

Kinetics of formation of the novel peroxide FC(O)OO(O₂)SF

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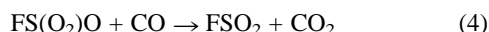
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The high-pressure rate coefficient for the formation of the new peroxide FC(O)OO(O₂)SF from recombination of FC(O)O and FS(O₂)O radicals has been determined by laser flash photolysis at 296 K; density functional theory calculations indicate peroxide stabilization and allow estimation of an O–O bond dissociation energy of 20.6 ± 3 kcal mol⁻¹.

Early syntheses of fluorinated peroxides involved the coupling of oxy-radicals to form the peroxide bond.¹ In fact, the photolysis of the mixtures of peroxides SF₅OOSF₅/CF₃OOCF₃ and SF₅OOSF₅/FS(O₂)OO(O₂)SF have been employed by Cady and coworkers to prepare SF₅OOCF₃ and SF₅OO(O₂)SF.¹ The fluorinated peroxides allow study of the role that the electron-withdrawing effect of electronegative groups plays on their reactivity, energetics and conformation. Here we report the determination of the rate coefficient for the recombination of FC(O)O and FS(O₂)O radicals to form the new peroxide FC(O)OO(O₂)SF at 296 K. In addition, the rate coefficient for the reaction of FS(O₂)O with CO has been determined for the first time.

A laser flash photolysis–absorption spectroscopy configuration described in detail elsewhere,^{2–7} was employed in the present experiments. Typically, samples of 30–40 mbar of FS(O₂)OF in the presence of 130–300 mbar of CO, 15 mbar of O₂ and up to 900 mbar of SF₆ were irradiated with the emission of an excimer laser operating on the 193 nm ArF transition. No more than 30 single shot experiments from fresh samples were averaged and analysed up to 5 ms for each set of conditions. In the photolysis, electronically excited FS(O₂)O radicals in the B²E state are initially formed and afterwards collisionally deactivated to the X²A₂ ground state via a manifold of low-lying vibrationally excited states.^{4,5} After *ca.* 250 μs the excited radicals are thermalized.⁵ On the other hand, photolytically generated F atoms are rapidly consumed by recombination with CO to form FCO radicals, which subsequently recombine with O₂ and yield FC(O)O₂ radicals. Finally, these radicals form FC(O)O radicals by self-reaction. The whole reaction mechanism is detailed in refs. 6–9. FCO and FC(O)O₂ are almost quantitatively consumed at 200 μs. Thus, the well established mechanisms involved in the FS(O₂)O^{2–5} and FC(O)O_x (x = 0, 1, 2)^{6–9} radical chemistries lead to the conclusion that over 300 μs only FS(O₂)O and FC(O)O survive and the mechanism reduces to eqns. (1)–(5)



Under the present conditions, reactions (1) and (2) are pressure independent with high-pressure rate coefficients of $k_{\infty,1} = 5.5 \times 10^{-13}$ s and $k_{\infty,2} = 4.6 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, respectively.³ Second-order plots of the absorbance monitored at 450 nm after photolysis of FS(O₂)OO(O₂)SF/CF₄ and FS(O₂)OF/CO/O₂/SF₆ mixtures are depicted in Fig. 1. In the first case, the generated FS(O₂)O radicals [absorption cross-

sections $\sigma(\text{FS(O}_2\text{)O}) = 3.64 \times 10^{-18}$ cm² molecule⁻¹]¹³ react exclusively according to reaction (2). In the latter case, a fast component due to the above mentioned thermalization of excited FS(O₂)O radicals is followed by a second component with a slope much higher than the observed for the first mixture. Absorbance vs. time profiles were numerically fitted employing the mechanism described by reactions (1)–(5). The modelling leads to radical concentrations such that the absorbance may be mostly attributed to FS(O₂)O absorption with a small contribution due to FC(O)O radicals [$\sigma(\text{FC(O)O}) = 6.7 \times 10^{-19}$ cm² molecule⁻¹].⁸ Moreover, the calculations show that the higher slope observed in signal (B) of Fig. 1 is predominantly due to FS(O₂)O consumption by reaction (3). At longer times and higher CO pressures these radicals are also consumed in reaction (4). However, the low FSO₂ concentration precludes the determination of k_5 , for which reasonable values ranging from 2×10^{-12} to 7×10^{-11} cm³ molecule⁻¹ s⁻¹ do not affect the modelling results. Between *ca.* 175 and 1060 mbar the rate coefficients determined for reaction (3) remain independent on total pressure such that they can be certainly ascribed to the limiting high pressure value. All experimental results are very well reproduced using the $k_{\infty,1}$, $k_{\infty,2}$ and k_5 values given above as well as $k_{\infty,3} = (1.2 \pm 0.3) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and $k_4 = (1.8 \pm 0.7) \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ for reactions (3) and (4). The errors quoted are 2σ. The value of $k_{\infty,3}$ is normal for this type of reaction¹⁰ while the low value of k_4 is quite consistent with the measured activation energy of 7 kcal mol⁻¹.¹¹ The experimental study is supplemented by density functional theory thermochemical computations to determine the bond dissociation energies of O–O, C–O and O–S bonds in FC(O)OO(O₂)SF. For this, standard enthalpies of formation of the peroxide and the relevant radicals were calculated. The value for FC(O)OO(O₂)SF was estimated using the isodesmic reaction: FOOF + FC(O)OH + HSO₃F → FC(O)OO(O₂)SF + 2FOH. Energy calculations were carried out on optimized geometries and harmonic frequencies evaluated employing the hybrid B3LYP density functional with the 6-311++G(d,p) basis

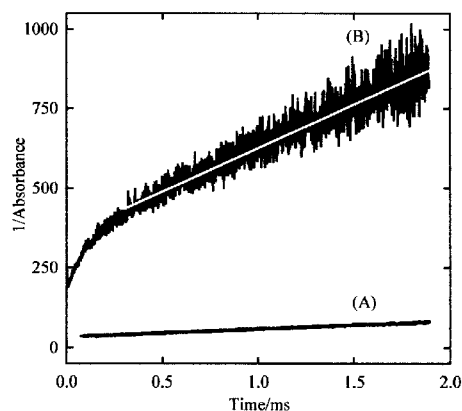


Fig. 1 Plot of the inverse of the absorbance vs. time. (A) 8.1 mbar of FS(O₂)OO(O₂)SF and 16.4 mbar of CF₄; (B) 29.3 mbar of FS(O₂)OF, 132.4 mbar of CO, 14.3 mbar of O₂ and 890.0 mbar of SF₆. The solid line is the result of the modelling described in the text.

set.¹² Unless otherwise indicated, the experimental enthalpies of formation of the species involved in this and other isodesmic reactions given here are from ref. 10. According to the experimental uncertainties, an error level for all derived thermochemical properties of this work of ± 3 kcal mol⁻¹ is estimated. From the calculated enthalpy of the isodesmic reaction of $\Delta H_r^0 = 44.7$ kcal mol⁻¹, the value $\Delta H_{f,298}^0(\text{FC}(\text{O})\text{OO}(\text{O}_2)\text{SF}) = -229.4$ kcal mol⁻¹ was derived. The enthalpy of formation for $\text{FS}(\text{O}_2)\text{O}$ was estimated from the experimental bond dissociation energy, $D_e(\text{FS}(\text{O}_2)\text{O}-\text{F}) = 33.1$ kcal mol⁻¹,² and $\Delta H_{f,298}^0(\text{FS}(\text{O}_2)\text{OF}) = -136.9$ kcal mol⁻¹ obtained from the isodesmic reaction $\text{FO}_2 + \text{HSO}_3\text{F} \rightarrow \text{FS}(\text{O}_2)\text{OF} + \text{HO}_2$ ($\Delta H_r^0 = 40.0$ kcal mol⁻¹). In this way, $\Delta H_{f,298}^0(\text{FS}(\text{O}_2)\text{O}) = -122.8$ kcal mol⁻¹ results. Using the above enthalpies of formation for $\text{FC}(\text{O})\text{OO}(\text{O}_2)\text{SF}$ and $\text{FS}(\text{O}_2)\text{O}$ together with $\Delta H_{f,298}^0(\text{FC}(\text{O})\text{O}) = -86.0$ kcal mol⁻¹,¹³ we obtain the enthalpy change $\Delta H_{298}^0(\text{FC}(\text{O})\text{O}-\text{O}(\text{O}_2)\text{SF}) = 20.6$ kcal mol⁻¹ which is similar to the value measured for the $\text{FS}(\text{O}_2)\text{O}-\text{O}(\text{O}_2)\text{SF}$ bond of 22.1 kcal mol⁻¹.³

Finally, using $\Delta H_{f,298}^0(\text{FS}(\text{O}_2)\text{OO}) = -110.2$ kcal mol⁻¹, estimated using the isodesmic reaction $\text{FO}_2 + \text{HSO}_3\text{F} \rightarrow \text{FS}(\text{O}_2)\text{OO} + \text{FOH}$ ($\Delta H_r^0 = 40.4$ kcal mol⁻¹), and $\Delta H_{f,298}^0(\text{FCO}) = 44.6$ kcal mol⁻¹,⁷ $\Delta H_{f,298}^0(\text{FC}(\text{O}_2)\text{OO}) = -76.1$ kcal mol⁻¹,⁶ and $\Delta H_{f,298}^0(\text{FSO}_2) = -96.2$ kcal mol⁻¹,¹⁴ dissociation energies for other bonds in $\text{FC}(\text{O})\text{OO}(\text{O}_2)\text{SF}$ were evaluated. The resulting values are: $\Delta H_{298}^0(\text{FC}(\text{O})\text{OO}-\text{O}(\text{O}_2)\text{SF}) = 57.1$ and $\Delta H_{298}^0(\text{FC}(\text{O})-\text{OO}(\text{O}_2)\text{SF}) = 74.6$ kcal mol⁻¹. These results indicate that no energetically feasible exit channels for the peroxide decomposition exist. The minimum-energy pathways for the recombination reaction (3) and for $\text{FC}(\text{O})-\text{OO}(\text{O}_2)\text{SF}$ and $\text{FC}(\text{O})\text{OO}-\text{O}(\text{O}_2)\text{SF}$ dissociations show a smooth energy profile without a maximum: no transition state was found on the B3LYP/6-311 + G(d) surface. Thus the enthalpy changes can be assimilated to the respective bond dissociation energies. Scarcely probable is the competition between the reaction $\text{FC}(\text{O})\text{O} + \text{FS}(\text{O}_2)\text{O} \rightarrow \text{CO}_2 + \text{FS}(\text{O}_2)\text{OF}$ and reaction (3). This assumption is supported by the fact that most fluorine abstraction reactions by either $\text{FS}(\text{O}_2)\text{O}$ or other radicals exhibit relatively large activation energy values (ca. 10–30 kcal mol⁻¹) and consequently very small room temperature rate coefficients. In particular, for the similar reaction $\text{FNO}_2 + \text{FS}(\text{O}_2)\text{O} \rightarrow \text{NO}_2 + \text{FS}(\text{O}_2)\text{OF}$ an activation energy of ca. 30 kcal mol⁻¹ can be estimated from the measured value of 10 kcal mol⁻¹ for the reverse reaction,¹⁵ the enthalpies of formation of FNO_2 and NO_2 molecules¹⁰ and the above values for $\text{FS}(\text{O}_2)\text{O}$ and $\text{FS}(\text{O}_2)\text{OF}$. The present results indicate that after formation by reaction (3), the new peroxide is mostly collisionally stabilized at room temperature. However, the low O–O bond dissociation energy leads to

significant decomposition as temperatures rises, such that a gaseous sample of $\text{FC}(\text{O})\text{OO}(\text{O}_2)\text{SF}$ finally degrades to the more stable peroxide $\text{FC}(\text{O})\text{OO}(\text{O})\text{CF}$.^{6–9}

Further experimental and theoretical work on $\text{FC}(\text{O})\text{OO}(\text{O}_2)\text{SF}$ is underway.

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