Journal of Photochemistry, 11 (1979) 139 - 144

Short Communication

Chlorine nitrate ultraviolet absorption spectrum at stratospheric temperatures

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(Received November 13, 1978)

1. Introduction

Chlorine nitrate $ClONO_2$ is a species which plays an important role in the chemistry of the stratosphere [1 - 3]; it is formed as a result of the recombination of NO_2 and ClO radicals and it is destroyed primarily by solar photolysis. Above 35 km photolysis occurs predominantly in the wavelength range 200 - 220 nm where $ClONO_2$ has absorption cross sections of the order of 3×10^{-18} cm^2. Below 30 km the dominant wavelength range for photolysis is 300 - 400 nm where the $ClONO_2$ cross sections are of the order of 10^{-21} cm^2.

Smith *et al.* [4] have reported O and ClONO as the primary photodissociation products in the photolysis of $ClONO_2$, whereas according to Chang *et al.* [5] these products are Cl and NO_3; the discrepancy might be due in part to the different photolytic wavelengths employed in the two experiments. Both studies indicate that the quantum yield for photodecomposition is unity.

Ultraviolet absorption cross sections are often temperature dependent, the effect being most pronounced in the wings of an absorption band. For CF_2Cl_2 the cross section at 295 K and 210 nm is approximately a factor of 2 larger than the value at 212 K [6] and for N_2O the 296 K cross section at 230 nm is a factor of 3 larger than the value at 225 K [7]. This effect can usually be attributed to transitions originating from vibrationally excited ground state molecules; as the temperature increases the relative populations of these states increase. In the case of diatomics the theoretical predictions are in very good agreement with experiment [8].

Our earlier $ClONO_2$ cross section measurements [1] have been corroborated by the work of Birks *et al.* [9]. These two sets of measurements agree within experimental error; both were carried out at room temperature using a short (10 cm) cell. We have reinvestigated the absorption spectrum of $ClONO_2$ as a function of temperature using a long path cell to increase the sensitivity at the crucial long wavelength range. We found the temperature effect to be negligible around 190 - 220 nm, while at the longer wavelengths

the cross sections decrease by up to 30% between 296 K and 227 K. Furthermore, at room temperature the cross sections obtained from these higher sensitivity measurements with highly purified $ClONO_2$ samples are 15 - 20% smaller than the cross sections reported in our earlier work [1].

2. *Experimental*

The absorption measurements were made with a Cary-14 UV-VIS spectrophotometer using a spectral slit width of about 0.2 nm. Two cells were used: a 10.0 cm quartz cell with an insulated sealed glass jacket and a 180 cm quartz cell (base path length 90 cm, with 2 passes) wrapped with a copper coil. Low temperature runs were performed by pumping cooled methanol through the glass jacket or copper coil; the temperature stability was ± 1 °C.

The procedure employed to synthesize chlorine nitrate from Cl_2O and excess N_2O_5 has been described previously [10]. Cl_2, N_2O_5, HNO_5, OClO, and NO_2 are all possible impurities in the $ClONO_2$ produced; Cl_2, N_2O_5 and HNO_3 were easily removed from $ClONO_2$ by distillation. The IR spectrum of $ClONO_2$ verified the absence of N_2O_5 and HNO_3. The absorption maximum of Cl_2 at 330 nm decreased with the first few distillations; these were continued until the UV–visible spectra showed no change in the 200 - 400 nm wavelength region. The only detectable impurities were NO_2 and OClO; we were able to detect less than 0.01% of NO_2 and less than 0.005% OClO present in the $ClONO_2$ sample using the 180 cm cell.

3. *Results and discussion*

The results are presented in Table 1. The absorption spectra measured with three different batches of $ClONO_2$ agreed with each other very well after the small contribution from NO_2 or OClO absorption was taken into account. The measurements were carried out at pressures between 0.5 Torr and the vapor pressure, and within experimental error Beer's law was obeyed at all pressures and wavelengths. We were not able to determine the cross sections at 243 K and 227 K at wavelengths greater than 400 nm owing to the low vapor pressures of $ClONO_2$ at these temperatures. The standard deviation was about 2% in the 200 - 350 nm range and about 5% in the 350 - 400 nm range.

TABLE 1

Absorption cross sections $\sigma(cm^2\ molecule^{-1} \times 10^{20})$ of $ClONO_2$ as a function of temperature

λ (nm)	296 K	243 K	227 K
450	0.005	—	—
445	0.007	—	—
440	0.009	—	—
435	0.013	—	—

(continued on facing page)

TABLE 1 *(continued)*

λ (nm)	296 K	243 K	227 K
430	0.016	—	—
425	0.020	—	—
420	0.027	—	—
415	0.035	—	—
410	0.044	—	—
405	0.055	—	—
400	0.064	0.058	0.056
395	0.077	0.070	0.069
390	0.090	0.083	0.082
385	0.108	0.100	0.098
380	0.122	0.114	0.113
375	0.139	0.130	0.128
370	0.162	0.140	0.142
365	0.179	0.159	0.155
360	0.208	0.173	0.170
355	0.218	0.183	0.182
350	0.246	0.205	0.198
345	0.285	0.223	0.214
340	0.323	0.255	0.246
335	0.397	0.307	0.283
330	0.514	0.381	0.353
325	0.655	0.502	0.463
320	0.895	0.681	0.630
315	1.23	0.954	0.893
310	1.69	1.35	1.28
305	2.38	1.89	1.80
300	3.30	2.61	2.51
295	4.56	3.83	3.74
290	6.36	5.36	5.45
285	8.80	7.33	7.50
280	11.9	9.98	10.4
275	16.1	13.5	13.9
270	21.5	18.0	18.3
265	26.9	23.1	23.3
260	34.6	30.1	30.7
255	44.7	39.1	39.8
250	57.7	50.9	52.6
245	77.0	—	70.6
240	106	—	98.5
235	149	—	141
230	210	—	206
225	286	—	282
220	344	—	348
215	360	—	362
210	329	—	330
205	299	—	293
200	307	—	293
195	381	—	358
190	589	—	555

A comparison between the results of this work and those reported earlier [1] is shown in Fig. 1. The discrepancy increases at the longer wavelengths, becoming about 40% around 400 nm.

Figure 2 shows the cross sections at 227 K and at 243 K relative to the 296 K values. The maximum temperature effect occurs around 330 nm and it decreases at longer wavelengths. This result indicates that the 320 — 450 nm shoulder which appears in the spectrum (see Fig. 1) is not due to the same electronic transition responsible for the maximum around 220 nm; the assumption is that the temperature effect is largest at the wings of the absorption bands. The peak of the weak band seems to be located around 370 - 380 nm.

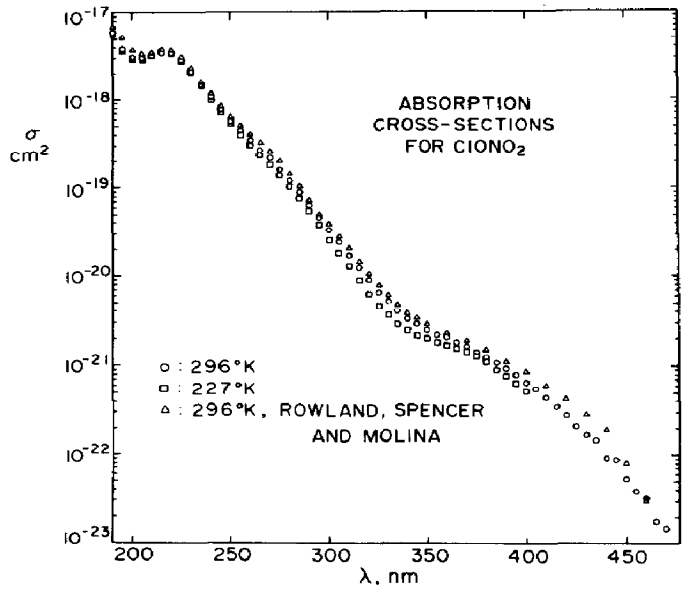

Fig. 1. Absorption spectrum of $ClONO_2$.

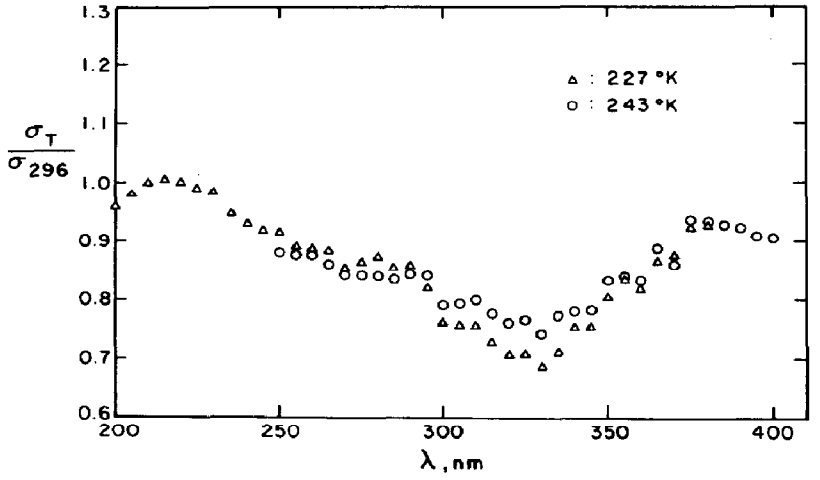

Fig. 2. Temperature effect on $ClONO_2$ cross sections.

4. Photodissociation rates in the stratosphere

We have calculated the stratospheric photodissociation rate of $ClONO_2$ using the cross sections given in Table 1 and assuming a quantum yield of unity for overhead sun conditions and including multiple scattering effects. The calculation was carried out using altitude and wavelength dependent solar fluxes as computed by Chang and Wuebbles [11]. The cross sections were assumed to be linearly dependent on temperature (at 243 K the values calculated by linear interpolation between 227 K and 296 K agree with the measured values within experimental error). The results are shown in Fig. 3. Figure 4 shows the contribution to the photodissociation rate for each wavelength interval at various altitudes. Figure 3 also shows, for comparison, the photodissociation rates calculated assuming room temperature cross sections throughout as well as the rates calculated with the cross sections reported earlier [1]. The discrepancy is largest below 30 km, where the temperature is lowest and where photolysis occurs predominantly at the longer wavelength; at these lower altitudes the new photodissociation rates are about 35% smaller than the rates calculated with the earlier data. The effect of using these new data on photochemical models of the stratosphere can be estimated from sensitivity studies such as that reported by Butler [12]; his most recent study [13] indicates that a 40% reduction in the $ClONO_2$ cross sections would result in the predicted long term ozone depletion due to the release of chlorofluoromethanes to drop from 19.7% to 18.2%, assuming continued release at 1975 rates.

In summary, our new $ClONO_2$ cross sections will not affect ozone depletion calculations in a major way; these cross sections are nevertheless sufficiently different from the earlier ones to warrant inclusion in current chemical models of the atmosphere.

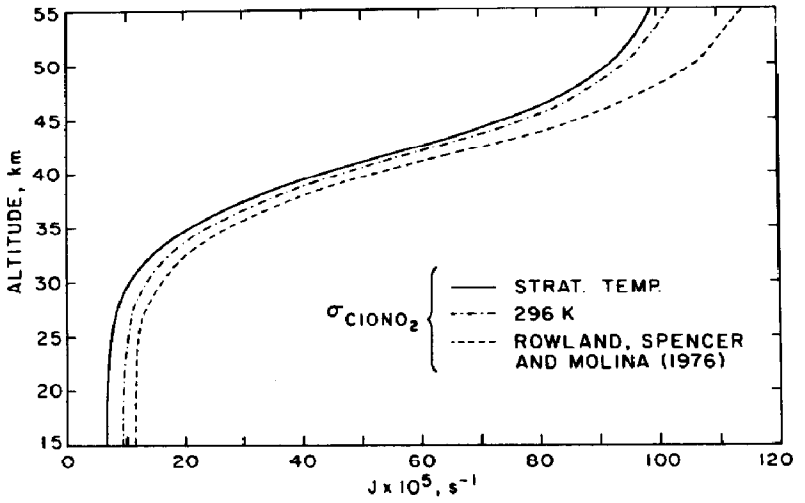

Fig. 3. Photodissociation rate of $ClONO_2$ in the stratosphere.

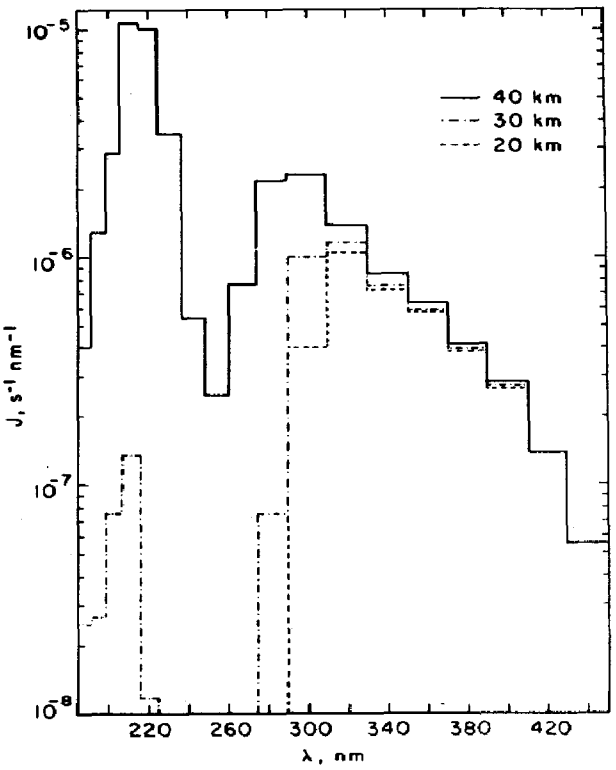

Fig. 4. Contribution to the photodissociation rate of $ClONO_2$ resulting from each wavelength interval.

Acknowledgment

This research has been supported by the National Aeronautics and Space Administration under Grant No. NSG-7208.

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