



Formation and dissociation kinetics of the FC(O)OOO(O)CF, FS(O₂)OOO(O₂)SF and FC(O)OOO(O₂)SF trioxides: A theoretical study



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ABSTRACT

A SACM/CT study of the FC(O)O + FC(O)OO → FC(O)OOO(O)CF, FS(O₂)O + FS(O₂)OO → FS(O₂)OOO(O₂)SF, FC(O)OO + FS(O₂)O → FC(O)OOO(O₂)SF and FC(O)O + FS(O₂)OO → FC(O)OOO(O₂)SF recombination reactions and their reverse dissociation processes was performed. The electronic energy along the reaction pathways was calculated at the G3S(MP2)//B3LYP/6-311+G(3df) level of theory. The respective high pressure rate coefficients obtained at 298 K are 3.2×10^{-12} , 4.3×10^{-13} , 8.5×10^{-13} , 1.1×10^{-12} cm³ molecule⁻¹ s⁻¹. The first calculated value compares very well with the available experimental one. From the corresponding thermal dissociation rate coefficients, lifetimes of about 170 days, 4 days and 1 min are predicted for FC(O)OOO(O)CF, FC(O)OOO(O₂)SF and FS(O₂)OOO(O₂)SF.

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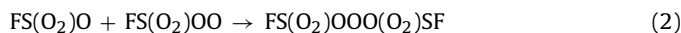
1. Introduction

Long before any direct kinetic evidence of the existence of the fluoroformylxyl FC(O)O and fluoroformylperoxy FC(O)OO radicals were available, their central participation in mechanistic studies had been postulated. In fact, they play a predominant role in the thermal reactions between F₂ and CO [1] and F₂O and CO [2], both in the presence of O₂, as well as in the photolysis of CF₂(OF)₂ at 254 nm in the presence of CO and O₂ [3,4]. Motivated by the potential chemical importance of these radicals in the stratosphere, several time-resolved studies appeared in the last two decades [5–12]. On the other hand, a number of fluorine- and sulphur-bearing radicals play a significant role in some regions of the atmosphere. In particular, for the fluorosulfate FS(O₂)O radical, several experimental and theoretical kinetic investigations have been reported [13–22]. Interesting compounds could be generated by association reactions between these radicals [23–25]. In fact, the FC(O)OOO(O)CF is formed as a byproduct in the thermal reaction between F₂ and CO in the presence of O₂ [26,27]. Also it is formed in the 248-nm laser flash photolysis of (FCO)₂ in the presence of O₂ at total SF₆ pressures ranging from 100 to 250 Torr [11],



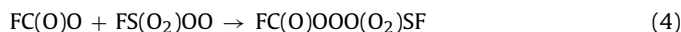
Under these conditions, a room temperature high pressure rate coefficient of $k_{\text{rec},\infty} = (3.7 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ was determined [11]. In addition, from conformational and thermochemical theoretical studies, a FC(O)O–OO(O)CF bond dissociation enthalpy at 298 K of 32.2 kcal mol⁻¹ has been derived [12,28].

The formation of FS(O₂)OOO(O₂)SF through the barrierless recombination reaction (2) has been recently proposed [29],



The predicted well-depth at 298 K of 25.0 kcal mol⁻¹ suggests that this trioxide presents a considerable thermal stability [28]. As a comparison, the O–O bond dissociation enthalpy for the well known related peroxide FS(O₂)OO(O₂)SF is 22.1 kcal mol⁻¹ [18]. The FS(O₂)OO radical has been proposed to be formed in the photolysis of FS(O₂)OF in the presence of O₂, SO₂ and SO₃ [13], in the thermal reaction between FS(O₂)OF and CO [14], and more recently, the room temperature rate coefficient for the FSO₂ + O₂ → FS(O₂)OO recombination reaction has been experimental and theoretically determined [29].

On the other hand, the asymmetric trioxide FC(O)OOO(O₂)SF could be generated according to reactions (3) and (4):



The theoretical dissociation enthalpies at 298 K for the FC(O)OO–O(O₂)SF and FC(O)O–OO(O₂)SF bonds of 29.1 and 30.1 kcal mol⁻¹ indicate that asymmetric trioxide is stable at room temperature [28].

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The present theoretical study is concerned with the kinetics of the reactions (1)–(4) and their reverse breaking processes at 298 K. High pressure rate coefficients using the statistical adiabatic channel model/classical trajectory SACM/CT [30,31] complemented with molecular information provided by quantum-chemical methods were calculated.

2. Computational details

2.1. Quantum chemical calculations

All calculations were performed with the GAUSSIAN 09 program package [32]. The hybrid B3LYP density functional [33–35] combined with the extended 6-311+G(3df) Pople's basis set [36] was used to compute fully optimized structural geometries and harmonic vibrational frequencies. Electronic potentials were computed with the G3(MP2)B3 [37,38], G3S(MP2) [39] and G4(MP2) [40] *ab initio* composite models. In particular, improved versions G3(MP2)//B3LYP/6-311+G(3df) and G3S(MP2)//B3LYP/6-311+G(3df) based on B3LYP/6-311+G(3df) molecular structures and vibrational frequencies were employed in the present work. The GAUSSIAN-3 (G3) treatment provides an economic way to obtain quadratic configuration interaction total energies, QCISD(T, full), with the extended G3Large basis set. Spin-orbit, core and higher-level empirical corrections are explicitly accounted for in the model [37,38]. The G3S(MP2) model corrects for deficiencies in the G3(MP2) model at large bond elongations *via* detailed higher-level empirical corrections, and presents a mean absolute deviation of 1.35 kcal mol⁻¹ [39]. The G4(MP2) model is based on B3LYP/6-31G(2df,p) optimized structures and harmonic vibrational frequencies scaled by a factor 0.9854, and provides CCSD(T, full) energy values with an extrapolated complete basis set. The stated average absolute deviation of this model is 1.04 kcal mol⁻¹ [40].

2.2. Kinetics calculations

Unimolecular bond fission reactions and the reverse radical recombination reactions at the high pressure limit are dominated by the intramolecular time evolution of molecules excited above the reaction threshold. In particular, the bond O–O forming reactions (1)–(4) involve potential energy profiles without a maximum, with a smooth transition between the rotational energy of the radicals and the vibrational energy of the trioxide transitional modes. This type of reactions can be appropriately treated by the SACM/CT [30,31]. This model combines the statistical adiabatic channel model, SACM, with classical trajectory, CT, calculations performed on standard valence potentials.

For convenience, the limiting high pressure rate coefficient for a recombination reaction can be expressed as [41,42],

$$k_{\text{rec},\infty} = f_{\text{rigid}} k_{\text{rec},\infty}^{\text{PST}} \quad (I)$$

Here, $k_{\text{rec},\infty}^{\text{PST}}$ denotes the phase space theory rate coefficient derived from the isotropic part of the potential, and f_{rigid} the thermal rigidity factor which account for the anisotropy of the potential energy surface.

Assuming that the anisotropic potential can be described by a Morse function $V = D_e [1 - \exp(-\beta(r - r_e))]^2$, $k_{\text{rec},\infty}^{\text{PST}}$ can be easily calculated as

$$k_{\text{rec},\infty}^{\text{PST}} = \frac{f_e f_{\text{sym}} (8\pi kT/\mu)^{1/2} (31.153 - 18.158X + 0.8685X^2)}{\beta^2} \quad (II)$$

In this expression β is the Morse parameter, D_e is the dissociation energy, $r_e = r_{\text{cm}}$ is the distance between the centers of mass of the two combining species, μ is the collisional reduced

mass, f_e is the electronic degeneracy factor, f_{sym} is a stoichiometric coefficient equal to 1/2 for identical rotors or 1 for different and $X = \ln(kT/D_e) - \beta r_e + 4$ [30].

On the other hand, f_{rigid} is estimated as [30]

$$f_{\text{rigid}} \approx \left[1 - 2.3C(\beta r_e)^{1/2} \exp\left(\frac{X'}{2.044}\right) \right] (1 + 0.75Z + Z^4)^{-1/4} \quad (III)$$

where $X' = X - 4$ and the anisotropy effects are accounted for $Z = (dC)^n$. As for other atom + polyatomic [43–46] and polyatomic + polyatomic reactions [15,47,48], we approach the FC(O)O, FC(O)OO, FS(O₂)O and FS(O₂)OO radicals as quasi-linear rotors. For the adducts formed with two different rotors of angle θ between both rotor axes and molecular axis the following expressions of C , n and d were used [31]

$$C = \frac{\{2\varepsilon_s^2 \varepsilon_a^2 \varepsilon_t^2 / [B_1 B_2 (B_1 + B_2)]\}^{1/3}}{2D_e} \quad (IV)$$

$$n = 1 - 0.5 \sin^2 \theta + \sin^4 \theta \quad (V)$$

$$d = c_1 + c_2 \sin^2 \theta + \frac{c_3}{\sin^2 \theta} + (\chi_a^2 \chi_s^2)^{1/3} \left(c_4 + c_5 \sin^2 \theta + \frac{c_6}{\sin^2 \theta} \right) + \chi_a^2 \cos^2 \theta \left(c_7 + c_8 \sin^2 \theta + \frac{c_9}{\sin^2 \theta} \right) + \chi_s^2 \cos^2 \theta \left(c_{10} + c_{11} \sin^2 \theta + \frac{c_{12}}{\sin^2 \theta} \right) \quad (VI)$$

with $\chi_a \approx \varepsilon_a/\varepsilon_t$ and $\chi_s \approx \varepsilon_s/\varepsilon_t$ and the values $c_1 = 1.757$, $c_2 = -1.337$, $c_3 = -0.393$, $c_4 = 1.444$, $c_5 = -0.509$, $c_6 = -7.730 \times 10^{-2}$, $c_7 = 0.357$, $c_8 = -0.557$, $c_9 = 0.247$, $c_{10} = -1.932$, $c_{11} = 0.385$, $c_{12} = 1.529$. In the above expressions ε_t , ε_a and ε_s are the equilibrium vibrational frequencies for the torsion, asymmetrical and symmetrical deformations modes of the trioxides, while B_1 and B_2 are the rotational constants of the reagents.

3. Results and discussion

3.1. Recombination rate coefficients $k_{\text{rec},\infty}$ on standard Morse potentials

From a kinetic point of view, high energy regions located at long interfragment distances constitute the more relevant part of the potential energy surface. Two approaches to the anisotropic radial potential have been followed. In the first, standard Morse functions were employed to describe the potentials of reactions (1)–(4). In Table 1 are listed the molecular parameters employed in the kinetic calculations. From the D_e values and the equilibrium force constants for the O–O stretching modes $F_{\text{O-O}}$ obtained from B3LYP/6-311+G(3df) calculations, the Morse parameters $\beta_{\text{eq}} = (F_{\text{O-O}}/2D_e)^{1/2}$ were derived.

A strong vibrational coupling was observed along the minimum energy paths of reactions (1)–(4) computed at the B3LYP/6-311+G(3df) level, that precluded the determination of the r dependence of their respective transitional modes. Therefore, the simple expression $\varepsilon(r) \approx \varepsilon(r_e) \exp[-\alpha(r - r_e)]$ was employed [49]. As for other recombination reactions, looseness parameter values of $\alpha \equiv (0.5 \pm 0.1)\beta$ were here used [42].

In the case of the FC(O)O + FC(O)OO → FC(O)OOO(O)CF reaction, this approach leads to $k_{\text{rec},\infty}^{\text{PST}} = 1.1 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ and $f_{\text{rigid}} = 0.023$. Therefore, the predicted SACM/CT rate coefficient is 2.5×10^{-12} cm³ molecule⁻¹ s⁻¹, and ranging from 1.1×10^{-12} to 5.2×10^{-12} cm³ molecule⁻¹ s⁻¹ when the α/β ratio is varied between 0.4 and 0.6. This result is in good agreement with the experimental value of $(3.7 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ [11]. A five times smaller high pressure rate coefficient,

Table 1

Molecular input data employed in the kinetics calculations. Structural parameters (μ in g mol^{-1} ; r_{CM} in \AA ; angle in degree; rotational constants B_1 and B_2 in cm^{-1} ; and β in \AA^{-1}) and harmonic vibrational frequencies (in cm^{-1}) computed at the B3LYP/6-311+G(3df) level [28]. D_e and ΔH_0 (in kcal mol^{-1}) obtained from isodesmic reactions at the G3(MP2)//B3LYP/6-311+G(3df) and G4(MP2) levels [28].

Parameter	FC(O)O + FC(O)OO	FS(O ₂)O + FS(O ₂)OO	FC(O)OO + FS(O ₂)O	FC(O)O + FS(O ₂)OO
μ	35.05	53.20	43.94	40.70
D_e	35.9	28.1	32.5	33.6
ΔH_0	32.1	24.6	29.1	30.2
$F_{\text{O-O}}$	6.11	6.09	6.28	8.99
r_{cm}	3.55	4.03	3.79	3.70
β_{eq}	3.50	3.95	3.73	4.39
θ	70	55	78	90
ε_t	51.6	33.0	45.6	55.9
ε_s	146.9	150.3	176.0	176.0
ε_a	218.7	279.0	334.4	334.4
B_1	0.292	0.171	0.136	0.292
B_2	0.136	0.0929	0.171	0.0929

$(7.0 \pm 1.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, has been measured for the related reaction $\text{FC(O)O} + \text{FC(O)O} \rightarrow \text{FC(O)OO(O)CF}$ [9].

Similar calculations were performed for the reactions (2)–(4). All resulting values are listed in Table 2. As in the previous case, the rate coefficient for the reaction between $\text{FS(O}_2\text{)O}$ and $\text{FS(O}_2\text{)OO}$ radicals is higher than the measured for the reaction to form the corresponding peroxide $\text{FS(O}_2\text{)O} + \text{FS(O}_2\text{)O} \rightarrow \text{FS(O}_2\text{)OO(O}_2\text{)SF}$, of $(4.5 \pm 0.6) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [18,20].

Finally, for the $\text{FC(O)OOO(O}_2\text{)SF}$ trioxide the two possible recombination channels (3) and (4) were considered. Contrary to the previous cases, the $k_{\text{rec},\infty}$ values predicted for this trioxide are smaller than the determined for the formation reaction of the analogous peroxide, $\text{FC(O)O} + \text{FS(O}_2\text{)O} \rightarrow \text{FC(O)OO(O}_2\text{)SF}$, of $(1.0 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [22]. Also, as can be seen in Table 2, the rate coefficient for both channels lie between the corresponding values derived for the symmetrical trioxides.

3.2. Recombination rate coefficients $k_{\text{rec},\infty}$ on *ab initio* electronic potentials

In this section the potential energy curves for the trioxides at different O–O bond distances along the reaction path were calculated. For this, the remaining geometrical parameters were fully optimized. The normalized V/D_e curves obtained for the FC(O)OOO(O)CF at the G3(MP2)//B3LYP/6-311+G(3df), G3S(MP2)//B3LYP/6-311+G(3df), and G4(MP2) *ab initio* composite levels are depicted in Figure 1. Due to the fact that only in the G3S(MP2) model the higher-level correction (the so-called HLC term) depends on molecular geometry, the medium to large interfragment region of the potentials is expected to be better described by this formulation than by the other employed GAUSSIAN models [39]. As Figure 1 shows, the G3(MP2)//B3LYP/6-311+G(3df) potential curve for the O–O bond breaking in FC(O)OOO(O)CF leads to V/D_e values larger than 1 above 2.4 \AA , while the G4(MP2) results approach more asymptotically to this value. In contrast, the G3S(MP2)//B3LYP/6-311+G(3df) potential exhibits a more reasonable shape at large elongations. A similar behavior has been observed for the potential curves of reaction $\text{Cl} + \text{FC(O)O} \rightarrow \text{FC(O)OCl}$ [45]. The G3S(MP2)//B3LYP/6-311+G(3df) and G4(MP2) potentials for FC(O)OOO(O)CF can be fitted with

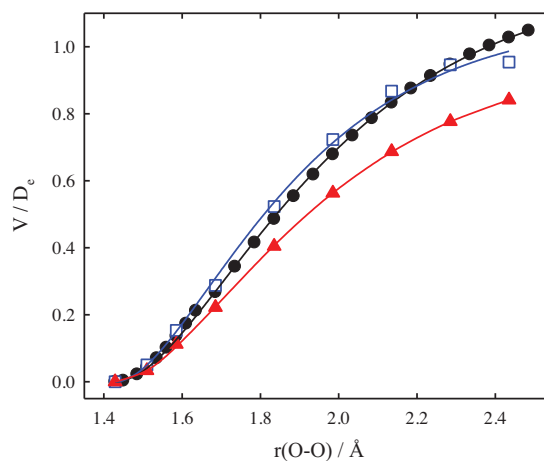


Figure 1. Dependence of the normalized electronic potential of FC(O)OOO(O)CF on the O–O bond distance. (●) G3(MP2)//B3LYP/6-311+G(3df) ($D_e = 26.4 \text{ kcal mol}^{-1}$); (▲) G3S(MP2)//B3LYP/6-311+G(3df) ($D_e = 27.7 \text{ kcal mol}^{-1}$); (□) G4(MP2) ($D_e = 23.6 \text{ kcal mol}^{-1}$). For the fits, see the text.

Morse functions using β of 2.52 and 2.96 \AA^{-1} and D_e (obtained from the energy of the separated fragments) of 27.7 and 23.6 kcal mol^{-1} . These D_e values are considerably smaller than the one obtained from the theoretical thermochemical analysis of Ref. [28] (see Table 1).

As before, V/D_e values larger than 1 were obtained with the G3(MP2)//B3LYP/6-311+G(3df) and G4(MP2) models at O–O bond distances near to 2.4 \AA for the other trioxides investigated. On the other hand, as Figure 2 shows, the G3S(MP2)//B3LYP/6-311+G(3df) potentials calculated for the $\text{FS(O}_2\text{)O-O(O}_2\text{)SF}$ ($\beta \equiv 1.96 \text{ \AA}^{-1}$ and $D_e = 29.1 \text{ kcal mol}^{-1}$) and $\text{FC(O)OO-O(O}_2\text{)SF}$ ($\beta \equiv 1.79 \text{ \AA}^{-1}$ and $D_e = 29.7 \text{ kcal mol}^{-1}$) dissociations exhibit curves similar to the reported for the FC(O)O-O(O)CF bond fission. However, the larger part of the $\text{FC(O)O-O(O}_2\text{)SF}$ potential ($\beta \equiv 2.19 \text{ \AA}^{-1}$ and $D_e = 29.5 \text{ kcal mol}^{-1}$) seems to be slightly overestimated. It is known that in some particular cases the potential surfaces for bond breaking present regions of possible artifactual behavior [50] and, to our knowledge, no potential energy calculations for other trioxide species are available for comparison.

Table 2

Phase space theory rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), thermal rigidity factors and rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) calculated using standard Morse potentials.

	FC(O)O + FC(O)OO	FS(O ₂)O + FS(O ₂)OO	FC(O)OO + FS(O ₂)O	FC(O)O + FS(O ₂)OO
$k_{\text{rec},\infty}^{\text{PST}}$	1.1×10^{-10}	9.3×10^{-11}	9.9×10^{-11}	8.9×10^{-11}
f_{rigid}	0.023	0.003	0.006	0.008
$k_{\text{rec},\infty}$	2.5×10^{-12}	2.8×10^{-13}	5.9×10^{-13}	7.1×10^{-13}

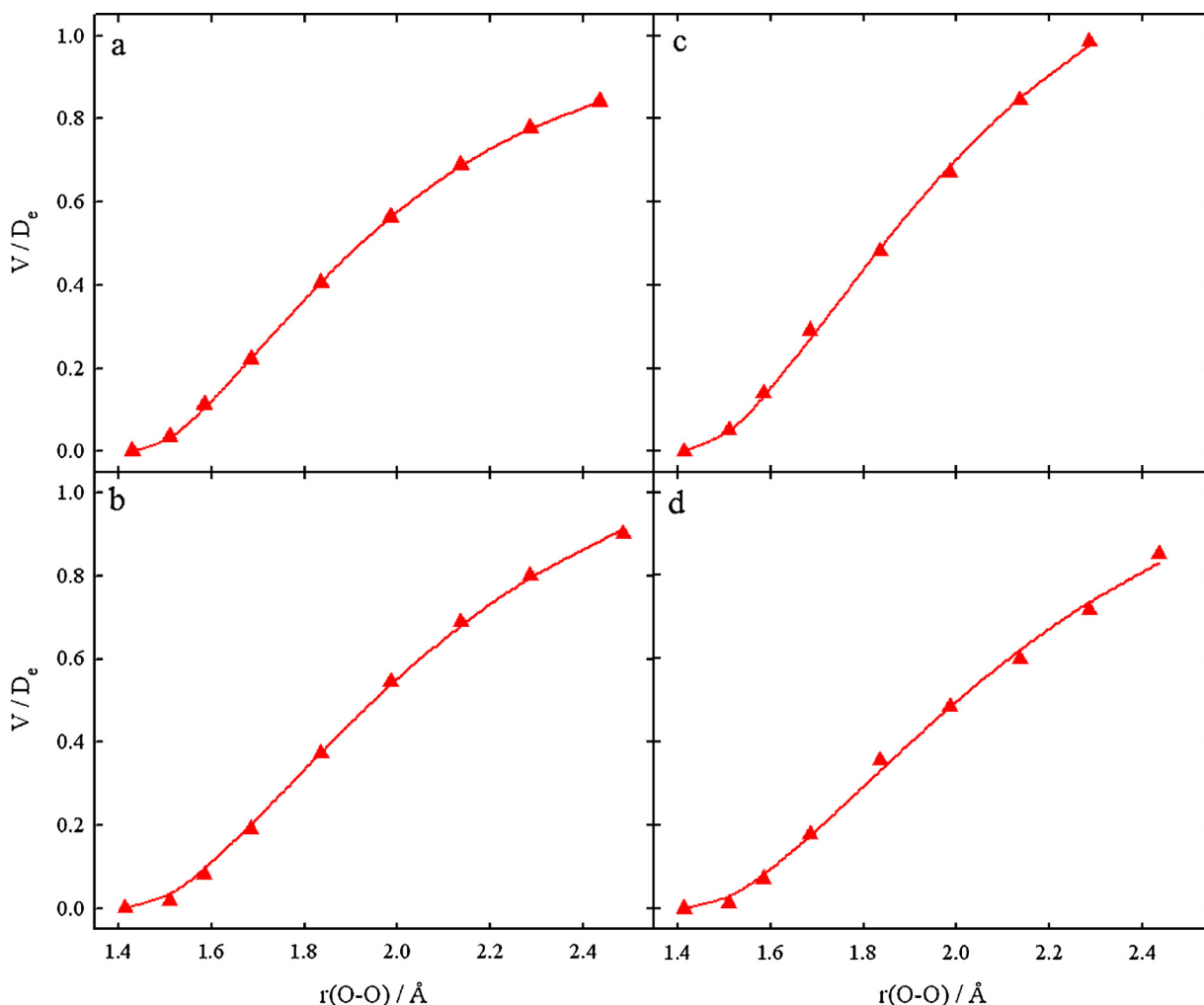


Figure 2. Dependence of the normalized electronic potential of (a) FC(O)OOO(O)CF ($D_e = 27.7 \text{ kcal mol}^{-1}$), (b) $\text{FS(O}_2\text{)OOO(O}_2\text{)SF}$ ($D_e = 29.1 \text{ kcal mol}^{-1}$), (c) $\text{FC(O)O-OO(O}_2\text{)SF}$ ($D_e = 29.5 \text{ kcal mol}^{-1}$), and (d) $\text{FC(O)OO-O(O}_2\text{)SF}$ ($D_e = 29.7 \text{ kcal mol}^{-1}$) trioxides on the O–O bond distance at the G3S(MP2)//B3LYP/6-311+G(3df) level of theory. For the fits, see the text.

The G3S(MP2)//B3LYP/6-311+G(3df) potential curves were employed to study the recombination kinetics of reactions (1)–(4). For this, the above β and the D_e values given in Table 1 together with a standard α/β ratio of 0.5 were employed. Table 3 summarizes the derived kinetic results. Thus, the calculated rate coefficient obtained for reaction (1) of $3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ agrees very well with the experimental value of $(3.7 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [11]. It should be noted that the G4(MP2) potential leads to a slightly smaller rate coefficient of $2.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. To analyze the influence of the anisotropic part of the potential energy surface on the reaction (1) rate coefficients, the α/β ratio was varied over the normally estimated error range of 0.4–0.6 [42]. As before, the resulting rate coefficients lie approximately within a factor of two from the value obtained with $\alpha/\beta \equiv 0.5$. In fact, $k_{\text{rec},\infty}$ values of 1.4×10^{-12} and $6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were calculated with $\alpha/\beta \equiv 0.4$ and 0.6 respectively.

The calculated rate coefficients and the rigidity factors for reactions (1)–(4) are presented in Table 3. The $k_{\text{rec},\infty}$ values span over one order of magnitude range and are about 20–35% larger than those obtained in Section 3.1 using standard Morse parameters derived from thermochemical and spectroscopic data.

3.3. Dissociation rate coefficients $k_{\text{diss},\infty}$ and lifetimes

Room temperature high pressure dissociation rate coefficients for the three trioxides were calculated using the more precise $k_{\text{rec},\infty}$ values of Table 3 and estimated equilibrium constants K_C , $k_{\text{diss},\infty} = k_{\text{rec},\infty}/K_C$. To this end, molecular parameters, harmonic vibrational frequencies and reaction enthalpies at 0K listed in Table 1 were employed. For all cases, the internal rotations of the trioxides were considered as hindered motions. The corresponding torsional potential curves, calculated in a previous work, are summarized in Figures A and B of the Supplementary material [28].

Table 3
Phase space theory rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), thermal rigidity factors and rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) calculated using the G3S(MP2)//B3LYP/6-311+G(3df) potentials.

	$\text{FC(O)O} + \text{FC(O)OO}$	$\text{FS(O}_2\text{)O} + \text{FS(O}_2\text{)OO}$	$\text{FC(O)OO} + \text{FS(O}_2\text{)O}$	$\text{FC(O)O} + \text{FS(O}_2\text{)OO}$
$k_{\text{rec},\infty}^{\text{PST}}$	1.4×10^{-10}	1.6×10^{-10}	1.8×10^{-10}	1.5×10^{-10}
f_{rigid}	0.023	0.0027	0.0047	0.0073
$k_{\text{rec},\infty}$	3.2×10^{-12}	4.3×10^{-13}	8.5×10^{-13}	1.1×10^{-12}

Table 4Equilibrium constants (in cm³ molecule⁻¹) and dissociation rate coefficients (in s⁻¹) for the studied trioxides.

	FC(O)OO—O(O)CF	FS(O ₂)OO—(O ₂)SF	FC(O)OO—O(O ₂)SF	FC(O)O—OO(O ₂)SF
K_C	4.7×10^{-5}	3.4×10^{-11}	1.8×10^{-7}	1.2×10^{-6}
$k_{\text{diss},\infty}$	6.8×10^{-8}	1.3×10^{-2}	4.7×10^{-6}	9.2×10^{-7}

The corresponding partition functions were estimated using the following Troe's interpolation expression [42]

$$Q_{\text{rot int}} = Q_{\text{tors}} \left[\exp\left(\frac{-RT}{V_0}\right) \right]^{1.2} + Q_{\text{free}} \left[1 - \exp\left(\frac{-RT}{V_0}\right) \right]^{1.2} \quad (\text{VII})$$

Here, $Q_{\text{tors}} = [1 - \exp(-\hbar\nu_{\text{tors}}/RT)]^{-1}$ and $Q_{\text{free}} = (2\pi I_m k/h^2)^{1/2}$ are the partition functions for totally restricted internal rotations (torsions) and for completely free rotors, respectively. The employed values for the rotational barrier heights V_0 ranging between 5.7 and 12.4 kcal mol⁻¹, reduced moments of inertia $I_m = I_A I_B / (I_A + I_B)$ and torsion values ν_{tors} were taken from information given in Ref. [28] (Table A of the Supplementary material). The resulting K_C and $k_{\text{diss},\infty}$ values are listed in Table 4. If all torsional modes are assumed harmonic oscillators, equilibrium constants about a factor of two higher result.

From the kinetic data, dissociation lifetimes at 298 K of about 170 days, 4 days and 1 min were obtained for FC(O)OOO(O)CF, FC(O)OOO(O₂)SF and FS(O₂)OOO(O₂)SF, respectively. Therefore, the trioxides present in a given atmospheric region might produce FC(O)O_x and FS(O₂)O_x (with $x = 1$ or 2) radicals in remote zones by transportation and subsequent decomposition.

4. Conclusions

SACM/CT kinetics calculations on an G3S(MP2)//B3LYP/6-311+G(3df) electronic potential allow to reproduce very well the experimental high pressure rate coefficient of the FC(O)O + FC(O)OO → FC(O)OOO(O)CF reaction. Kinetics data for the association reactions between the FS(O₂)O and FS(O₂)OO, FC(O)OO and FS(O₂)O, and FC(O)O and FS(O₂)OO radicals are predicted. On the basis of the reverse dissociation rate coefficients, lifetimes for the respective trioxides were estimated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2014.10.024.

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