On the Photodecomposition of $ClONO_2$ in the Middle Ultraviolet

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Photodecomposition of gaseous $ClONO_2$ was investigated in a static system at wavelengths 265 nm and 313 nm. From the quantitative determination of the products O_2, N_2O_5, and $ClO^{15}NO_2$ formed, and from $\Phi(-ClONO_2)$ it is concluded that the predominant primary step is $ClONO_2 + h\nu \rightarrow Cl + NO_3$ (3).

Chlorine nitrate, $ClONO_2$, is considered to be formed in the stratosphere via the pressure dependent recombination reaction

$$ClO + NO_2 + N_2 \rightarrow ClONO_2 + N_2 . \qquad (1)$$

As its major removal process the photodissociation of atmospheric $ClONO_2$ in the ultraviolet is discussed. It has repeatedly been pointed out that significance should be attributed to the pathways of chlorine nitrate formation and its destruction since this compound might be involved in the ozone depletion mechanism through both the ClO_x and NO_x atmospheric cycles.

This communication summarizes our results on the photodecomposition of gaseous chlorine nitrate in the middle ultraviolet using a static experimental set-up. Its publication is prompted by a report [1] containing in essence conclusions which are in agreement with an earlier letter by Smith et al. [2] but being at variance with our results [3, 4] and those of others [5].

All experiments were carried out in thermostated all-quartz cells. One set of cells was equipped with an additional set of sealed-on Si windows which are transparent in the ir region of interest. Illumination occurred with a Hanovia medium pressure Hg-lamp. The Schott filters UV-250 and UV-340 were used either separately or in combination with cut-off filters. The effective wavelength in the experiments was either $\lambda = 265$ nm with a relative total intensity $< 1\%$ for $\lambda < 263$ nm or $\lambda = 313$ nm with no measurable contributions at $\lambda < 300$ nm. Irradiations were performed in the temperature range +20 to −30 °C. The $ClONO_2$ pressure was adjusted between 3 and 50 mbar depending on the wavelength. Conversion was always $\lesssim 5\%$. At 265 nm, HI was used for actinometry. At 313 nm, ClNO or NO_2 were applied for this purpose. Product analysis was carried out mass spectrometrically and/or by uv and ir absorption measurements.

Three major routes are energetically available for the photodecomposition of $ClONO_2$ at wavelengths $\lambda \geqq 265$ nm. They are listed in the table below.

The energy requirements for simple one center fragmentations are also given using recommended values [6] and more recent data [7] from this laboratory.

Process				ΔH_0^0 [kJ/mole]
$ClONO_2$	$\rightarrow ClO$	$+ NO_2$;	(2)	104
	$\rightarrow Cl$	$+ NO_3$;	(3)	162
	$\rightarrow ClONO$	$+ O(^3P)$;	(4)	270 [7]

The molecular elimination processes

$$ClONO_2 \rightarrow ClNO + O_2 \qquad (5)$$

and

$$ClONO_2 \rightarrow ClO_2 + NO \qquad (6)$$

are not included, although energetically feasible, because of their inherent low probability. Also, the spin-allowed dissociation

$$ClONO_2 \rightarrow ClONO + O(^1D) \qquad (7)$$

is not considered. The energy required for this process to occur is given as 460 kJ/mole equivalent to $\lambda < 260$ nm.

Results

To obtain information about the relative importance of the pathways (2)–(4) in the photode-

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composition of gaseous chlorine nitrate we have performed a series of different experiments. The experimental details and the results are as follows:

1. Irradiation experiments with excess $^{15}NO_2$ were designed to yield information by ir spectroscopy on the relative importance of (2) upon irradiation at 265 nm. If (2) were the predominant photochemical pathway, recombination should produce labelled chlorine nitrate with a high quantum yield. In addition, using the compensation technique [8] one should observe the initial rate of $ClO^{15}NO_2$ formation to be balanced by the initial rate of $ClONO_2$ disappearance.

The experiments performed at 253 K indicated, however, that whereas $ClONO_2$ disappeared with a quantum yield of $\Phi = 1.15 \pm 0.02$, the rate of $ClO^{15}NO_2$ formation corresponded to $\Phi(2) \leqq 0.05$. The main product detected by ir-spectroscopy was N_2O_5.

It must be pointed out that corrections are necessary in the evaluation of the ir data in order to take into account the thermally induced pressure dependent exchange reaction reported earlier [8]. The value for Φ (2) given above mainly reflects the uncertainty in this correction.

2. In order to estimate the relative importance of pathway (4) in the photodecomposition of $ClONO_2$, experiments were carried out at 265 nm in the presence of up to 10% NO_2. If oxygen atoms are formed at this wavelength they will be captured by the added scavenger to yield O_2 or by the parent compound depending on their relative abundance according to

$$k(O + NO_2) = 9.3 \times 10^{-12}\,\mathrm{cm^3\,s^{-1}},$$
$$k(O + ClONO_2) = 1.9 \times 10^{-13}\,\mathrm{cm^3\,s^{-1}}$$

(see [6]).

The experiments resulted in $\Phi(O_2) = 0.08 \pm 0.02$. The absolute cross section for light absorption at 265 nm is roughly a factor 6 smaller for NO_2 than for $ClONO_2$ [6, 9]. Due to a less favourable absorption ratio NO_2 could not be used as scavenger in the photolysis at 313 nm. Oxygen formation in the absence of added NO_2 will be described later.

Applying appropriate corrections for the light absorption by the additive and for the competition in O-atom scavenging the experiments at 265 nm resulted in a primary yield of $\Phi(4) = 0.10 \pm 0.02$.

This result is disturbingly different from that of Smith et al. [2] who postulated process (4) to be the major photolytic decomposition pathway. It is also in contradiction with the conclusion presented by Adler-Golden et al. [1]. These authors interpret their atomic absorption spectroscopy data in the vacuum uv in favor of a predominant $O(^3P)$ production with the quantum yield for $Cl(^2P)$ production being less than 4%. Our experimental findings on the probability of step (4) are in full agreement with the results of Chang et al. [5] obtained in a very low pressure photolysis study of $ClONO_2$ in which $O(^3P)$ production was observed to an extent of about 10%.

Experimental support for our conclusion that process (3) describes the predominant pathway in the photolytic decomposition of $ClONO_2$ in the gas phase was obtained from different circumstantial observations.

3. The low temperature photolysis of $ClONO_2/NO_2$ mixtures at 265 nm in the presence of up to 1 bar inert N_2 reduced the quantum yield of $ClONO_2$ consumption from 1.7–1.9 as obtained in studies of the pure compound to $\Phi = 1.00 \pm 0.07$. The nitrogen was added to increase the removal of photoproduced Cl-atoms via the recombination process

$$Cl + NO_2 + N_2 \rightarrow ClONO + N_2\,. \tag{8}$$

Removal of Cl-atoms prevents their attack on the parent compound (see below).

At the low temperatures NO_2 also acts as scavenger for photoproduced NO_3. The determination of N_2O_5 in low temperature experiments by ir analysis at 1245 $\mathrm{cm^{-1}}$ yielded $\Phi(N_2O_5) = 0.90 \pm 0.05$. In the same experiments the NO_2 consumption was $\Phi = 0.8 \pm 0.1$.

4. Preliminary results obtained in the photolysis of molecular chlorine using the 340 nm filter in the presence of $ClONO_2$ yielded evidence that Cl-atoms attack $ClONO_2$ via the reaction

$$Cl + ClONO_2 \rightarrow Cl_2 + NO_3 \tag{9}$$

with nearly unit yield. Nitrogen pentoxide resulted as a major product of the overall process [10].

5. A number of photolysis experiments were carried out at 265 nm and at 313 nm, respectively, without any additive to determine the overall production of O_2 at the both wavelengths. Quantum yields $\Phi(O_2) = 0.43 \pm 0.02$ were found in all runs independent of illumination conditions. A quantum yield $\Phi(O_2) = 0.5$ would be expected if (3) is the only primary photolytic decomposition channel and all the oxygen results from the decomposition of NO_3 to form NO_2. These assumptions also lead to $\Phi(N_2O_5) = 1$ in the presence of excess NO_2.

Discussion and Conclusions

In carrying out the different experiments on the problem under discussion it became apparent that the mechanism of the photoinduced $ClONO_2$ decomposition is better understood in experiments being performed at the lower temperatures than at room temperature.

It is recognized that due to the temperature dependent equilibrium (1, −1) the photofragments encounter collisions not only with the parent $ClONO_2$ but also with ClO and NO_2, the concentration of which is sensitively depending on temperature. It can be easily calculated that reducing the gas temperature from +20 to −30 °C the encounter probability with these species is reduced by more than 4 orders of magnitude [8]. Inversely, if in an pulsed experiment the temperature should be suddenly increased a higher degree of thermal dissociation would result.

All our experimental results can be interpreted in a straight-forward way under the assumption that not step (4) but reaction (3) is the predominant pathway in the photodecomposition of chlorine nitrate. With this assumption the formation of chlorine dioxide might be understood as an oxidation product of thermally produced ClO with NO_3.

On the basis of the results presented above the following overall equation for the stoichiometry of the photodecomposition of $ClONO_2$ in the presence of NO_2 can be formulated:

$$\nu_1\,ClONO_2 + \nu_2\,NO_2 = \tfrac{1}{2}\nu_1\,Cl_2 + \nu_3\,O_2 + \nu_4\,N_2O_5\,. \qquad \text{(a)}$$

Mass balance requires

$$\nu_1 = \nu_2 + 4\nu_3 \quad \text{and} \quad \nu_4 = \tfrac{1}{2}\nu_1 + \tfrac{1}{2}\nu_2\,.$$

With the measured yields

$$\Phi(-NO_2) = 0.8 \;\pm 0.1 \;\equiv \nu_2$$

and

$$\Phi(O_2) = 0.08 \pm 0.02 \equiv \nu_3$$

one obtains from the above overall equation (a):

$$\nu_1 = \Phi(-ClONO_2) = 1.12 \pm 0.2$$

and

$$\nu_4 = \Phi(N_2O_5) \quad = 0.96 \pm 0.15$$

in agreement with the experiments.

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Note added in Proof: Recently published results on the chlorine nitrate photochemistry [11] are in agreement with the statement presented above.

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