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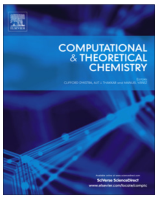

A theoretical study of the thermal stability of the $FS(O_2)OSO_2$ radical and the recombination kinetics with the FSO_3 radical

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ABSTRACT

The kinetics of the thermal reaction of $FS(O_2)OO(O_2)SF$ with SO_2 have been theoretically studied. Experimental investigations performed at 293–323 K indicate that the FSO_3 radical, in equilibrium with the peroxide $FS(O_2)OO(O_2)SF \rightleftarrows 2\ FSO_3$ (1, -1), initially attacks the SO_2 forming the $FS(O_2)OSO_2$ radical which afterwards may dissociate back, $FSO_3 + SO_2 \rightleftarrows FS(O_2)OSO_2$ (2, -2), or recombine with FSO_3 generating the final product, $FSO_3 + FS(O_2)OSO_2 \rightarrow (FS(O_2)O)_2SO_2$ (3). Several DFT formulations and composite ab initio models were employed to characterize $FS(O_2)OSO_2$ molecular properties and to determine relevant potential energy surfaces features of reactions (2), (-2) and (3). Transition state theory calculations lead to the high pressure rate coefficients $k_{\infty,2} = 9.1 \times 10^{-14} \exp(-5.2\ \text{kcal mol}^{-1}/\ RT)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ and $k_{\infty,-2} = 4.9 \times 10^{15} \exp(-13.9\ \text{kcal mol}^{-1}/RT)\ \text{s}^{-1}$ while statistical adiabatic channel model (SACM/CT) calculations predict for the barrierless reaction (3) the expression $k_{\infty,3} = 2.9 \times 10^{-11}(T/300)^{0.4}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. The experimental phenomenological rate coefficients are very well reproduced by these rate coefficients.

1. Introduction

The knowledge of the thermal stability and the kinetics of small radicals formed from atmospheric species deserves considerable interest. In particular, a set of RSO_2 radicals are formed by association of R radicals with the important pollutant SO_2, such as HSO_2, SO_3 or $HOSO_2$. Among these, the $HOSO_2$ radical is probably the most important compound [1,2]. In addition to these termolecular processes, metastable excited adducts RSO_2^* generated by reaction of SO_2 with other atmospheric radicals such as ClO, HO_2 or NO_2, could participate as intermediates in relevant complex-forming bimolecular reactions [1,2]. The molecular properties of other SO_2-containing radicals such as FSO_2 [3–6], $ClSO_2$ [7] and CF_3OSO_2 [8] have been estimated. Species of varied stability have been postulated to participate in the reaction mechanisms, in which the fluorosulphate radical, FSO_3, is involved. In fact, the stable species $FS(O_2)ONO$ [9], $FS(O_2)ONO_2$ [10,11] and the labile complexes $FS(O_2)OOO$ [12,13], $FS(O_2)OSF_4$ [14,15] and $FS(O_2)OSO_2$ [15,16] have been reported.

The FSO_3 is an interesting radical formed by direct association of F atoms with SO_3 [17]. Under pseudo-first order conditions, the $FS(O_2)OO(O_2)SF \rightleftarrows 2\ FSO_3$ equilibrium is established [14,18–20]. This equilibrium plays a relevant role in the synthesis of numerous inorganic and organic substances realized with the peroxide $FS(O_2)OO(O_2)SF$, because the system reactivity is exclusively accounted for by the FSO_3 [21]. In addition, this system has been found particularly appropriate for studies of light-induced bistability [22], stabilization of unstable states [23] and oscillatory behavior [24].

Kinetic studies of FSO_3 reactions have received considerable attention. Pioneering kinetic and mechanistic investigations were performed by Schumacher and coworkers employing manometric methods [9–11,14–17,24–31]. More recently direct laser flash-photolysis studies have been reported [12,20,32–38]. On the other hand, early systematic spectroscopic studies of FSO_3 [39–46] have been improved by detailed infrared [47] and microwave [48] investigations.

Cady and Roberts [49] and Castellano and Schumacher [16] found that the $(FS(O_2)O)_2SO_2$ is formed as only product in the thermal reaction between $FS(O_2)OO(O_2)SF$ and SO_2. In a subsequent study, Castellano and Schumacher postulated the participation of the $FS(O_2)OSO_2$ radical to explain the $(FS(O_2)O)_2SO_2$ formation at 293–323 K [15],

$$FS(O_2)OO(O_2)SF \rightleftarrows 2FSO_3 \qquad (1,\text{-}1)$$

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$$FSO_3 + SO_2 \rightleftarrows FS(O_2)OSO_2 \qquad (2,\text{-}2)$$

$$FSO_3 + FS(O_2)OSO_2 \rightarrow (FS(O_2)O)_2SO_2 \qquad (3)$$

As aforementioned, the equilibrium constant for (1, -1), $K_{C,1}$, has been precisely determined [14,18–20]. In addition, the high pressure rate coefficients for the individual dissociation $k_{\infty,1}$ [10,33,50] and the recombination $k_{\infty,\text{-}1}$ processes have also been determined experimentally between 293 and 525 K and interpreted theoretically [20,34]. However, no studies for reactions (2), (-2) and (3) have been reported so far. Assuming that at the stationary state the equilibria (1, -1) ($K_{C,1} = k_1/k_{-1}$) and (2, -2) ($K_{C,2} = k_{-2}/k_2$) are established, the phenomenological rate coefficient $k_I = k_3\ K_{C,1}/K_{C,2} = 2.1 \times 10^{-13}\ \exp(-15.7\text{kcal mol}^{-1}/RT)$ cm^3 molecule^{-1} s^{-1} was determined [15]. From this analysis, and assuming that reaction (3) is barrierless, a dissociation energy for the $FS(O_2)O\text{-}SO_2$ bond of 7.7 ± 1 kcal mol^{-1} was obtained [16].

The aim of the present study is to predict relevant molecular properties of $FS(O_2)OSO_2$ and to test the above reaction mechanism. For this, a large number of methods of the density functional theory (DFT) along high-level ab initio composite models were employed. Besides, rate coefficients for reaction (2), (-2) and (3) were derived using suitable reaction rate theories.

2. Computational methods

Due to the elusive nature of the exchange-correlation functional and to the difficulty to establish *a priori* the best DFT model, the following hybrid functionals were employed: B3LYP [50,51], B98 [52], B97-2 [53], mPW1PW91 [54], PBE1PBE [55], O3LYP [56], X3LYP [57], BMK [58], M05-2X [59], M06 [60], M06HF [61], M06-2X [60], mPW1LYP [54], mPW1PBE [54], mPW3PBE [54], TPSSh [62], τ-HCTHhyb [63], PBEh1PBE [64], LC-ωPBE [65], CAM-B3LYP [66], ωB97X-D [67] and HSEh1PBE [68]. All of them were combined with the Pople's 6-311++G(3df,3pd) triple split valence basis set [69]. The valence electrons of $FS(O_2)OSO_2$ were accommodated in molecular orbitals which comprise 328 basis functions based on 492 primitive Gaussians.

The correlation energy was more accurately accounted for by using ab initio multilevel models. The employed CBS-QB3 model relies on projected MP2 energies in the limit of a complete basis set [70,71]. The computed energies with the G3B3 [72] and G4 [73] model chemistries approach very well to those obtained at the QCISD(T, full)/G3Large//B3LYP/6-31G(d) and CCSD(T, full)/CBS//B3LYP/6-31G(2df,p) levels with a strong reduction in the computational resources. Besides, the G4MP2 model which uses a reduced order perturbation theory was employed in the calculations [74]. The average absolute deviations of these composite models from well-known experimental heats of formation values are close to the considered chemical accuracy of ±1 kcal mol^{-1} [70–74]. An additional improvement to the predictive capability of the G3B3 method was carried out by using the bond additivity correction (BAC) procedure [75]. This empirical model applies atomic, molecular and pairwise bond corrections to the theoretical G3B3 enthalpies of formation reducing the mean absolute deviation to about 0.4 kcal mol^{-1}.

The geometries of the molecules were fully optimized using analytical gradient methods without symmetry constraints. Harmonic vibrational frequencies employed to estimate zero-point energy corrections (ZPE) were calculated with analytical second derivative methods. In all cases, real vibrational frequencies were obtained assuring that computed structures correspond to stable species. Standard enthalpies of formation (ΔH_f°) for $FS(O_2)OSO_2$ at 298 K were derived from atomization and isodesmic energies. These values, in combination with the enthalpies of formation of FSO_3 and SO_2 molecules of −120.9 [37,76] and −70.94 kcal mol^{-1} [1] were afterwards employed to calculate the $FS(O_2)O\text{-}SO_2$ bond dissociation enthalpies.

The UV/Vis absorption spectrum of $FS(O_2)OSO_2$ was predicted employing the time-dependent density functional theory (TD-DFT) [77] with the 6-311+G(3df) basis set. To cover the relevant part of the spectrum, the first fifteen electronic states of the radical were calculated.

All electronic structure calculations were performed using the Gaussian set of computer codes with default integration grids [78]. Increasing the integration grid to tight limits, such that cartesian coordinates converge to 10^{-4} Å or better, does not improve the results.

The kinetic calculations for reaction (2) were performed using the canonical version of the transition state theory (CTST) [79]. The rate coefficients for the barrierless reaction (3) were carried out with the statistical adiabatic channel model/classical trajectory (SACM/CT) formulation developed for linear rotor + linear rotor type of reactions [80,81]. For both cases, the molecular information was provided by the quantum chemical calculations. All calculations were performed within the rigid rotor/harmonic oscillator approximation.

3. Results and conclusions

3.1. Molecular conformers and harmonic vibrational frequencies of FS(O$_2$)OSO$_2$

The $FS(O_2)OSO_2$ radical exhibits internal rotations around the $FS(O_2)\text{-}OSO_2$ (dihedral angle FSOS) and $FS(O_2)O\text{-}SO_2$ (dihedral angle SOSO) bonds. To investigate the hindrance degree of the conformers, the corresponding electronic barriers were calculated. To this end, the total energy as a function of the dihedral angles was computed, allowing the remaining molecular structural parameters to be fully optimized. The resulting torsional potentials for the six conformers derived at the G4MP2 level of theory are depicted in Fig. 1. The $FS(O_2)\text{-}OSO_2$ potential energy curve presents a global minimum at a FSOS dihedral angle of 79.1° and a transition state for total rotation located at 5.9°. These structures are connected by an electronic barrier of 4.3 kcal mol^{-1}. On the other hand, the more stable conformer obtained from rotation around the $FS(O_2)O\text{-}SO_2$ bond lies at 174.8°. The corresponding critical configuration is located at 272° and presents a barrier height of 3.6 kcal mol^{-1}. The imaginary vibrational frequencies for these transition states

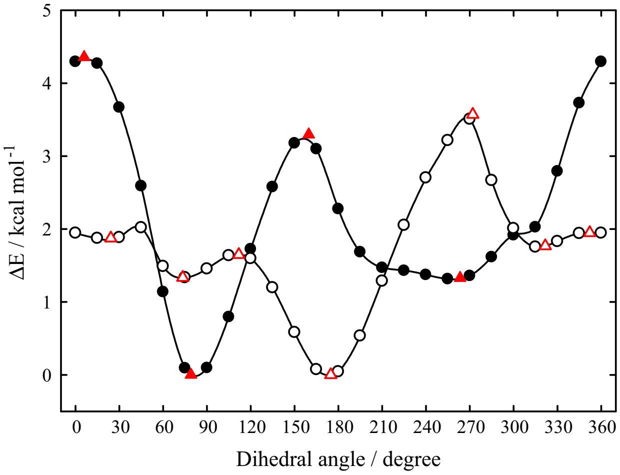

Fig. 1. Potential energy barriers for internal rotation around $FS(O_2)\text{-}OSO_2$ (●) and $FS(O_2)O\text{-}SO_2$ bonds (○) computed at the G4MP2 level. (▲) and (△) correspond to full optimized geometries at the same level.