formation from atomization energy at one of the best levels of theory employed here, BAC-G3(MP2)//B3LYP/6-311+G(3df). The resulting value of -236.5 kcal mol^{-1} leads to a $FC(O)O—O(O_2)SF$ bond dissociation enthalpy of 27.7 kcal mol^{-1}. This value is smaller than the corresponding related trioxide of 29.6 kcal mol^{-1}. According to these results, the studied trioxides present a higher stability compared to their related peroxides. In addition, it is interesting to note that the value for the enthalpy of formation derived for the asymmetrical trioxide is around the average of the corresponding values for the symmetrical trioxides.

The above determined energies for the O—O bonds of the trioxides of 32.2, 25.0 and 29.6 kcal mol^{-1} for FC(O)OOO(O)CF, $FS(O_2)$-$OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$, respectively, allow for an estimation of their thermal stability. Assuming a typical high pressure pre-exponential value of 3×10^{15} s^{-1} (this value is similar to the experimentally obtained for the $FS(O_2)OO(O_2)SF$ dissociation reaction [16]), lifetimes of about 4 years, 12 min and 20 days are obtained respectively at room temperature of 298 K. These values are higher than those previously estimated for FC(O)OOO(O)CF [53] and determined from experimental kinetic study of 1 min for $CF_3OC(O)OOO(O)COCF_3$ [4]. Therefore, these species eventually produced in certain atmospheric regions might be transported and afterwards decompose to deliver $FC(O)O_x$ and $FS(O_2)O_x$ (with $x = 1$ or 2) radicals in remote zones.

4. Conclusions

DFT and composite *ab initio* models have been employed to estimate molecular geometries and conformational mobilities, harmonic vibrational frequencies, infrared intensities and assignments along with standard enthalpies of formation for the most stable conformers of FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$ trioxides. The results presented here for the two last novel trioxides may aid in their experimental determination.

Employing the obtained enthalpies of formation of -195.4, -255.6 and -226.5 kcal mol^{-1}, O—O bond dissociation enthalpies of 32.2, 25.0 and 29.6 (average of both O—O bonds) kcal mol^{-1} were respectively calculated for FC(O)OOO(O)CF, $FS(O_2)OOO(O_2)SF$ and $FC(O)OOO(O_2)SF$. These values suggest that all studied trioxides are, at least up to about room temperature, relatively stable species.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2012.12.025.

References

[1] L.R. Anderson, W.B. Fox, Reaction of oxygen difluoride. Addition to carbonyl fluoride to produce bis(trifluoromethyl) trioxide, J. Am. Chem. Soc. 89 (1967) 4313–4315.

[2] P.G. Thompson, Bis(perfluoroalkyl) trioxides, J. Am. Chem. Soc. 89 (1967) 4316–4319.
[3] J. Czarnowski, H.J. Schumacher, The kinetics and the mechanism of the thermal decomposition of bis (trifluoromethyl) trioxide. The influence of carbonmonoxide on its decomposition, Int. J. Chem. Kinet. 13 (1981) 639–649.
[4] S. von Ahsen, P. García, H. Willner, M. Burgos Paci, G.A. Argüello, The open-chain trioxide $CF_3OC(O)OOOC(O)OCF_3$, Chem. Eur. J. 9 (2003) 5135–5141.
[5] M.D. Manetti, M.A. Burgos Paci, G.A. Argüello, Trifluoromethyl fluoroformyl trioxicarbonate, $CF_3OC(O)OOOC(O)F$: the first nonsymmetric acyl trioxide, J. Phys. Chem. A 113 (2009) 8523–8528.
[6] N. Fukuhara, L.A. Bigelow, The action of elementary fluorine upon organic compounds. X. The vapor phase fluorination of acetone, J. Am. Chem. Soc. 63 (1941) 788–791.
[7] H. Pernice, H. Willner, R. Eujen, The reaction of dioxygenyl salts with ^{13}CO: formation of $F^{13}C(O)^{13}C(O)F$, J. Fluorine Chem. 112 (2001) 277–281.
[8] H. Pernice, H. Willner, K.L. Bierbrauer, M. Burgos Paci, G.A. Argüello, Fluoroformic acid anhydride, FC(O)OC(O)F, Angew. Chem. 114 (2002) 3987–3989. Angew. Chem. Int. Ed. 41 (2002) 3832–3834..
[9] A.J. Arvia, P.J. Aymonino, C.H. Waldow, H.J. Schumacher, Bis-monofluorcarbonyl-peroxyd, Angew. Chem. 72 (1960) 169.
[10] H.-G. Mack, C.O. Della Védova, H. Oberhammer, Bis(fluorocarbonyl) peroxide; an unusual molecular structure, Angew. Chem. 103 (1991) 1166–1167. Angew. Chem. Int. Ed. Engl. 30 (1991) 1145–1146..
[11] G. Bednarek, G.A. Argüello, R. Zellner, FTIR-spectroscopic study of reactions of FCO and FC(O)OO radicals in the presence of O_2 and NO_2, Ber. Bunsenges. 100 (1996) 445–454.
[12] H. Pernice, M. Berkei, G. Henkel, H. Willner, G.A. Argüello, M.L. McKee, T.R. Webb, Bis(fluoroformyl)trioxide, FC(O)OOOC(O)F, Angew. Chem. Int. Ed. 43 (2004) 2843–2846.
[13] A. Russo, D.D. DesMarteau, Chloroxyfluoroxydifluoromethane, Inorg. Chem. 34 (1995) 6221–6222.
[14] M.P. Badenes, E. Castellano, C.J. Cobos, A.E. Croce, M.E. Tucceri, Rate coefficient for the reaction $FCO + FC(O)O_2 \rightarrow 2\ FC(O)O$ at 296 K, Chem. Phys. Lett. 303 (1999) 482–488.
[15] M.E. Tucceri, M.P. Badenes, A.E. Croce, C.J. Cobos, Experimental and theoretical study of the recombination reaction $FSO_2 + O_2 \rightarrow FS(O_2)OO$, Chem. Phys. Lett. 465 (2008) 15–19.
[16] C.J. Cobos, A.E. Croce de Cobos, H. Hippler, E. Castellano, Direct determination of the limiting high-pressure rate constants of the system $FSO_3 + FSO_3 \rightarrow F_2S_2O_6$ over the temperature range 293–381 K, J. Phys. Chem. 93 (1989) 3089–3094.
[17] W.H. Basualdo, H.J. Schumacher, Die photochemischen Reaktionen von Fluorfluorsulfonat, F_2SO_3, mit Schwefeltrioxid und Schwefeldioxid im Licht der Wellenlänge 2537 Å, Z. Physik. Chem. NF 47 (1965) 57–64.
[18] R. Gatti, J.E. Sicre, H.J. Schumacher, Die Kinetik der thermischen Reaktion zwischen Bis-Fluorsulfurylperoxid, $F_2S_2O_6$, und Kohlenmonoxid, Z. Physik. Chem. NF 47 (1965) 323–336.
[19] E. Vasini, H.J. Schumacher, Die Kinetik der thermischen Reaktion zwischen Fluorfluorsulfonat, Kohlenmonoxid und Sauerstoff, Z. Physik. Chem. NF 104 (1977) 219–228.
[20] E. Castellano, H.J. Schumacher, Die Kinetik der thermischen Reaktion zwischen Fluor und Bisfluorsulfurylperoxid, Z. Physik. Chem. NF 44 (1965) 57–66.
[21] A.E. Croce de Cobos, C.J. Cobos, E. Castellano, Pressure and temperature dependence of the reaction fluorine atom + fluorosulfate + M → fluorine fluorosulfate + M, J. Phys. Chem. 93 (1989) 274–278.
[22] A.E. Croce, C.J. Cobos, E. Castellano, Pulsed laser photolysis study of the reaction $Cl + FSO_3 + M \rightarrow FSO_2OCl + M$, Chem. Phys. Lett. 158 (1989) 157–160.
[23] C.J. Cobos, A.E. Croce, E. Castellano, Excimer laser-induced temperature jump-measurements on the recombination kinetics of the gas-phase $FSO_3 + FSO_3 \Leftrightarrow F_2S_2O_6$ equilibrium between 415 and 525 K, Int. J. Chem. Kinet. 22 (1990) 289–297.
[24] M.E. Tucceri, M.P. Badenes, A.E. Croce, C.J. Cobos, Kinetics of formation of the novel peroxide $FC(O)OO(O_2)SF$, Chem. Commun. 1 (2001) 71–72.
[25] M.E. Tucceri, M.P. Badenes, A.E. Croce, C.J. Cobos, Experimental and theoretical study of the recombination reactions of $FS(O_2)O$ with FC(O)O and CO, Phys. Chem. Chem. Phys. 3 (2001) 1832–1839.
[26] D.J. Mckay, J.S. Wright, How long can you make an oxygen Chain?, J Am. Chem. Soc. 120 (1998) 1003–1013.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
[28] A.D. Becke, Density-functional thermochemistry. III. The role of exact Exchange, J. Chem. Phys. 98 (1993) 5648–5652.
[29] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behaviour, Phys. Rev. A 38 (1988) 3098–3100.
[30] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–789.
[31] M.J. Frisch, J.A. Pople, J.S. Binkley, Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets, J. Chem. Phys. 80 (1984) 3265–3269. and references therein.
[32] Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor. Chem. Account 120 (2008) 215–241.
[33] A.G. Baboul, L.A. Curtiss, P.C. Redfern, K. Raghavachari, Gaussian-3 theory using density functional geometries and zero-point energies, J. Chem. Phys. 110 (1999) 7650–7657.
[34] L.A. Curtiss, P.C. Redfern, V. Rassolov, G. Kedziora, J.E. Pople, Extension of Gaussian-3 theory to molecules containing third-row atoms K, Ca, Ga–Kr, J. Chem. Phys. 114 (2001) 9287–9295.
[35] L.A. Curtiss, P.C. Redfern, K. Raghavachari, Gaussian-4 theory using reduced order perturbation theory, J. Chem. Phys. 127 (2007). pp. 124105–124105-8.
[36] B. Anantharaman, C.F. Melius, Bond additivity corrections for G3B3 and G3MP2B3 quantum chemistry methods, J. Phys. Chem. A 109 (2005) 1734–1747.
[37] A.P. Scott, L. Radom, Harmonic vibrational frequencies: an evaluation of Hartree–Fock, Møller–Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors, J. Phys. Chem. 100 (1996) 16502–16513.
[38] K.I. Gobbato, M.F. Klapdor, D. Mootz, W. Poll, S.E. Ulic, H. Willner, H. Oberhammer, Bis(trifluorpmethyl)trioxide: first structure of a straight-chain trioxide, Angew. Chem. 107 (1995) 2433–2434. Angew. Chem. Int. Ed. Engl. 34 (1995) 2244–2245..
[39] F. Aubke, B. Casper, H.S.P. Müller, H. Oberhammer, H. Willner, Vibrational spectra and gas phase structures of fluorine fluorosulfate ($FOSO_2F$) and chlorine fluorosulfate ($ClOSO_2F$), J. Mol. Struct. 346 (1995) 111–120.
[40] M.W. Chase, Jr., NIST-JANAF Thermochemical Tables, fourth ed. J. Phys. Chem. Ref. Data, 1998, Monograph No. 9.
[41] C.E. Moore, Atomic Energy Levels, NBS467, 1949.
[42] K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Co., 1979.
[43] L.A. Curtiss, P.C. Redfern, D.J. Frurip, Theoretical Methods for Computing Enthalpies of Formation of Gaseous Compounds, in: K.B. Lipkowitz, D.B. Boyd (Eds.), Reviews in Computational Chemistry, vol. 15, Wiley-VCH, New York, 2000, pp. 147–211.
[44] C.W. Bauschlicher Jr., A. Ricca, Accurate Heats of Formation for SF_n, SF_n^+, and SFn- for $n = 1–6$, J. Phys. Chem. A 102 (1998) 4722–4727.
[45] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.
[46] R.J. Berry, D.R.F. Burgess Jr., M.R. Nyden, M.R. Zachariah, M. Schwartz, Halon thermochemistry: ab initio calculations of the enthalpies of formation of fluoromethanes, J. Phys. Chem. 99 (1995) 17145–17150.
[47] S.P. Sander, R.R. Friedl, J.R. Barker, D.M. Golden, M.J. Kurylo, P.H. Wine, J.P.D. Abbatt, J.B. Burkholder, C.E. Kolb, G.K. Moortgat, R.E. Huie, V.L. Orkin, Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, NASA/JPL Data Evaluation, JPL Publication 06-2 Evaluation No. 17, NASA, Pasadena, CA, June 1, 2011, <http://jpldataeval.jpl.nasa.gov/>.
[48] K.E. Gutowski, D.A. Dixon, Ab initio prediction of the gas- and solution-phase acidities of strong Brønsted acids: the calculation of pK_a values less than −10, J. Phys. Chem. A 110 (2006) 12044–12054.
[49] D.J. Grant, D.A. Dixon, J.S. Francisco, D. Feller, K.A. Peterson, Heats of formation of the $H_{1,2}O_mS_n$ ($m, n = 0–3$) molecules from electronic structure calculations, J. Phys. Chem. A 113 (2009) 11343–11353.
[50] M.P. Badenes, A.E. Croce, C.J. Cobos, Experimental and theoretical study of the recombination reaction $F + FC(O)O + M \rightarrow FC(O)OF + M$, Phys. Chem. Chem. Phys. 6 (2004) 747–755.
[51] M.P. Badenes, A.E. Croce, C.J. Cobos, Theoretical thermochemistry of the FSO_x ($x = 1$ to 5) radical series, in: A.G. Mirskiy (Ed.), Thermochemistry and Advances in Chemical Research, Nova Science Publishers, Inc., New York, EE, UU, 2009, pp. 311–321.
[52] M.A. Burgos Paci, G.A. Argüello, Arrhenius parameters for the thermal decomposition of FC(O)OOC(O)F, J. Argentine Chem. Soc. 93 (2005) 175–182.
[53] M.P. Badenes, E. Castellano, C.J. Cobos, A.E. Croce, M.E. Tucceri, Kinetics of the reactions of $FC(O)O_2$ radicals with F atoms and F_2, Chem. Phys. 253 (2000) 205–217.