

On the Photodecomposition of ClONO₂ in the Middle Ultraviolet

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Z. Naturforsch. **38a**, 893–895 (1983); received October 22, 1982

Herrn Professor G. O. Schenck zu seinem 70. Geburtstag gewidmet

Photodecomposition of gaseous ClONO₂ was investigated in a static system at wavelengths 265 nm and 313 nm. From the quantitative determination of the products O₂, N₂O₅, and ClO¹⁵NO₂ formed, and from $\Phi(-\text{ClONO}_2)$ it is concluded that the predominant primary step is $\text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_3$ (3).

Chlorine nitrate, ClONO₂, is considered to be formed in the stratosphere via the pressure dependent recombination reaction



As its major removal process the photodissociation of atmospheric ClONO₂ 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 ClONO₂ pressure was adjusted be-

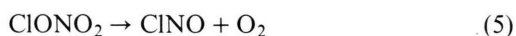
tween 3 and 50 mbar depending on the wavelength. Conversion was always $\lesssim 5\%$. At 265 nm, HI was used for actinometry. At 313 nm, ClNO or NO₂ were applied for this purpose. Product analysis was carried out mass spectrometrically and/or by uv and ir absorption measurements.

Three major routes are energetically available for the photodecomposition of ClONO₂ at wavelengths $\lambda \geq 265$ 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° [kJ/mole]
ClONO ₂ → ClO + NO ₂ ; (2)	104
→ Cl + NO ₃ ; (3)	162
→ ClONO + O(³ P); (4)	270 [7]

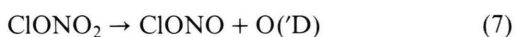
The molecular elimination processes



and



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



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 ¹⁵NO₂ 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 ClO¹⁵NO₂ formation to be balanced by the initial rate of ClONO₂ disappearance.

The experiments performed at 253 K indicated, however, that whereas ClONO₂ disappeared with a quantum yield of $\Phi = 1.15 \pm 0.02$, the rate of ClO¹⁵NO₂ formation corresponded to $\Phi(2) \leq 0.05$. The main product detected by ir-spectroscopy was N₂O₅.

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 $\Phi(2)$ given above mainly reflects the uncertainty in this correction.

2. In order to estimate the relative importance of pathway (4) in the photodecomposition of ClONO₂, experiments were carried out at 265 nm in the presence of up to 10% NO₂. If oxygen atoms are formed at this wavelength they will be captured by the added scavenger to yield O₂ or by the parent compound depending on their relative abundance according to

$$\begin{aligned} k(\text{O} + \text{NO}_2) &= 9.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}, \\ k(\text{O} + \text{ClONO}_2) &= 1.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \end{aligned}$$

(see [6]).

The experiments resulted in $\Phi(\text{O}_2) = 0.08 \pm 0.02$. The absolute cross section for light absorption at 265 nm is roughly a factor 6 smaller for NO₂ than for ClONO₂ [6, 9]. Due to a less favourable absorption ratio NO₂ could not be used as scavenger in the photolysis at 313 nm. Oxygen formation in the absence of added NO₂ 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 ClONO₂ 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 ClONO₂ in the gas phase was obtained from different circumstantial observations.

3. The low temperature photolysis of ClONO₂/NO₂ mixtures at 265 nm in the presence of up to 1 bar inert N₂ reduced the quantum yield of ClONO₂ 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



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

At the low temperatures NO₂ also acts as scavenger for photoproduced NO₃. The determination of N₂O₅ in low temperature experiments by ir analysis at 1245 cm⁻¹ yielded $\Phi(\text{N}_2\text{O}_5) = 0.90 \pm 0.05$. In the same experiments the NO₂ 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 ClONO₂ yielded evidence that Cl-atoms attack ClONO₂ via the reaction



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 O₂ at the both wavelengths. Quantum

yields $\Phi(\text{O}_2) = 0.43 \pm 0.02$ were found in all runs independent of illumination conditions. A quantum yield $\Phi(\text{O}_2) = 0.5$ would be expected if (3) is the only primary photolytic decomposition channel and all the oxygen results from the decomposition of NO₃ to form NO₂. These assumptions also lead to $\Phi(\text{N}_2\text{O}_5) = 1$ in the presence of excess NO₂.

Discussion and Conclusions

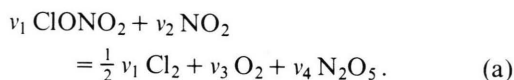
In carrying out the different experiments on the problem under discussion it became apparent that the mechanism of the photoinduced ClONO₂ decomposition is better understood in experiments being performed at the lower temperatures than at room temperature.

It is recognized that due to the temperature dependent equilibrium (1, -1) the photofragments encounter collisions not only with the parent ClONO₂ but also with ClO and NO₂, 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 NO₃.

On the basis of the results presented above the following overall equation for the stoichiometry of the photodecomposition of ClONO₂ in the presence of NO₂ can be formulated:



Mass balance requires

$$v_1 = v_2 + 4 v_3 \quad \text{and} \quad v_4 = \frac{1}{2} v_1 + \frac{1}{2} v_2.$$

With the measured yields

$$\Phi(-\text{NO}_2) = 0.8 \pm 0.1 \equiv v_2$$

and

$$\Phi(\text{O}_2) = 0.08 \pm 0.02 \equiv v_3$$

one obtains from the above overall equation (a):

$$v_1 = \Phi(-\text{ClONO}_2) = 1.12 \pm 0.2$$

and

$$v_4 = \Phi(\text{N}_2\text{O}_5) = 0.96 \pm 0.15$$

in agreement with the experiments.

Acknowledgements

The authors are indebted to Mrs. H. Alberti and Dr. W. Stockmann for providing their experimental results. The work was supported in part by the Bundesminister für Forschung und Technologie (BMFT) within project FKW 10.

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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