Thermal Stability of Peroxy Acyl Nitrates Formed in the Oxidation of C\textsubscript{x}F\textsubscript{2x+1}CH\textsubscript{2}C(O)H (x = 1.6) in the Presence of NO\textsubscript{2}

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ABSTRACT: The formation of C\textsubscript{x}F\textsubscript{2x+1}CH\textsubscript{2}C(O)OONO\textsubscript{2} (x = 1.6) from the photooxidation of C\textsubscript{x}F\textsubscript{2x+1}CH\textsubscript{2}C(O)H (x = 1.6) in the presence of NO\textsubscript{2} was investigated. The infrared spectrum of C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)OONO\textsubscript{2} is reported for the first time, and thermal stability for both peroxy nitrates at 295 K and 9.0 mbar is informed. Kinetic parameters (activation energy and pre-exponential factor) for C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)OONO\textsubscript{2} at 9.0 and 1000 mbar are: 108 ± 2 kJ/mol, 1.5 × 10\textsuperscript{13} and 114 ± 2 kJ/mol, 2.4 × 10\textsuperscript{16}, respectively. A comparison is made between fluoro and hydrogenated peroxy acyl nitrates.

INTRODUCTION

The oxidation of telomeric alcohols (FTOHs), which have a wide variety of industrial applications, leads to the formation of fluorinated telomeric aldehydes (FTAHs, C\textsubscript{n}F\textsubscript{2n+1}C(O)H) and perfluorocarboxylics acids \textsuperscript{1} (PFCAs, C\textsubscript{n}F\textsubscript{2n+1}C(O)OH), which are highly persistent in the environment and have been found to be present in fauna from the Great Lakes\textsuperscript{2} up to the Arctic.\textsuperscript{3} In particular, C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)H (FTAL 6:2) is formed from the degradation of FTOH 6:2,\textsuperscript{4} whereas CF\textsubscript{3}CH\textsubscript{2}C(O)H has been reported as the primary oxidation product of CF\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}OH.\textsuperscript{5}

The UV absorption cross sections and the photochemistry of FTAL 6:2 were studied\textsuperscript{6} as well as its reaction with both chlorine atoms,\textsuperscript{7,8} for which the authors measured a rate constant of (2.1 ± 0.5) × 10\textsuperscript{-12}, (2.8 ± 0.7) × 10\textsuperscript{-12}, and (1.8 ± 0.2) × 10\textsuperscript{-11} cm\textsuperscript{3} molec\textsuperscript{-1} s\textsuperscript{-1}, respectively, and OH radicals,\textsuperscript{9} with a reported coefficient of (2.2 ± 0.3) × 10\textsuperscript{-12} cm\textsuperscript{3} molec\textsuperscript{-1} s\textsuperscript{-1}. Its oxidation in the absence of NO, gives n-C\textsubscript{6}F\textsubscript{13}C(O)H, CF\textsubscript{3}O, CO\textsubscript{2}, and CO as the only products. Chiappero et al.\textsuperscript{4} concluded that most of the reaction between C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)H and chlorine atoms occurs via abstraction of the aldehyde hydrogen atom, not being substantially modified by the length of the fluorinated C-F\textsubscript{2n+1} group.

Kelly et al.\textsuperscript{5} have measured the quantum yield of the photoysis of CF\textsubscript{3}CH\textsubscript{2}C(O)H, \textphi < 0.04 and its rate constant with OH radicals (2.96 ± 0.04) × 10\textsuperscript{-12} cm\textsuperscript{3} molec\textsuperscript{-1} s\textsuperscript{-1} and chlorine atoms (25.7 ± 0.4) × 10\textsuperscript{-12} cm\textsuperscript{3} molec\textsuperscript{-1} s\textsuperscript{-1}. Its oxidation in the absence of NO leads to the formation of C\textsubscript{6}F\textsubscript{13}C(O)H, C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(OH), and C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)OH.\textsuperscript{5} When NOx is present, CF\textsubscript{3}O and CF\textsubscript{3}CH\textsubscript{2}C(O)OONO\textsubscript{2} are additionally formed.\textsuperscript{5,9}

As it is well known, peroxy acyl nitrates (RC(O)OONO\textsubscript{2}) are formed in situ by photochemical reactions involving volatile organic compounds (aldehydes, hydrocarbons, ketones, etc.) and nitrogen oxides, and they are also important reservoir species due to their stability. Among them, peroxyacetyl (CH\textsubscript{3}C(O)OONO\textsubscript{2}, PAN), peroxypropionyl (CH\textsubscript{3}CH\textsubscript{2}C(O)-OONO\textsubscript{2}, PPN), peroxybutyryl (PBN, ((CH\textsubscript{3})\textsubscript{2}CHC(O)-OONO\textsubscript{2}), peroxyisobutyryl (PiBN, ((CH\textsubscript{3})\textsubscript{2}CHC(O)OONO\textsubscript{2}), and peroxybenzoyl (C\textsubscript{6}H\textsubscript{5}C(O)C(O)OONO\textsubscript{2}, PBN) nitrates have been detected in the atmosphere.\textsuperscript{10–14} To provide information about the thermal stability of the peroxynitrates formed by the oxidation of FTAL 6:2 and CF\textsubscript{3}CH\textsubscript{2}C(O)H in the presence of NO\textsubscript{2}, we prepared both and measured their decomposition rate constants as a function of temperature and total pressure.

EXPERIMENTAL SECTION

Reagents. Samples of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanal and 3,3,3-trifluoropropionaldehyde (TFPA, CF\textsubscript{3}CH\textsubscript{2}C(O)H) were used as provided without any special purification. Oxygen (5.0), nitrogen (5.0), and nitrogen monoxide (5.1) were provided by AGA. Cl\textsubscript{2} (>99%) was prepared by dehydration of HCl, and NO\textsubscript{3} (>99%) was obtained from thermal decomposition of Pb(NO\textsubscript{3})\textsubscript{2}.

Procedure. Gas samples were manipulated in a glass vacuum line equipped with two capacitance pressure gauges. All photolyses were carried out in a 5 L glass flask, using black lamps (\lambda > 330 nm) to initiate the oxidation from chlorine atoms.

Synthesis and Characterization. C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)OONO\textsubscript{2}. Photolyses of mixtures containing C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)H (0.6 mbar), Cl\textsubscript{2} (0.9 mbar), Cl\textsubscript{2} (1.0 mbar), and O\textsubscript{3} (1000 mbar) were performed at 295 K. Their progress was monitored at 0, 30, 50, and 75 min by transferring portions of the mixtures to a long path infrared gas cell (optical path: 9 m) and recording infrared spectra. It was stopped before the NO\textsubscript{2} was
COMpletely consumed to shift the equilibrium \( \text{ROONO}_2 \rightleftharpoons \text{ROO}^* + \text{NO}_2 \) to the peroxynitrate formation (see below).

After infrared analysis, the resulting mixture was collected by passing it through traps at liquid nitrogen temperature to remove oxygen excess. Subsequent distillation at 193 K allowed elimination of carbonyl fluoride (CF\(_3\)O), CINO, and carbon dioxide formed as photooxidation products. The remains were kept with other different batches for further purification. They contained peroxynitrate, CF\(_3\)CH\(_2\)ONO\(_2\), and CF\(_3\)F\(_2\)CH\(_2\)-C\((\text{O})\)H, three substances which are difficult to separate from each other by trap-to-trap distillation under vacuum. Therefore, to obtain the infrared spectra of CF\(_3\)CH\(_2\)ONO\(_2\) and CF\(_3\)F\(_2\)CH\(_2\)-C\((\text{O})\)ONO\(_2\), we distilled in our three U-trap system (233, 213, and 77 K) the mixture as much as possible until every U-trap contained mostly one of each component. From successive subtraction the spectra of both nitrate and peroxynitrate were obtained. The content of the U-trap containing mainly the peroxynitrate was transferred to the infrared cell, and NO was added to study its thermal stability.

Thermal stability was determined by the addition of NO, in the temperature range between 288 and 307 K, at 9.0 and 1000 mbar of total pressure. At 307 K, pressure dependence of the rate constant was analyzed between 3.3 and 1000 mbar.

**RESULTS AND DISCUSSION**

**Photooxidation Mechanism of CF\(_3\)CH\(_2\)C\((\text{O})\)H in the Presence of NO\(_2\).** Figure 1 depicts the infrared spectra obtained in the photooxidation of CF\(_3\)CH\(_2\)C\((\text{O})\)H before and 30 min after irradiation and their subtraction showing the resulting products. Observation of the whole infrared spectrum of the products (middle trace in Figure) reveals the formation of CINO (around 1800 cm\(^{-1}\)) and CO\(_2\) (667 cm\(^{-1}\)) and the appearance of peaks at 795, 1749 and 825, 1694 cm\(^{-1}\) corresponding to CF\(_3\)F\(_2\)CH\(_2\)-C\((\text{O})\)ONO\(_2\) and CF\(_3\)F\(_2\)CH\(_2\)-ONO\(_2\). Not even at 30 min was CF\(_3\)O detected as a product, which is in accordance with the high NO\(_2\) concentrations still present in the system (see below).

Infrared spectra of peroxynitrate and nitrate were included for comparison.

Table 1 lists the main peaks of the products identified in this work together with those corresponding to hydrogenated and fluorinated peroxynitrates as well as nitrates of similar structures.

**Table 1. Comparison of Selected Wavenumbers for Similar Peroxynitrates (RC(O)OONO\(_2\)) and Nitrates (RONO\(_2\))**

| R      | \(\nu_{as}(\text{NO}_2)\) cm\(^{-1}\) | \(\delta_s(\text{NO}_2)\) cm\(^{-1}\) | Reference |
|--------|-------------------------------------|-------------------------------------|-----------|
| CH\(_3\) | 1741 | 794 | 15 |
| CF\(_3\)CH\(_2\) | 1750 | 794 | 9 |
| CF\(_3\)F\(_2\) | 1749 | 791 | 16 |
| CF\(_3\)F\(_2\)CH\(_2\) | 1749 | 795 | **this work** |
| CF\(_3\) | 1761 | 793 | 17 |
| CH\(_3\) | 1672 | 854 | 18 |
| CF\(_3\)CH\(_2\) | 1694 | 826 | 19 |
| CF\(_3\)F\(_2\) | 1695 | | 16 |
| CF\(_3\)F\(_2\)CH\(_2\) | 1694 | 825 | **this work** |
| CF\(_3\) | 1748 | 788 | 20 |

**Scheme 1. Mechanism of Photooxidation of CF\(_3\)F\(_2\)CH\(_2\)-C\((\text{O})\)H**

![Figure 1. Infrared spectra obtained in the photooxidation of CF\(_3\)F\(_2\)CH\(_2\)-C\((\text{O})\)H in the presence of NO\(_2\). From top to bottom: before photolysis; after 30 min irradiation; products; CF\(_3\)F\(_2\)CH\(_2\)-C\((\text{O})\)ONO\(_2\); and CF\(_3\)F\(_2\)CH\(_2\)-ONO\(_2\). The last two traces correspond to reference spectra.](image-url)
C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)H is initiated by the attack of chlorine atoms to the hydrogen atom of the aldehyde group to form C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}CO\textsuperscript{•} radicals (reaction 1)\textsuperscript{8}
\[
\text{C}_6\text{F}_{13}\text{CH}_2\text{C(O)}\text{H} + \text{Cl}^* \rightarrow \text{C}_6\text{F}_{13}\text{CH}_2\text{CO}^* + \text{HCl}
\] (1)
which follows a series of typical reactions occurring when O\textsubscript{2} and NO\textsubscript{2} are present, leading mainly to peroxy and nitrate. The formation of the peroxy nitrate is consistent with the relatively high concentration of NO\textsubscript{2}, which reacts with the C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)OO\textsuperscript{•} radical.

The formation of C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}ONO\textsubscript{2} needs some explanation, however. C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}O\textsuperscript{•} radicals could either react with either NO\textsubscript{2} or O\textsubscript{2} or decompose (reactions 2–4):
\[
\text{C}_6\text{F}_{13}\text{CH}_2\text{O}^* + \text{O}_2 \rightarrow \text{C}_6\text{F}_{13}\text{CH}_2\text{C(O)}\text{H} + \text{HO}_2^* 
\] (2)
\[
\text{C}_6\text{F}_{13}\text{CH}_2\text{O}^* + \text{NO}_2 \rightarrow \text{C}_6\text{F}_{13}\text{CH}_2\text{ONO}_2 
\] (3)
\[
\text{C}_6\text{F}_{13}\text{CH}_2\text{O}^* \rightarrow \text{C}_6\text{F}_{13}^* + \text{CH}_2\text{O} 
\] (4)
but given the scarcity of direct measurements for rate constants of long chain alkoxy radicals (>C4), those for reactions 2 and 3 have been assigned the values of 1 \times 10^{-14} and 3 \times 10^{-13} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}, respectively employing for the radical C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}O\textsuperscript{•} a similar strategy as that used by Sulbaek Andersen et al.\textsuperscript{16} for the C\textsubscript{3}F\textsubscript{7}CH\textsubscript{2}O radical using the database of Orlando et al.\textsuperscript{21} Within this assumption, reaction 3 is favored under our experimental conditions. Furthermore, the formation of nitrate is observed in the infrared spectrum of the products shown in Figure 1, while the peak at 1777 cm\textsuperscript{-1} (corresponding to C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)H\textsuperscript{•}) is absent.

The unimolecular decomposition of the alkoxy radical does not compete effectively with reaction 2 at oxygen pressures higher than 7 mbar,\textsuperscript{22,23} suggesting that formaldehyde will not be formed. This agrees with the nonobservation of their characteristic and intense infrared signals, which for our experimental conditions would impose a detection limit of 5.3 \times 10^{-4} mbar.

**Thermal Decomposition of C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)OO\textsubscript{•}**

The rate constant of the thermal decomposition of C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)\textsubscript{H} was experimentally measured at 9.0 mbar and 295 K. The peroxy nitrate was introduced into the long path infrared gas cell, NO was added, and total pressure was obtained by the addition of N\textsubscript{2}. The thermal decomposition of C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)\textsubscript{O}ONO\textsubscript{2} leads mainly to peroxynitrate and NO\textsubscript{2}, which follows a series of typical reactions occurring when O\textsubscript{2} and NO\textsubscript{2} are present, leading mainly to peroxy and nitrate.

The activation energy for CF\textsubscript{3}C(O)OO\textsuperscript{•} radical. The formation of the peroxy nitrate is consistent with the relatively high concentration of NO\textsubscript{2}, which reacts with the C\textsubscript{6}F\textsubscript{13}CH\textsubscript{2}C(O)OO\textsuperscript{•} radical.

The temperature dependence of the first-order rate constant was measured at two different pressures (9.0 and 1000 mbar) and temperatures ranging from 288 to 307 K. The decomposition
\[
\text{CF}_3\text{CH}_2\text{C(O)}\text{ONO}_2 \rightarrow \text{CF}_3\text{CH}_2\text{C(O)}\text{O}^* + \text{NO}_2 
\] (8)
was carried out adding an excess of NO in the system sufficient to titrate the peroxy radicals formed
\[
\text{CF}_3\text{CH}_2\text{C(O)}\text{O}^* + \text{NO} \rightarrow \text{CF}_3\text{CH}_2\text{C(O)}\text{O}^* + \text{NO}_2 
\] (9)
The experimental values obtained are plotted in Figure 2 and fitted with a linear regression to obtain the Arrhenius parameters. Additional measurements of k\textsubscript{5} at 307 K show that the rate constant is dependent on the total pressure (Figure 3), and even at 1000 mbar the behavior is similar to the one shown for CF\textsubscript{3}C(O)OO\textsubscript{•} at 315 K.\textsuperscript{24}

The Arrhenius parameters are presented in Table 2 and compared with those of similar fluorinated and hydrogenated peroxy nitrites.

As it can be observed, the activation energy for CF\textsubscript{3}CH\textsubscript{2}C(O)\textsubscript{O}ONO\textsubscript{2} decreases with total pressure (114 and 108 kJ/mol at 1000 and 9.0 mbar, respectively). It can also be seen that when an acyl-peroxynitrate is completely fluorinated (cf. rows 2 and 4) the activation energy increases beyond experimental uncertainty. Nevertheless, if the CF\textsubscript{3} group has a methylene bridging the carbonyl moiety, the former conclusion is not so
Table 2. Kinetic Parameters for Selected Peroxynitrates at Different Pressures

| Peroxynitrinate          | Ea (kJ/mol) | A (s⁻¹) | Ref. |
|--------------------------|-------------|---------|------|
| CF₃CH₂C(O)OONO₂          | 114 ± 2     | 2.4 x 10⁸ | this work |
| CH₃C(O)OONO₂             | 113 ± 2     | 2.5 x 10⁸ | 15   |
| CH₃CH₂C(O)OONO₂          | 116 ± 2     | 7.2 x 10⁸ | 25   |
| CF₃C(O)OONO₂             | 119 ± 5     | 6.0 x 10⁸ | 24   |

| Peroxynitrinate          | Ea (kJ/mol) | A (s⁻¹) | Ref. |
|--------------------------|-------------|---------|------|
| CF₃CH₂C(O)OONO₂          | 108 ± 2     | 1.5 x 10⁹ | this work |
| CH₃C(O)OONO₂             | 106         | 15      |      |
| CH₃CH₂C(O)OONO₂          | 107 ± 3     | 1.5 x 10⁹ | 25   |

“Uncertainty for the activation energy of CF₃CH₂C(O)OONO₂ was calculated from the fitting of the experimental data points of the rate constants used in the Arrhenius plot. ×Measured at 11.5 mbar.

CONCLUSIONS

The results obtained have significant implications for understanding of the atmospheric oxidation mechanism of CF₃CH₂CH₂OH in the presence of O₂ and NO₂. The atmospheric fate of CF₃CH₂CH₂OH is reaction with OH radicals, leading to the formation of CF₃CH₂CH₂COO⁺, which in an environment with high NO₂ concentrations could give CF₃CH₂CH₂(O)NO₂⁻. The high stabilities of CF₃CH₂CH₂(O)NO₂⁻ (x = 1,6) that are similar to the stability of the most abundant peroxytrinitrates in the atmosphere (PAN, PPN), as Figure 4 shows, point out that the peroxytrinitrates formed from telomeric aldehydes can act as reservoir species for NO₂ and peroxy radicals in the atmosphere.

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Notes
The authors declare no competing financial interest.

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