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# Photolysis of n-propyl Formate in the Presence of O and NO. Peroxy Formyl Propyl Nitrate CHCHCHOC(O)OONO, Synthesis and Characterization

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Photolysis of n-propyl Formate in the Presence of O<sub>2</sub> and NO<sub>2</sub>. Peroxy Formyl Propyl Nitrate CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)OONO<sub>2</sub>, Synthesis and Characterization Jesús A. Vila, Gustavo A. Argüello, Fabio E. Malanca\*
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Abstract:

The photo-oxidation of n-propyl formate (initiated by chlorine atoms) was studied in the presence of NO<sub>2</sub> and the products were identified. The Cl atom attack to the molecule occurs in four sites leading to the formation of formic acid, carbon dioxide, dicarbonylic products, nitrates, peroxy propionyl nitrate (CH<sub>3</sub>CH<sub>2</sub>C(O)OONO<sub>2</sub>, PPN), and a new peroxynitrate, peroxy formyl propyl nitrate (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)OONO<sub>2</sub>, PFPN). In order to characterize bulk quantities of the PFPN, its synthesis was carried out by the photolysis of mixtures of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)H, NO<sub>2</sub>, Cl<sub>2</sub>, and O<sub>2</sub>. After purification, its infrared spectrum and thermal stability were determined. The main infrared absorption bands and their corresponding cross-sections are: 796, 1219, 1302, 1741, and 1831 cm<sup>-1</sup> (1.16, 3.11, 0.88, 2.42, and 1.34 x 10<sup>18</sup> cm<sup>2</sup> molec<sup>-1</sup>, respectively). Thermal decomposition was studied as a function of pressure from 6.0 to 1000 mbar at 298 K and the activation energy was determined between 293 and 304 K at total pressures of 9.0 and 1000 mbar (E<sub>a</sub> = 98  $\pm$  3 and  $110 \pm 2$  kJ/mol, respectively). The atmospheric thermal lifetimes were obtained from kinetic parameters.

Keywords: Peroxynitrate. Atmospheric degradation. Propyl formate. Thermal stability.

Peroxy Formyl Propyl Nitrate.

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# Introduction

Esters are important volatile organic compounds. They are used as industrial solvents, as reagents during the manufacture of perfumes and food flavoring, and as fumigant of stored foodstuffs due to its pesticide properties<sup>1-4</sup>. They are also emitted naturally to the atmosphere by vegetation and could be formed in the atmospheric degradation of alcohols, ethers, and new biofuels. Propyl formate (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)H) is emitted from some fruits<sup>5</sup> and is formed as a degradation product from the family of glycol ethers used in many domestic and industrial products.<sup>6</sup> Though there are not reliable estimates of the total atmospheric burden of either the formate or the peroxynitrate itself, the latter should be considered as a potential source of pollution, and therefore, the study and understanding of its chemistry is highly needed.

Kinetic studies of reactions of formates with <sup>•</sup>OH radicals or chlorine atoms, as well as determinations of the photo-oxidation mechanisms in the presence and absence of nitrogen dioxide have been performed by several authors who aimed to predict the possible impact of their emissions to the atmosphere. The rate coefficient for methyl, ethyl, n-propyl and n-butyl formates with <sup>•</sup>OH radicals at 298 K ( $1.80 \times 10^{-13}$ ,  $8.43 \times 10^{-13}$ ,  $1.82 \times 10^{-12}$ ,  $3.82 \times 10^{-12}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> respectively)<sup>7</sup> show that these species can react in the troposphere, with the concomitant formation of degradation products. On the other hand, the rate coefficient of these formates with chlorine atoms has been determined by several authors.<sup>7-11</sup> The rate coefficient for n-propyl formate at 298 K ranges from 4.3 to 5.6 x  $10^{-11}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1.8,10</sup>

The reaction mechanism initiated by chlorine atoms in the presence and absence of  $NO_2$ , as well as the branching ratio for the attack of chlorine atoms to the different hydrogen atoms of the molecule were determined for methyl- and ethyl formates by Wallington et al. (2001), Hansen et al. (2002), Malanca et al. (2009) and Orlando et al. (2010), respectively.<sup>1,12-14</sup> Many studies have concluded that the oxidation of either hydrogenated or fluorinated compounds in the presence of NO<sub>2</sub> leads to the formation of peroxynitrates (ROONO<sub>2</sub>), important reservoir species in the atmosphere.<sup>15-18</sup> In particular, the photo-oxidation of formates in the presence of NO<sub>2</sub> should lead to the formation of an important family of thermally stable peroxy acyl nitrates,  $CxH_{2x+1}OC(O)OONO_2$ , of which only the shorter chain (x=1,2) congeners have been reported.<sup>1,18</sup>

In this work, we have studied the oxidation of n-propyl formate in the presence of NO<sub>2</sub>, determined its reaction mechanism, quantified the main products formed, and characterized the new peroxynitrate (identified as peroxy formyl propyl nitrate CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)OONO<sub>2</sub> PFPN) as well as determined some of its physicochemical properties.

#### Experimental

#### <u>Materials</u>

Commercially available samples of propyl formate (Sigma Aldrich), NO (AGA) and  $O_2$  (AGA) were used. NO<sub>2</sub> was synthetized by the thermal decomposition of Pb(NO<sub>3</sub>)<sub>2</sub>. Cl<sub>2</sub> was prepared by the reaction between HCl and KMnO<sub>4</sub>, and was then distilled.

# Procedure

Gases were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (0 – 760 Torr, MKS Baratron; 0 – 70 mbar, Bell and Howell).

Photolyses of mixtures of  $CH_3CH_2CH_2OC(O)H$  (3.0 mbar)/  $Cl_2$  (1.5 mbar)/  $NO_2$  (0 or 0.7 mbar)/  $O_2$  (1000 mbar) were carried out in an IR gas cell (optical path 23.0 cm; silicon windows), using two black lamps, following the temporal variation of reactant and products through IR spectroscopy. Spectra were acquired in the range 4000 - 400 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>

using a FTIR spectrophotometer BRUKER IR IFS28. This set-up was also used to quantify the products formed.

Additionally, to identify the products formed in the photo-oxidation in the absence of NO<sub>2</sub>, samples were photolyzed in a 5 L glass flask. The resulting mixture was transferred to a set of three cold traps where its components were distilled using baths at different temperatures (-100, -70 and -50°C). The resulting fractions were transferred to the infrared gas cell and their spectra were analyzed.

In order to characterize the PFPN, it was synthesized and further purified. The syntheses were carried out in a photo-reactor maintained at low temperature (0 to 3 °C) to avoid its thermal decomposition. The progress of the reaction was checked every 30 min. by taking small samples from the reactor and recording the infrared spectra. The photolysis was stopped when 50% of the reactant had disappeared. The resultant mixture was collected by slowly passing it through three traps kept in liquid N<sub>2</sub> in order to remove excess O<sub>2</sub>, and non-condensable products. The distillation from -80 °C to -120 °C led to the elimination of CINO and CO<sub>2</sub>, and successive distillations from -50°C to -100°C allowed the removal of propyl formate, nitrates, and most of the formic acid. The remnant fraction contained mainly PFPN and a small amount (<2%) of formic acid.

Thermal stability of PFPN was determined between 293 and 304 K using a proven methodology frequently employed,<sup>15,18</sup> that adds NO (1.0 mbar) to the reaction vessel in order to capture the peroxy radicals formed in the decomposition. The temporal variation of the peroxynitrate concentration for 0.4 mbar samples of PFPN was monitored by infrared spectroscopy using the bands at 796 and 1742 cm<sup>-1</sup>. The results were analyzed according to a first-order rate law at each temperature and thus an Arrhenius plot was obtained.

Theoretical calculations to give the infrared spectrum were performed with the Gaussian 03 program suite.<sup>19</sup> Geometric optimizations, and calculations of the vibrational frequencies of PFPN were carried out by applying Density Functional Theory (DFT) methods, using the B3LYP exchange functional with 6-311++ G(d,p) basis.

Gas chromatography/mass spectrometry (GC/MS) analyses were performed in a Shimadzu GC-MS-QP 5050 spectrometer equipped with a capillary column Zebron 2B-5MS (30 m × 0.25 mm × 0.25  $\mu$ m) using helium as eluent at a flow rate of 1.1 mL / min. Both injector and ion source temperatures were 280°C, the oven heating ramp was 15 °C / min. from 25 °C up to 280 °C. The pressure in the MS instrument was 10<sup>-5</sup> torr, precluding ion-molecule reactions from taking place, and MS recording were made in the electron impact (EI) mode with ionization energy of 70 eV.

#### **Results and discussions**

#### Photo-oxidation of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)H in the presence of NO<sub>2</sub>

Figure 1 shows the sequence of infrared spectra obtained in the photolysis of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)H, Cl<sub>2</sub>, NO<sub>2</sub>, and O<sub>2</sub> mixtures. The first and second traces correspond to t=0 and t=60 min. of irradiation, respectively. The third trace (A), obtained from the subtraction of reactants to the second one, shows the products formed. It is clear that formic acid is formed (peaks at 1105 and 1775 cm<sup>-1</sup>). In the fourth trace (B), formic acid has been subtracted and the spectrum shows two peaks characteristic of peroxynitrates (796 and 1742 cm<sup>-1</sup>). The fifth trace (C) shows the reference spectrum of PFPN, obtained as will be explained in a subsequent section. Its subtraction from the fourth trace (paying special attention to the band centered at 1219 cm<sup>-1</sup> that we independently know that belongs to PFPN) leads to the sixth trace (D) and

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reveals still another peroxynitrate formed in the photolysis. The next (seventh) trace shows the reference spectra of peroxy propionyl nitrate (PPN), whose subtraction from the sixth trace leads to the last one, in which circles highlight the formation of nitrates (bands at 1650, 1280, and 850 cm<sup>-1</sup>) and asterisks point to the formation of other carbonylic compounds (bands at 1758 and 1166 cm<sup>-1</sup>). Carbon dioxide is also formed in the photolysis (though it is not shown in the Figure).



**FIGURE 1** 

Information about the identity of the carbonyl products was obtained from similar experiments carried out in the absence of nitrogen dioxide. Figure 2 shows the spectrum of products obtained in the photolysis of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)H, Cl<sub>2</sub>, and O<sub>2</sub> mixtures after 60 minutes of irradiation (first trace). The subtraction of a reference spectrum of formic acid to this first trace leads to a new one that shows the presence of the same carbonylic signals as those of trace F of Figure 1, though their intensities are higher in the absence of NO<sub>2</sub>. This could be

explained by taking into account that the photolysis in the presence of nitrogen dioxide leads to the formation of both nitrate and peroxynitrate and, consequently, the formation of carbonylic products is decreased.



FIGURE 2

Identification of these carbonylic compounds required photolysis of bulk quantities in the absence of NO<sub>2</sub> and appropriate fractionation using cold baths. The most abundant products identified by FTIR were carbon dioxide and formic acid, while the less volatile fraction shows other carbonylic compounds that needed to be analyzed by gas chromatography coupled to mass spectrometry. A typical chromatogram shows three peaks at retention times ranging from 3 to 4 minutes. Based on their fragmentation patterns, we are led to conclude that the species are CH<sub>3</sub>C(O)CH<sub>2</sub>OC(O)H (m/e: 15, CH<sub>3</sub><sup>+</sup>; 43, CH<sub>3</sub>CO<sup>+</sup>; 59, C<sub>3</sub>H<sub>7</sub>O<sup>+</sup>; 87, M- CH<sub>3</sub>; 101, M<sup>+</sup>), CH<sub>3</sub>CH<sub>2</sub>C(O)OC(O)H ( $m/e: 27, C_2H_3^+; 29, C_2H_5^+, CHO^+; 45, CO_2H^+; 59, C_3H_7O^+; 74, C_3H_6O_2^+; 87, M-CH_3; 101 M^+$ ) and HC(O)CH<sub>2</sub>CH<sub>2</sub>OC(O)H (29, CHO<sup>+</sup>; 44, CO<sub>2</sub><sup>+</sup>; 58, C<sub>3</sub>H<sub>6</sub>O<sup>+</sup>; 73, C<sub>3</sub>H<sub>5</sub>O<sub>2</sub><sup>+</sup>), all of them formed from the reaction of oxy radicals with molecular oxygen, as will be discussed.

The explanation of the products observed (in the presence and absence of nitrogen dioxide) could be as follows; chlorine atoms attack n-propyl formate at four different sites forming the respective radicals (*Reaction 1a-d*)

$$CH_{3}CH_{2}CH_{2}OC(O)H + CI^{\bullet} \rightarrow {}^{\bullet}CH_{2}CH_{2}OC(O)H + HCI$$
 1a

$$\rightarrow CH_3CH^{\bullet}CH_2OC(O)H + HCl$$
 1b

$$\rightarrow CH_3CH_2CH^{\bullet}OC(O)H + HCl 1c$$

$$\rightarrow CH_3CH_2CH_2OC(O)^{\bullet} + HCl \qquad 1d$$

In the presence of  $O_2$ , all these radicals lead to the formation of peroxy radicals:  $^{\circ}OOCH_2CH_2CH_2OC(O)H$ ,  $CH_3CH(OO^{\circ})CH_2OC(O)H$ ,  $CH_3CH_2CH(OO^{\circ})OC(O)H$ , and  $CH_3CH_2CH_2OC(O)OO^{\circ}$ . From these radicals, the only one that could lead directly to a stable peroxynitrate in the presence of nitrogen dioxide is the last one, which gives  $CH_3CH_2CH_2OC(O)OONO_2$ . The other peroxy radicals form the oxy radicals  $^{\circ}OCH_2CH_2CH_2OC(O)H$  (R1),  $CH_3CH(O^{\circ})CH_2OC(O)H$  (R2), and  $CH_3CH_2CH(O^{\circ})OC(O)H$  (R3) after interaction with either chlorine atoms or nitrogen monoxide formed from the photolysis of  $NO_2$ . These C4 alkoxy radicals still have some reaction paths available: either reaction with  $O_2$  to form dicarbonylic compounds; breaking of C-C or C-O bonds to form shorter chain compounds;  $\alpha$ -ester rearrangement to form acids; or isomerization via a 1,5-H atom shift that preserves the length of the carbon chain.<sup>20</sup>

As might be expected by analogy to non-substituted radicals of similar structure, reaction with  $O_2$  is a major fate for R1 to form 3-oxopropyl formate (HC(O)CH<sub>2</sub>CH<sub>2</sub>OC(O)H), while decomposition via C-C bond cleavage appears to dominate for R2.<sup>20,21</sup> The rearrangement process could, a priori, be the major fate for R3, on account of its analogy with the CH<sub>3</sub>CH(O<sup>•</sup>)OC(O)CH<sub>3</sub> radical, though reactions with  $O_2$ , decomposition via C-C or C-O bond scission, or isomerization may also occur to a smaller degree as pointed out by Piquet et al and Tuazon et al.<sup>21,22</sup> Nevertheless, R2 and R3 could still lead to minor quantities of CH<sub>3</sub>C(O)CH<sub>2</sub>OC(O)H and CH<sub>3</sub>CH<sub>2</sub>C(O)OC(O)H because of the reaction with  $O_2$ . In the presence of nitrogen dioxide, an additional path to form nitrates opens.

Scheme 1 shows the reaction mechanism in the presence of NO<sub>2</sub>. The reactions following the formation of  $CH_3CH_2CH_2OC(O)OO^{\bullet}$  lead to PFPN ( $CH_3CH_2CH_2OC(O)OONO_2$ ). Further decomposition of PFPN could lead to  $CO_2$  and  $CH_3CH_2CH_2O^{\bullet}$  radicals that, in the presence of nitrogen dioxide, mainly end in n-propyl nitrate formation. As can be seen from the yields presented in the Scheme, the formation of PFPN accounts for about 10% of the disappearance of the formate.

On the other hand, R3 leads to the formation of formic acid, PPN (15 %), carbon dioxide, CH<sub>3</sub>CH<sub>2</sub>C(O)OC(O)H, and ethyl nitrate, all of them identified by infrared or mass spectroscopy. The radical R2, leads to the formation of CH<sub>3</sub>C(O)CH<sub>2</sub>OC(O)H and formic acid. Finally, the radical R1 leads to the formation of HC(O)CH<sub>2</sub>CH<sub>2</sub>OC(O)H. As expected, the quantities of formic acid formed (25 %) are not modified by the addition of NO<sub>2</sub>, considering that its formation occurs through a  $\alpha$ -ester rearrangement. The quantification of total nitrates formed in the photolysis with NO<sub>2</sub> explains about (26 ± 3) of the disappearance of the precursor formate.

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# Infrared spectrum of PFPN

Figure 3 shows the experimental and calculated spectra of PFPN as well as the infrared absorption cross-sections. There is a good concordance between both spectra. This feature could also be used as a confirmation corroborating the identity of PFPN. The calculated spectrum was obtained from the most stable conformer syn-syn (Figure 4), derived by structure optimization (see below). The calculation of the vibrational frequencies of possible conformers of PFPN were carried out by applying Density Functional Theory (B3LYP) methods with 6-311++ G(d,p) basis sets.







During the optimization process of the possible conformers, some common features, regardless of the starting structure were observed:

- The dihedral angle formed by the fragment H(1,2,3)-C1-C2-C3 adopts the configuration "anti" (180°) as well as the other dihedrals formed with the fragments C1-C2-C3-O1 and C2-C3-O1-C4.

- The dihedral angle formed by the fragment O3-04-N1-O5 adopts the configuration "syn" (close to 0°) similar to other peroxinitrates.<sup>23</sup>

Therefore, setting fixed values for these dihedral angles, the study focused on the remaining ones, that define the position of the C=O bond with respect to the peroxidic bond O3-O4. The conformers were named according to the following criteria: (a) the position of the C=O bond with respect to the O—O bond defines the first term, whether *syn* or *anti*; and (b) the position of the CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>—O bond with respect to the C=O bond defines the second *syn-anti* term. The calculations reveal that the most stable conformer is syn-syn in accordance with results obtained for CH<sub>3</sub>CH<sub>2</sub>OC(O)OONO<sub>2</sub> by Bossolasco et al. (2011).<sup>18</sup> Tables S1 and S2 show the calculated geometric parameters, and Cartesian coordinates. The calculated value for both the dihedral (C—O—O—N) and the O—O bond distance agree with literature values <sup>14, 18, 19, 24</sup> ACS Paragon Plus Environment



The temporal variation of the peroxynitrate concentration was followed by FTIR as was described previously, and the rate coefficient measured ( $k_{obs}$ ) was corrected using the following equation,

$$k_2 = k_{obs} \left( 1 + \frac{k_{-2} \left[ NO_2 \right]}{k_3 \left[ NO \right]} \right)$$

which takes into account that, during the thermal decomposition the nitrogen dioxide concentration increases. The rate coefficient for reactions (-2) and (3) were taken from literature values corresponding to similar radicals as has been done by many authors ( $k_{.2} = 1.12 \times 10^{-11}$ ,  $k_3 = 2.11 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).<sup>25, 26</sup> Nevertheless, this correction accounts for a 6 % of k<sub>obs</sub> at most. This percentage arises from the use of the reported rate coefficients for reaction (-2) and (3) as well as the experimental concentration for nitrogen monoxide added to the

system and the maximum nitrogen dioxide concentration formed as consequence of PFPN decomposition.

In order to establish the dependence of the rate coefficient of reaction (2) with pressure, a series of experimental runs were performed at 298 K at different total pressures. The results presented in Figure 5 show that the dependence is similar to that reported by Bossolasco et al. (2011)<sup>18</sup> for peroxy ethoxy formyl nitrate (PEFN), though we can not explain why the high pressure limit has not been reached at 1000 mbar for a molecule possessing a higher number of degrees of freedom.



FIGURE 5

The kinetic parameters ( $E_a$ , activation energy, A, pre-exponential factor) derived from the Figure give the following values at 9.0 and 1000 mbar:  $E_a = (98 \pm 3)$  kJ/mol and Ln A = (31 ± 1);  $E_a = (110 \pm 2)$  kJ/mol, and Ln A = (36.1 ± 0.8), respectively. The comparison of the values of  $E_a$  determined at 1000 mbar with those reported for  $CH_3OC(O)OONO_2$  (107 ± 5) kJ/mol<sup>27</sup> and  $C_2H_5OC(O)OONO_2$  (108 ± 5) kJ/mol<sup>18</sup> shows good agreement for the family  $C_xH_{2x+1}OC(O)OONO_2$ . The closeness of the values for  $E_a$ , all of them comprised within the experimental errors, preclude us to establish a definite trend in the stability of this family as a function of the length of the carbonated chain.

#### Conclusions

In this paper, we determined the main products resulting from the photo-oxidation of npropyl formate, both in the presence and in the absence of NO<sub>2</sub>, as well as the reaction mechanism. In the atmosphere, emissions of n-propyl formate could contribute to the formation of nitrates, dicarbonyl compounds, and PFPN.

The comparison of its thermal stability with peroxynitrates of the shorter carbonated chain  $C_xH_{2x+1}OC(O)OONO_2$  (x = 2, 3) leads to conclude that this family could act as reservoir species in the atmosphere. In particular, the lifetime of PFPN at an altitude of 2 Km is about one day. It rapidly increase up to 7 months at 6 km, reaching values of years near the tropopause.

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### **Supporting Information Available**

Geometric parameters for the *syn-syn* PFPN conformer (Table S1) and cartesian matrix for syn-syn PFPN (Table S2).

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#### Captions

**Figure 1.** Photooxidation of n-propyl formate in the presence of NO<sub>2</sub>. Traces from top to bottom: first, before irradiation; second, after 60 min photolysis; "A", reaction products "B" = "A"-HC(O)OH; "C" = PFPN reference spectra (see text below); "D" = "B" – PFPN; "E" = PPN; "F"= "D"– PPN. Arrows signal the peaks corresponding to formic acid. Circles and asterisks show the peaks corresponding to remnant nitrates and carbonylic compounds, respectively. **Figure 2.** Photooxidation of n-propyl formate in the absence of NO<sub>2</sub>. Traces from top to bottom:

"A", products after 60 min of photolysis; "B" = "A" – HC(O)OH; "C", trace "F" taken from Figure 1 for comparison.

Figure 3. Absorption cross-sections and calculated spectra of PFPN.

Figure 4. Calculated structure for the most stable conformer (syn – syn conformer).

Figure 5. Thermal decomposition of PFPN as a function of pressure. Errors bars represent one

standard deviation taken from the temporal variation of peroxynitrate at each pressure.

**Scheme 1.** Mechanism of oxidation in the presence of nitrogen dioxide.



**FIGURE 1** 



FIGURE 2



**FIGURE 3** 







# TABLES OF CONTENTS IMAGE

