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Fluorocarbonyl peroxynitrate ($FC(O)OONO_2$) Temperature dependence of the UV absorption spectrum

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Abstract

The ultraviolet absorption spectrum of gas phase $FC(O)OONO_2$ has been measured over the wavelength range 200–320 nm for temperatures between 298 and 245 K. Absorption cross-sections were found to increase significantly with increasing temperature at wavelengths longer than 250 nm. Implications for the atmospheric chemistry of $FC(O)OONO_2$ are discussed.

Keywords: UV absorption; Peroxynitrates; Peroxides; Fluorocarbonyl peroxynitrate; Temperature dependence

1. Introduction

The atmospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) leads to the formation of XYC(O) molecules, where X = Cl, F and Y = Cl, F or H [1–3]. These molecules could either react with OH (if Y = H) in the troposphere or be photolyzed in the stratosphere leading in both cases to the formation of FCO radicals.

Once formed in the atmosphere, the almost exclusive fate for FCO radicals is the reaction with O_2 [4] to form peroxyacyl radicals

$$FCO + O_2 + M \rightarrow FC(O)OO + M \tag{1}$$

which, in NO_2 rich areas, could be converted into $FC(O)OONO_2$ [5] through reaction (2)

$$FC(O)OO + NO_2 + M \rightarrow FC(O)OONO_2 + M \tag{2}$$

Thus, fluorocarbonyl peroxynitrate ($FC(O)OONO_2$) could be acting as a reservoir species in the atmosphere [6] like several other peroxynitrates do, sequestering FC(O)OO radicals and converting them into less reactive, electron paired, thermally stable molecules which are, at the same time, reservoir for NO_2 radicals. The formation and decomposition is a consequence of the equilibrium between reactions (2) and (2′)

$$FC(O)OONO_2 \rightarrow FC(O)OO + NO_2 \tag{2′}$$

that at 296 K has a $K_{eq} = 3.9 \times 10^{-8}$ (cm^3 $molecule^{-1}$) [7].

The thermal stability of other peroxy acyl nitrates has been reported [8]. Among them, peroxyacetyl nitrate (PAN, $CH_3C(O)OONO_2$) and peroxy propionyl nitrate (PPN, $CH_3CH_2C(O)OONO_2$) – two important NO_x reservoir species that can transport NO_x over large distances from polluted to unpolluted areas [9–12] – are the most stable ones and have been directly detected in the atmosphere.

$FC(O)OONO_2$, also an acyl nitrate, has already been thoroughly characterized [6,7]. Its spectroscopic properties, kinetic formation and thermal stability are known. $FC(O)OONO_2$ is stable thermally and could be transported to high altitudes where it can be photolyzed. Therefore, due to the changing temperatures of the troposphere which will affect not only the equilibrium constant value for thermal decomposition but the absorption cross-sections, it is important to know its ultraviolet absorption features at stratospheric temperatures. The first UV–vis spectrum was recorded by Scheffler et al. [6] between 200 and 290 nm at 298 K. Our aim in this work is to extended the range to 320 nm and to establish the dependence of cross-sections with temperature. These data are of relevance to calculate the atmospheric lifetime of $FC(O)OONO_2$. Wallington et al. [7] reported that below 3 km the thermal lifetime is short (shorter than 7 days),

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but at higher altitudes, it could take much longer values [7]. Nevertheless, at higher altitudes the radiation increases and the photochemical features could control its atmospheric lifetime. Our results indicate that after 4 km altitude the photochemical dissociation takes over the thermal decomposition.

2. Experimental

2.1. Chemicals

Frozen oxalyl fluoride obtained by an earlier synthesis from oxalyl chloride and NaF was taken from our reservoir and distilled prior to use. IR analysis were performed to check its purity, as well as the purity of all the other IR active reagents.

Commercially available samples of NO_2 (AGA) and O_2 (AGA) were used. Oxygen was condensed by flowing O_2 at atmospheric pressure through a trap immersed in liquid air. It was then pumped under vacuum several times and transferred to a glass bulb whilst the trap was still immersed in liquid air.

$FC(O)OONO_2$ was synthesized by the photolysis at 254 nm of a gaseous mixture of $(FC(O))_2$, NO_2 and O_2 kept at 0 °C in a 12 L reactor as is described in Scheffler et al. [6]. The pressures of each reactant were 3, 10 and 300 Torr, respectively. The progress in the synthesis reaction was followed by IR analysis taking small samples from the reactor and bringing them into the IR cell connected on-line. The photolysis was stopped when the absorption bands characteristic of $(FC(O))_2$ were no longer present. At this point some $FC(O)OONO_2$ could have been decomposed as well. Several batches from different syntheses were collected before attempting the purification in order to have a bigger amount of material. A coarse purification was made through vacuum distillation and after reaching the point where no improvements in purity were possible, ozone was introduced to oxidize the remnant NO_2. Finally, the purity of $FC(O)OONO_2$ was checked also by UV spectroscopy.

2.2. Methods

In order to measure the temperature dependence, the experimental set-up described in Ref. [13] was used. A standard quartz gas cell (optical path 10 cm) inside an evacuated metal box located in the UV–vis spectrometer path with diode array detector was employed. The temperature was regulated between 298 and 245 K using a cryostat. Temperatures were maintained constant to within ±1 K and read using a thermocouple. The pressures of the reagent were measured using a Bell & Howell 60 mbar full scale capacitance manometer.

Reagent pressures were selected taking into account two needs: first, the avoidance of condensation within the cell at low temperatures and second, the minimization of photometric errors – whenever possible – by keeping the absorbances between 0.3 and 0.8. The baseline drift with temperature was less than 1×10^{-3} absorbance units corresponding to a cross-section near to $2 \times 10^{-22}\,cm^3\,molecule^{-1}$. The particular pressures used to record the UV spectra ranged between 1.28 ± 0.04 and 30.0 ± 0.2 mbar.

Atmospheric half-lives with respect to photolysis were calculated using the TUV 4.2 program [14] as a function of altitude and solar zenith angle. A pressure independent quantum yield of unity at all wavelengths was assumed.

3. Results and discussion

The samples of $FC(O)OONO_2$ distilled from different syntheses batches were introduced into the cell and UV–vis spectra were measured taking first the spectrum at 298 K, then lowering the temperature down to 245 K and recording another spectrum to begin warming up the sample and sequentially taking spectra at 261, 273, 285 K and repeating the spectrum at 298 K to check for consistency of our results.

During manipulation there is always production of NO_2 (reaction (2′)). This species exists also in equilibrium with N_2O_4. NO_2 and N_2O_4 absorb in the wavelength range studied, N_2O_4 being a particularly strong absorber. Consequently, these two species were subtracted from the spectrum of the samples taking care of observing the relative concentrations as temperature changed. At low temperatures a greater fraction of the NO_2 exists in the form of N_2O_4. The NO_2 absorption features subtracted were those recommended in Sander et al. [15] looking particularly at the region of maximum absorption (390–420 nm). Then, the amount of N_2O_4 dictated by the NO_2/N_2O_4 equilibrium constant at that particular temperature [15] was calculated and, using as a reference the absorption cross-sections given by Merienne et al. [16], the subtraction was carried out without any manipulation. The consistency of this procedure was checked using known equilibrated samples of NO_2/N_2O_4 at the same temperatures as those used for the peroxynitrate samples.

The absorption cross-sections obtained are given in Table 1. The increase in absorption cross-sections with temperature are small at some wavelengths; but they represent a genuine temperature change since the data were taken with the same sample without any manipulation but the different temperatures. The increase is consistent with an increased population of the vibrational and rotational levels of the ground electronic state of the molecule at higher temperatures [17].

Fig. 1 shows the spectra of $FC(O)OONO_2$ at three temperatures and a comparison with data obtained at 298 K by Scheffler et al. [6]. The upper inset (a) shows the linear behavior expected at the pressures used for a system that follows Beer Lambert Law. The particular temperature of this plot was 298 K. The cross-sections determined were an average of all the measurements.

Spectra at 298 K are in a good agreement as can be observed in the lower inset (b) that shows the percent difference between ours and Scheffler's results. It is also clear a significant decrease in absorption for wavelengths longer than 250 nm as the temperature decreases.

Fig. 2 shows the spectra of PAN [12], PPN [18] and $FC(O)OONO_2$, between 200 and 320 nm, all at 298 K. The three spectra are similar in shape (the bigger differences in cross-sections between our substance and the other peroxynitrates lie at shorter wavelengths) as could be expected for species sharing the structure of the acylperoxynitrate moiety with small influ-

Table 1
$FC(O)OONO_2$ UV absorption cross-sections at different temperatures

λ (nm)	Scheffler	This work					
	298 K	298 K	285 K	273 K	261 K	253 K	245 K
200	221	226 (6)	230	234	230	232	224
205	154	158 (5)	162	167	173	179	163
210	101	105 (5)	107	110	114	122	110
215	68.2	72 (5)	73	74	76	71	74
220	52.1	52 (3)	53	53	54	55	53
225	41.2	42 (3)	42	41	42	42	41
230	33.4	33 (3)	32	33	33	33	32
235	26.9	27 (2)	27	26	26	25	25
240	21.4	22 (2)	21	21	20	20	19
245	16.8	17 (1)	17	17	18	18	18
250	13.1	13 (1)	12	12	11	11	11
255	10	9.5 (0.9)	8.8	8.5	8.3	7.9	7.9
260	7.4	6.8 (0.6)	6.6	6.3	6.1	5.9	5.6
265	5.3	4.9 (0.5)	4.8	4.6	4.6	4.4	4.1
270	3.7	3.3 (0.3)	3.2	3.1	2.9	2.7	2.6
275	2.5	2.0 (0.3)	2.0	1.9	1.7	1.6	1.5
280	1.7	1.3 (0.2)	1.3	1.2	1.2	1.1	1.1
285	1.2	0.9 (0.1)	0.8	0.7	0.7	0.7	0.6
290	0.8	0.68 (0.09)	0.61	0.53	0.46	0.45	0.43
295	–	0.52 (0.08)	0.46	0.40	0.35	0.30	0.27
300	–	0.38 (0.07)	0.33	0.28	0.23	0.19	0.17
305	–	0.25 (0.07)	0.21	0.17	0.13	0.11	0.10
310	–	0.16 (0.05)	0.13	*0.09*	*0.07*	*0.06*	*0.05*
315	–	*0.09 (0.04)*	*0.07*	*0.05*	*0.04*	*0.03*	*0.02*
320	–	*0.04 (0.01)*	*0.03*	*0.02*	*0.01*	–	–

All the values are in units of 10^{-20} cm^2 $molecule^{-1}$. Bracketed values correspond to a standard deviation and they are the same for every temperature at a particular wavelength. The deviation was obtained as an average from independent measurements at different pressures. Values in italics bear higher relative errors. Cross-sections averaged over 5 nm intervals.

ence of the substituents attached to the carbon atom as discussed by Wallington et al. [7]. This small influence can also be related to the "blocking effect" of the carbonyl moiety as reported by Burgos Paci and Argüello [19].

Table 1 summarizes the absorption cross-sections of $FC(O)OONO_2$ at different temperatures together with the data obtained by Scheffler et al. at 298 K.

The cross-sections show a dependence with temperature. This dependence is more pronounced towards the longer wavelength tail. The representation of $\log_{10}(\sigma) = B \times T + \log_{10}(\sigma_0)$, where σ and σ_0 are the cross-sections in cm^2 $molecule^{-1}$ at T and 0 K, respectively, gives good straights. The intercepts σ_0 and slopes B obtained by linear regression analysis for some selected wavelengths are given in Table 2. Note that B increases with wavelength as a consequence of the larger temperature dependence at longer wavelengths. The coefficients derived from the plot of $\log_{10}(\sigma)$ versus T can be used to obtain cross-sections outside the experimental range by extrapolation.

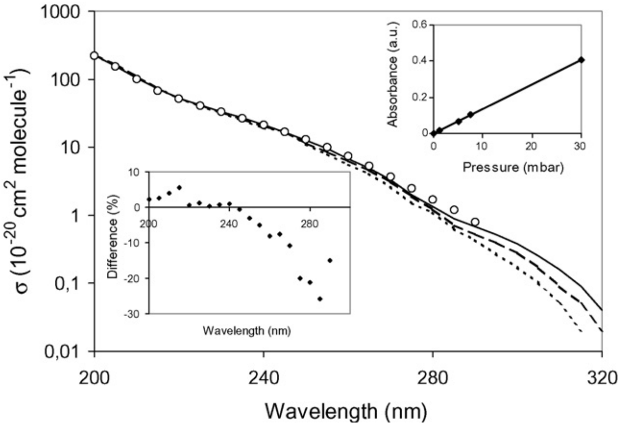

Fig. 1. UV spectra of $FC(O)OONO_2$ measured in the present work at three different temperatures: 297 K, solid line; 273 K, dashed line; 245 K, dotted line. Values from Scheffler et al. [6] at 298 K are presented as open circles.

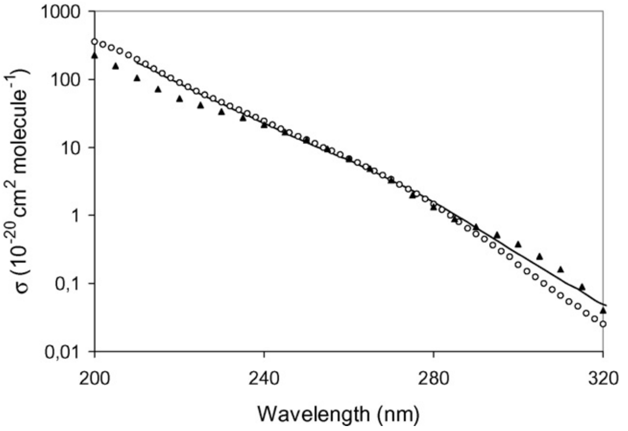

Fig. 2. UV spectra of PAN (open circles), PPN (solid line) and $FC(O)OONO_2$ (upper triangles) at 298 K.

Table 2
Parameters derived from $\log_{10}(\sigma) = B \times T + \log_{10}(\sigma_0)$ at selected wavelengths

λ (nm)	$B \times 10^3$ (K^{-1})	$\sigma_0 \times 10^{20}$ (cm^2 molecule^{-1})
260	1.5 (0.1)	2.4 (0.2)
270	2.0 (0.2)	0.85 (0.08)
280	1.5 (0.3)	0.48 (0.05)
290	4.0 (0.3)	0.045 (0.005)
300	6.8 (0.4)	0.004 (0.002)

Bracketed values correspond to a standard deviation.

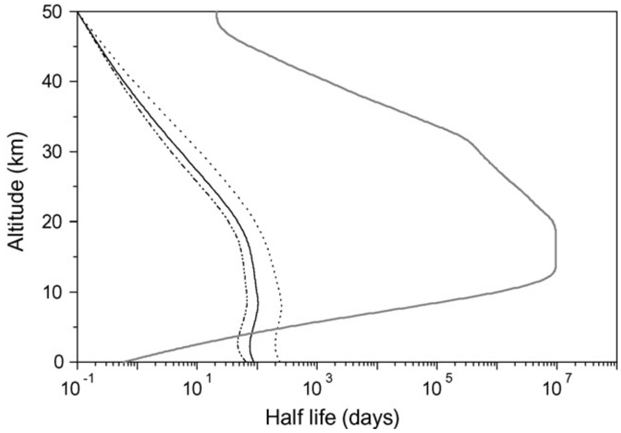

Fig. 3. Half-life profiles as a function of altitude. Thermal decomposition calculated using data from Bednarek et al. [5] (gray). Photochemical decomposition (black curves) at different latitudes: 30° (double dotted-dashed), 40° (solid) and 50° (dotted) calculated using the TUV program taking into account the temperature dependent cross-sections.

In the troposphere, the temperature decreases with increasing altitude up to the tropopause (approximately 12 km altitude). In this zone the temperature is close to 220 K. Under these conditions, the peroxynitrate UV absorption cross-sections are lower than those at room temperature. This means that its photodissociation rate will decrease. Fig. 3 shows the half-life of $FC(O)OONO_2$ and its dependence with altitude and latitude. The photochemical half-lives are the result of the average for 4 selected days; 2 solstices and 2 equinoxes. The counteracting effects of the decrease in absorption cross-sections with temperature and the increase in solar flux with altitude lead to a maximum half-life at around 8 km. This maximum lifetime varies between approximately 70 and 270 days for the latitude band 30–50°. Above the tropopause both, the cross-sections and the solar flux increase and consequently the half-life steadily decreases.

From the surface up to 4 km, loss via thermal decomposition dominates photolytic loss. The $FC(O)OONO_2$ half-life toward thermal decomposition increases substantially with altitude reaching values as long as 107 days, in very good accordance with the results from Ref. [7]. These findings show that the half-life of $FC(O)OONO_2$ in the atmosphere, though significantly shorter than the thermal lifetime, is of a duration (270 days) that favors its transport and distribution to non-production zones of the atmosphere.

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