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Quantum Yield for NO$_3$ Production from Photolysis of ClONO$_2$

By

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Abstract

Chlorine nitrate, ClONO$_2$, was photolyzed at 249 nm by a 10 ns pulse from an excimer laser, and the primary product NO$_3$ was followed by tunable dye-laser absorption at 662 nm. With Ar or Ar plus CH$_4$ as carrier gases between 20 and 100 Torr, the primary quantum yield for NO$_3$ was 0.55 (-0.1 to +0.3).
Introduction

There are several possible products of ClONO$_2$ photolysis, which are listed here with the threshold wavelengths (nm):

\[
\text{ClONO}_2 + h\nu \rightarrow \text{ClO} + \text{NO}_2 \quad \lambda \leq 1100 \quad (1)
\]
\[
\rightarrow \text{Cl} + \text{NO}_3 \quad 700 \quad (2a)
\]
\[
\rightarrow \text{Cl} + \text{NO} + \text{O}_2 \quad 652 \quad (2b)
\]
\[
\rightarrow \text{Cl} + \text{NO}_2 + \text{O}(^{3}\text{P}) \quad 318 \quad (2c)
\]
\[
\rightarrow \text{ClONO} + \text{O}(^{3}\text{P}) \quad 391 \quad (3a)
\]
\[
\rightarrow \text{ClONO} + \text{O}(^{1}\text{D}) \quad 241 \quad (3b)
\]

Three previous studies of this process have obtained apparently conflicting results.

Smith, Chou, and Rowland [1] photolyzed ClONO$_2$ at 302.5 nm. No direct measurements were made for ClO, Cl, ClONO, NO$_3$, or O; but they measured the final chemical products and overall quantum yields. They found O$_2$, Cl$_2$, and N$_2$O$_5$ to be the predominant final products, and the overall quantum yield for ClONO$_2$ destruction was 4. The lack of HCl as a product when C$_2$H$_6$ was added was interpreted as evidence against path (2). A multi-step mechanism involving homogeneous and heterogeneous reactions and with (3a) as the primary process was used to explain the results.

Chang, Barker, Davenport, and Golden [2] photolyzed ClONO$_2$ at low pressure in a silica Knudsen cell with molecular beam sampling into a mass spectrometer. Photolysis was by a filtered beam from a high-intensity, high-pressure xenon lamp. The wavelength band was 260 to 380 nm, and about half of the photolysis occurred below 300 nm. In the
The apparatus atomic chlorine, atomic oxygen, NO$_3$, and ClO could be observed if present. The authors reported the following primary quantum yields: 
\[ \phi(O) \leq 0.1, \phi(Cl) = 1.0 \pm 0.2, \phi(NO_3) = 0.5 \pm 0.3, \phi(ClO) \leq 0.04. \]
On the basis of these results, they concluded that (2a) was the predominant reaction pathway.

Adler-Golden and Wiesenfeld [3] photolyzed ClONO$_2$ with a broad-band flash lamp with a pulse width of 20 $\mu$s. The wavelength of the radiation extended from 200 nm to the infrared with a distribution comparable to a black-body at 6500 K. Atomic oxygen and atomic chlorine were followed by resonance absorption in the vacuum-ultraviolet region. They clearly detected atomic oxygen, but did not report a value for the quantum yield. They were also able to measure the pseudo first-order kinetics of the $O + ClONO_2$ reaction, beginning 200 $\mu$s after the initiation of the flash. Atomic Cl was looked for but not seen, and on the basis of the sensitivity of the apparatus they estimated that $\phi(Cl) \leq 0.04$. These authors favored (3a) as the primary path of ClONO$_2$ photolysis.

This study was designed to measure the primary NO$_3$ quantum yield using excimer-laser flash photolysis of ClONO$_2$ at 249 nm and a dye-laser absorption probe of the NO$_3$(0-0) band at 661.9 nm.

Experimental

The flash photolysis/laser absorption (FP/LA) technique was used to observe the NO$_3$ product from ClONO$_2$ photolysis. The apparatus is shown in Figure 1. The FP/LA cell consisted of a 191.5 cm long, 3.3 cm i.d. jacketed quartz cell equipped with stainless steel end caps and CaF$_2$ windows. The outputs from an Ar ion pumped CW dye laser (Spectra Physics
581A) with 0.05 nm bandwidth and an unstable-resonator excimer laser (Lumonics TE-860-2M) operating on KrF at 249 nm were propagated coaxially down the cell. A pair of calibrated masks served to define the excimer laser photolysis and dye laser probe beams so as to make the photolysis volume larger than the probe volume. This insured that the probe beam sampled only the photolysis volume, and minimized the effects of diffusion out of the probe volume. When set up with the "unstable resonator" option, the laser produced a compact, slowly diverging beam with rectangular cross sections, but it had a hole in the center of the rectangle. The intense portion of the beam excluding this hole was used. The dye laser was operated using R640 and tuned to the NO₃ A-X(0,0) transition at 661.9 nm using a 1 meter monochromator, operated in second order with a 1200 λ/mm grating blazed at 500 nm, and coupled to a vidicon tube and optical multichannel analyzer (OMA). The wavelength scale of the OMA was calibrated by overlaying the output from a Neon pilot lamp on to the dye laser signal. Photolysis laser energies were measured using a pyroelectric joulemeter (Gentec) calibrated by ClNO actinometry. Data were recorded using a fast photodiode detector/amplifier combination interfaced to a transient waveform recorder (Biomation 805) and signal averager. The photolysis laser was operated at 1 Hz and a typical experiment was the sum of 256 or 512 laser shots.

Flow rates were such that the residence times of chlorine nitrate in the photolysis cell was about 6 seconds. Chlorine nitrate was entrained in a stream of Ar passed through a saturator held at 157 K, and then diluted with either Ar or CH₄ to the desired pressure and concentration using needle valves placed in the carrier gas flow.
lines. After passing through the photolysis cell, the ClONO$_2$ concentration was measured by UV absorption at 215 nm in an absorption cell of one-meter pathlength. This system consisted of a chopped deuterium lamp whose output passed down the 1 meter cell and entered a 0.3 meter monochromator (0.3 nm resolution) equipped with a PMT and associated phase sensitive detection electronics. The UV monitoring cell was connected to the photolysis cell by a 3/4 inch O.D. Pyrex tube, which is large enough to eliminate pressure drops between the cells. This was confirmed by simultaneous measurement of flowing NO$_2$/N$_2$ mixtures in each cell. After exiting the monitoring cell the mixture was removed by a throttled and trapped roughing pump. The combination of short gas residence time, small photolysis volume, and low photodissociation efficiency, resulted in less than 3% ClONO$_2$ destruction in the cell. Absorption cross sections used at the monitoring and photolysis wavelengths ($\sigma_{215} = 3.60 \times 10^{-18}$ cm$^2$ molecule$^{-1}$, $\sigma_{249} = 6.39 \times 10^{-19}$ cm$^2$ molecule$^{-1}$) were those of Molina and Molina [4].

Chlorine nitrate was prepared via the reaction of Cl$_2$O with N$_2$O$_5$ by the method of Schmeisser [5]

$$\text{Cl}_2\text{O} + \text{N}_2\text{O}_5 \rightarrow 2 \text{ClONO}_2$$

(4)

Chlorine monoxide was condensed into a trap containing excess, freshly prepared N$_2$O$_5$. The trap was equipped with a P$_2$O$_5$ drying tube, placed in a trichloroethylene slush at 200 K, and allowed to warm to 273 K during which the reaction occurred. The ClONO$_2$ was distilled.
from the trap held at 175 K into a trap at 157 K, leaving behind any residual \( \text{NO}_2 \), \( \text{N}_2\text{O}_5 \), or \( \text{HNO}_3 \). The \( \text{ClONO}_2 \) was then pumped at 157 K to remove any \( \text{Cl}_2 \), \( \text{Cl}_2\text{O} \), or \( \text{OCIO} \) impurities. The final product was a faintly yellow liquid. A measurement of UV absorption cross sections agreed well with Molina and Molina [4]. No impurities were found above the detection limits of 0.4\%, \( \text{Cl}_2\text{O} \); 0.8\%, \( \text{NO}_2 \); 0.07\%, \( \text{OCIO} \); 4.2\%, \( \text{Cl}_2 \); 0.2\%, \( \text{N}_2\text{O}_5 \). Argon (> 99.99\%) and \( \text{CH}_4 \) (> 99.99\%) were supplied by Lawrence Berkeley Laboratories and used without further purification.

Results

The time domain behavior of \( \text{NO}_3 \) in a typical \( \text{ClONO}_2 \) photolysis experiment is shown in Figure 2. This experiment was conducted using \( 6.2 \times 10^{14} \) molecules cm\(^{-3}\) of \( \text{ClONO}_2 \), a laser fluence of \( 1.7 \times 10^{17} \) photons cm\(^{-2}\) per shot, 1 shot per second, time resolution of 2 \( \mu \)s/channel, and a carrier gas mixture of 17 Torr \( \text{CH}_4 \) and 3 Torr Ar. Argon was always present in these experiments since it (and never \( \text{CH}_4 \)) was used to flow through the \( \text{ClONO}_2 \) saturator. Figure 2 shows a prompt rise in the \( \text{NO}_3 \) concentration coincident with the laser pulse followed by a slow rise peaking after about 200 \( \mu \)s. The slowly-produced \( \text{NO}_3 \) was about 15\% of the initial increase in this example. This secondary \( \text{NO}_3 \) occurred both in pure argon and in the presence of methane, although its magnitude was less when \( \text{CH}_4 \) was present.

The amount of \( \text{NO}_3 \) initially formed, \( C \), was calculated from \( \ln I_0/I = \sigma L \), where \( \sigma \) was \( 1.90 \times 10^{-17} \) cm\(^2\) molecule\(^{-1}\) [6] and \( L \) was 192 cm. The primary quantum yield \( \phi_{\text{NO}_3}^0 \) is the ratio of this concentration
to the amount of ClONO₂ photolyzed as calculated from ClONO₂ concentration, laser pulse fluence, and the cross section of ClONO₂ \cite{4} for 249 nm radiation. The experimental conditions and experimental results are given in Table 1. The quantum yields are plotted against laser fluence in Figure 3. The initial quantum yields appear to be 0.55 ± 0.1 independent of fluence, ClONO₂ concentration, presence or absence of methane, and total pressure.

Discussion

These experiments had a short (10 ns) pulse width and narrow band (248 - 249 nm) photolysis wavelength. The product NO₃ appeared with about 0.55 quantum yield within 2 µs following the photolysis pulse. This NO₃ could not be the product of a secondary chemical reaction of some species with ClONO₂ unless the rate constant was greater than 5 x 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. This study did reveal some secondary production of NO₃ (Figure 2) with quantum yields between 0.1 and 0.2. Possible mechanisms for the secondary production of NO₃ include the following: (i) The reaction of atomic chlorine with chlorine nitrate

\begin{equation}
\text{Cl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3 \tag{5}
\end{equation}

(ii) The reaction of atomic chlorine with methane to produce methyl radicals which further react

\begin{equation}
\text{CH}_3 + \text{ClONO}_2 \rightarrow \text{CH}_3\text{Cl} + \text{NO}_3 \tag{6}
\end{equation}

and (iii) the formation of some NO₃ in excited vibrational states, which becomes measurable with the 0-0 transition only after deactivation to the ground vibrational state.
The observed quantum yield is consistently 0.55. If (7) is the cause of the secondary NO₃, then the observed quantum yield for NO₃ is about 0.75. Because of this uncertainty in interpreting the secondary NO₃, the value and error limits on \( \phi(\text{NO}_3) \) are considered to be 0.55 (–0.1 to +0.3). This study supports (2a) as the most important channel, but it does not exclude partial contributions from other channels.

It is difficult to compare these results with those of Smith et al. [1]. Their method was indirect, and their interpretations, based on final products, depend on a multi-step mechanism including homogeneous and heterogeneous reactions. They explicitly reject channel (2a), whereas this study indicates it to represent 55% or more of the primary products. It is possible to propose alternate paths for some of the products observed by Smith et al. For example, their product N₂O₅ might have come from NO₂ + NO₃ where the NO₂ was produced from NO₃ + hv + NO₂ + O. Their O₂ might have come from various reactions by these secondary oxygen atoms, and their Cl₂ might have been formed by Cl + ClONO₂. Although these considerations do not explain all of their results, it may be that a large component of (2a) is consistent with their data.

The present results tend to disagree with the article by Adler-Golden and Wiesenfeld [3], who conclude that the quantum yield from channels (2) is less than 0.04. They observed no chlorine atoms in the photolysis of ClONO₂. They stated that their observations of oxygen atoms started after 200 μs, but in this time small amounts of
Cl$_2$O impurity in the ClONO$_2$ might have scavenged chlorine atoms. The rate constant for the reaction, Cl + Cl$_2$O $\rightarrow$ Cl$_2$ + ClO, is $9.8 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [7], which is 445 fold larger than that for Cl + ClONO$_2$ [8]. Also, these authors concluded that atomic oxygen was the predominant primary product of ClONO$_2$ photolysis, whereas this study finds NO$_3$ to be a predominant primary product. A possible source of this disagreement may arise from their relatively slow (20 μs), broad band (200 - 1000 nm) flash lamp, which might be expected to produce secondary oxygen atoms from photolysis of NO$_3$. Their results showed a linear relation between atomic oxygen production and flash-lamp energy, and they state that secondary O production would show a quadratic dependence on energy. However, this conclusion depends on the magnitude of the photolytic constants for ClONO$_2$ and NO$_3$. Consider the mechanism

\begin{align*}
\text{ClONO}_2 + h\nu_1 & \rightarrow \text{Cl} + \text{NO}_3 \quad (2a) \\
\text{NO}_3 + h\nu_2 & \rightarrow \text{NO}_2 + 0 \quad (8)
\end{align*}

The rate of production of atomic oxygen is

$$
\frac{d[O]}{dt} = j_1[\text{ClONO}_2](1 - e^{-j_2\tau}) \quad (9)
$$

If the term $j_2\tau$ is small compared to one (where $\tau$ is the pulse duration), the integral of atomic-oxygen production over the pulse is quadratic in pulse energy

$$
\int_{\text{pulse}} d[O] = j_1j_2[\text{ClONO}_2]\tau^2/2 \quad (10)
$$

since both $j_1$ and $j_2$ are proportional to pulse energy.
On the other hand if \( j_2^\tau \) is larger than one, the oxygen signal is linear in pulse energy

\[
\int_{\text{pulse}} d[0] = j_1[\text{ClONO}_2]^\tau
\]

(11)

The article by Adler-Golden and Wiesenfeld [3] does not give quantitative values for photolytic rate constants, but approximate relative values can be inferred from the data given. The flash lamp has a radiation distribution similar to a black body at 6500 K, and "flash lamp operation led to substantial ClONO\(_2\) decomposition." By using cross sections for ClONO\(_2\) [4] between 200 and 360 nm, cross sections [9] and quantum yields [10] for NO\(_3\) photolysis between 400 and 650 nm, and a relative radiation distribution based on the Planck function for 6500 K, we estimate that NO\(_3\) photolysis to produce NO\(_2\) + O is more than six times as fast as ClONO\(_2\) photolysis in their experiments. If ClONO\(_2\) underwent "substantial decomposition," then NO\(_3\) would be almost completely photolyzed, and the linear relation (11) would be applicable even for this secondary production of atomic oxygen.

Chang et al. [2] found little or no production of atomic oxygen or ClO as primary products, and they found \( \phi(\text{Cl}) \) to be 1.0 ± 0.2 and \( \phi(\text{NO}_3) \) to be 0.5 ± 0.3. The present study finds \( \phi(\text{NO}_3) \) to be 0.55 (± 0.1 to + 0.3). These quite different methods give about the same quantum yield for NO\(_3\). These two studies agree that channel (2a) is the most important single process, and the two studies are in complete agreement if channels (2b) and/or (2c) contribute to the quantum yield of atomic chlorine.
Acknowledgment

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References


Table 1. The NO$_3$ quantum yields from laser flash photolysis at 249 nm and from laser absorption at 662 nm.

<table>
<thead>
<tr>
<th>[ClNO$_3$] $10^{14}$</th>
<th>Pressure $\text{Torr}$</th>
<th>$E$ $10^4$</th>
<th>Light abs $10^4$</th>
<th>$\phi_{\text{NO}_3}^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.88 a Ar CH$_4$ b</td>
<td></td>
<td>4.93</td>
<td>1.92</td>
<td>0.58</td>
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<tr>
<td>8.03 Ar CH$_4$ b</td>
<td></td>
<td>15.9</td>
<td>8.14</td>
<td>0.55</td>
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<tr>
<td>6.96 Ar CH$_4$ b</td>
<td></td>
<td>2.97</td>
<td>1.32</td>
<td>0.55</td>
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<tr>
<td>6.90 Ar CH$_4$ b</td>
<td></td>
<td>10.3</td>
<td>4.54</td>
<td>0.63</td>
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<tr>
<td>6.64 Ar CH$_4$ b</td>
<td></td>
<td>2.92</td>
<td>1.24</td>
<td>0.57</td>
</tr>
<tr>
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<td>17.6</td>
<td>7.06</td>
<td>0.59</td>
</tr>
<tr>
<td>6.15 Ar CH$_4$ b</td>
<td></td>
<td>15.1</td>
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<td>0.64</td>
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<td>4.49</td>
<td>1.71</td>
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<tr>
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<td>1.23</td>
<td>.555</td>
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<tr>
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<td>5.32</td>
<td>2.04</td>
<td>0.57</td>
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<td>3.72</td>
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</tr>
<tr>
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<td>4.30</td>
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<tr>
<td>6.80 Ar CH$_4$ b</td>
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<td>3.09 Ar CH$_4$ b</td>
<td></td>
<td>6.73</td>
<td>1.33</td>
<td>0.55</td>
</tr>
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</table>

$^a$Molecules cm$^{-3}$. $^b$Photons cm$^{-2}$ shot$^{-1}$. $^c$Photons cm$^{-3}$ shot$^{-1}$. 
Figure Captions

Figure 1. Schematic diagram of experimental method.

Figure 2. Example of experimental data during one run, showing NO$_3$ concentration as a function of time as measured by laser absorption at 662 nm. Photolysis of ClONO$_2$ was by excimer laser pulses at 249 nm, 10 ns pulse width. Each point is 2 µs wide and represents the average of 512 laser pulses at 1 Hz.

Figure 3. Primary NO$_3$ quantum yield from ClONO$_2$ at 249 nm as a function of laser fluence and composition of carrier gases: ○, 20 Torr Ar; ●, 20 Torr Ar + CH$_4$; △, 100 Torr Ar; +, 100 Torr Ar + CH$_4$. 
Figure 1
Figure 2

[NO3] (MOL/CM3 X 1E13) vs SWEEP TIME (US)
PRIMARY NO₃ QUANTUM YIELD FROM CINO₂ AT 249 nm

- 20 Torr Ar
- 20 Torr Ar + CH₄

Δ 100 Torr Ar
+ 100 Torr Ar + CH₄

Figure 3

Quantum Yield

Photons cm⁻² Pulse⁻¹/10¹⁶
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