The reaction of OH with ClNO₂ at 298 K: kinetics and mechanisms

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The kinetics of the gas phase reaction between OH and CINO₂ have been studied in a fast flow discharge system (FFDS) at 298 K. The rate constant for the reaction was determined in phosphoric acid or halocarbon wax coated flow tubes to be $(3.5\pm0.7)\times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, where the uncertainty takes into account possible systematic errors and is greater than 2σ . HOCl was shown by mass spectrometry to be the major product. Using for comparison the OH + ClNO reaction, these data show that channel (1a) OH + ClNO₂ → HOCl + NO₂ must account for $\ge 90\%$ of the OH + ClNO₂ reaction. A second possible channel (1b) OH + ClNO₂ → HNO₃ + Cl is not significant. The atmospheric implications of these results are discussed.

1. Introduction

The reaction of gaseous N_2O_5 with NaCl, HCl or HCl/ice mixtures produces nitryl chloride, ClNO₂ [1-6]. Recent studies have suggested that this molecule may play a role in photochemical air pollution in the polluted marine troposphere [5-7] as well as initiating ozone depletion in the stratosphere [2,3,8,9]. Knowledge of the kinetics and mechanisms of its reaction with other atmospheric constituents, such as OH, is therefore important.

Although several studies have probed the spectroscopy and photochemistry of $ClNO_2$ [10-14], only a few have interrogated its reactivity with other molecules or radicals. We report here the first determination of the room temperature rate constant, k_1 , for the reaction of $ClNO_2$ with hydroxyl radicals using a fast-flow discharge method:

$$HO+CINO_2 \xrightarrow{k_1} products.$$
 (1)

In addition, a room temperature product analysis using mass spectrometry was carried out to search for the products of two potential reaction channels analogous to those previously observed in the reaction of a closely related nitrogen oxychloride, ClNO [15– 18]:

$$HO + CINO_2 \rightarrow HOCI + NO_2, \qquad (1a)$$

$$HO + CINO_2 \rightarrow HONO_2 + Cl$$
. (1b)

The implications of these results for the atmospheric fate of $CINO_2$ are explored.

2. Experimental

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The fast-flow discharge system used for the kinetic studies has been previously described in detail [17]. Briefly, hydroxyl radicals were generated by the reaction of hydrogen atoms with an NO_2/He mixture $(\approx 15-20\%)$ added through the upstream end of a double concentric movable inlet. Hydrogen atoms were produced by passage of H_2 ($\approx 0.50\%$ UHP H_2 in UHP He, Union Carbide) through a microwave discharge and further diluted with He (99.9999%, Union Carbide) prior to entering the flow tube. CINO₂, stored in a darkened 5-L bulb, was added to the flow tube at the downstream part of the movable inlet, which could be moved along the longitudinal axis of the flow tube to produce variable reaction times. The concentrations of both CINO₂ and NO₂ were determined by measuring the pressure drop in calibrated volumes over time. For all experiments,

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pseudo-first-order conditions were maintained with ClNO₂ in excess. Typical ClNO₂ concentrations were in the range $(0.5-20) \times 10^{14}$ molecules cm⁻³. To ensure that the reaction of ClNO₂ with H atoms was negligible, the concentration of NO₂ ([NO₂]₀ = $(0.9-4.0) \times 10^{13}$ molecules cm⁻³) was kept sufficiently large so that at the point of addition of ClNO₂ the hydrogen atom concentration had fallen to $<5 \times 10^8$ atoms cm⁻³. The total pressure in the flow tube was 1.05 ± 0.05 Torr.

The reaction kinetics were monitored by following the decay of OH using resonance fluorescence at 309.5 ± 2.8 nm. Initial OH concentrations were in the range $(7-15)\times10^{11}$ radicals cm⁻³ as measured by gas phase titration [19].

For all kinetic studies described here, the flow tube used had an inner diameter of 2.4 cm. Three different wall coatings (boric acid, phosphoric acid and halocarbon wax) were used to minimize surface loss of OH and to test for potential interferences from heterogeneous wall reactions. For each coating, at least six complete sets of runs at different initial NO₂ and OH concentrations, each set consisting of six different ClNO₂ concentrations, were performed.

Product studies of the OH reaction with CINO₂ and with CINO were carried out using a fast-flow discharge system interfaced to an Extrel EMBA II quadrupole mass spectrometer described elsewhere [17,20]. The flow tube wall coating was either boric acid or halocarbon wax, and runs were at 298 K and a total pressure of 0.50 Torr. The relative product yields of HOCl and Cl₂ were determined by comparison of the peak heights at m/e=52 and 70, respectively, to those from the OH+CINO reaction where these products have been reported [15] to be formed in equal yields.

NO₂ was prepared by the reaction of NO (Union Carbide, 98.5%) with O₂ (Union Carbide, UHP, > 99.99%). ClNO was synthesized by the reaction of NO with Cl₂ at low temperatures and purified as described elsewhere [16,17]. ClNO₂ was synthesized using the method of Volpe and Johnston [21], by the reaction of HCl gas with a mixture of fuming nitric and sulfuric acids. This method of preparation yielded a crude ClNO₂ product which typically contained $\leq 8\%$ total of impurities, mainly Cl₂, ClNO, and NO₂. These impurities were removed using the following procedures. Chlorine was removed from

the crude product by vacuum distillation from a methanol/liquid nitrogen slush trap (175 K) to a liquid nitrogen trap (77 K). Nitrosyl chloride, ClNO, was destroyed by reaction with N₂O₅, which completely oxidized the ClNO impurity to ClNO₂ [1,22,23]. Dinitrogen pentoxide was prepared by the reaction of NO₂ with excess O₃, followed by condensing N₂O₅ in a dry ice/acetone trap while pumping off O_2/O_3 . The crude ClNO₂ was finally purified for NO₂ and HNO₃ by allowing ClNO₂ to distill under vacuum from a dry ice/acetone trap (196 K) to a liquid nitrogen trap (77 K), which left the NO₂ and HNO₃ behind. Nitryl chloride purified in this manner was shown by FTIR and mass spectrometry to contain less than 1.0% of the impurities ClNO, and NO₂, less than 0.1% HNO₃ and less than 2.5% Cl₂.

3. Results and discussion

3.1. Kinetics

Fig. 1 shows a typical decay of OH fluorescence intensity (I) as a function of reaction distance at various initial $CINO_2$ concentrations. The decay of [OH] in the presence of excess $CINO_2$ is expected to follow the pseudo-first-order kinetic expression



Fig. 1. Typical plot of OH resonance fluorescence intensity as a function of reaction distance in the presence of increasing concentrations of $CINO_2$ at 298 K. Error bars shown represent two standard deviations.

$$\ln[OH] / [OH]_{0} = \ln I / I_{0}$$

= - (k₁[ClNO₂]₀ + k_w)t
= - (k₁[ClNO₂]₀ + k_w)d/v, (I)

where k_1 is the rate constant for reaction (1), k_w represents the loss of OH to the walls in the absence of $CINO_2$, t is the reaction time (typically 5-35 ms), $[CINO_2]_0$ is the initial concentration of $CINO_2$, I_0 and I are the OH resonance fluorescence intensities at times t=0 and t when the concentrations of OH are $[OH]_0$ and [OH], respectively, d is the reaction distance, and v is the linear flow speed along the flow tube. The data from individual runs extrapolate back to an apparent negative reaction distance because the design of the mixing inlet, which forces CINO₂ upstream at the relatively high ClNO₂ flows needed to obtain significant reaction. From eq. (I) and the known linear flow speed, the slopes of the lines can be used to derive a value for the pseudo-first-order rate constant, which when plotted versus the corresponding initial CINO₂ concentrations yields the rate constant, k_1 . Fig. 2 displays typical plots of the pseudo-first-order decays of [OH] as a function of initial CINO₂ concentration for each type of flow tube wall coating studied.

The rate constant for OH loss at the wall, k_w , was measured immediately before and after each measurement of k_1 by monitoring the OH resonance flu-



Fig. 2. Plot of observed first-order rate constants for the decay of OH as a function of the initial $CINO_2$ concentration for the boric acid, phosphoric acid and halocarbon wax coated flow tubes.

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orescence signal decay in the absence of ClNO₂. The values of k_w determined in this manner are in very good agreement with the intercepts at $[ClNO_2]_0=0$ in plots such as fig. 2. The rate constant for wall loss, k_w , is a function of the wall coating and hence different $[ClNO_2]_0=0$ intercepts are observed for each coating used in this study. Typical values of k_w ranged from 3–20 s⁻¹, with halocarbon wax having the smallest rate constant for wall loss of OH and boric acid having the largest.

Table 1 summarizes the measurements of k_1 using the flow tubes with the three different wall treatments. The result in the boric acid tube is significantly larger than the mean of the other two results. The trend k_1 (boric acid) > k_1 (phosphoric acid) > k_1 (halocarbon wax) is analogous to that observed [17] in the reaction between CINO and OH where the higher boric acid flow tube results appeared to be due to heterogeneous wall reactions. The same may be true for the OH+CINO₂ reaction.

A list of the most likely impurities in ClNO₂ and their rate constants for reaction with OH at 298 K is given in table 2. Because the rate constants for the reactions of OH with the impurities exceed that for the CINO₂ reaction, it is important that their concentrations in the CINO₂ be minimized. CINO is particularly critical, as its room temperature rate constant is an order of magnitude greater than that for $OH+CINO_2$. As seen in table 2, based on the maximum concentrations in any run of each impurity in the CINO₂, their individual contributions to the measured value of k_1 never exceed 5%. In most cases, the impurity levels were much lower than the cited maxima. For example, fig. 3 shows a typical FTIR spectrum of purified CINO₂ with the region where CINO has its strong v_1 absorption around 1800 cm⁻¹ amplified to show the absence of ClNO $(\leq 0.5\%)$. Hence the individual contributions to the observed OH decays are typically much smaller than 5%.

Using only the results from the halocarbon wax and phosphoric acid coated tubes, $k_1 = (3.5 \pm 0.1) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ where the error represents 2σ . Corrections have not been made for axial and radial diffusion, but are expected to be $\leq 5\%$ [24]. Given this, as well as possible contributions from impurities in the CINO₂, $\pm 20\%$ is a more realistic assessment of the error, giving $k_1 = (3.5 \pm 0.7) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

Table 1

Values of the rate constants (cm³ molecule⁻¹ s⁻¹) determined for the OH+ClNO₂ reaction for the different wall coatings

Wall coating	[NO ₂] ₀ ^{a)}	[OH] ₀ ^{b)}	$10^{14}(k_1\pm 1\sigma)$	Average $10^{14}(k_1 \pm 2\sigma)$
phosphoric acid	1.5	1.5	3.3±0.1	
	1.9	1.5	3.5±0.3	
	3.4	1.5	3.4 ± 0.2	
	1.8	0.75	4.6 ± 0.4	
	0.94	0.75	3.9±0.7	
	1.3	1.0	4.1 ± 0.1	
	3.0	1.0	3.5 ± 0.5	3.8 ± 0.3
boric acid	0.91	1.5	4.6 ±0.6	
	1.6	1.5	4.2 ± 0.1	
	1.9	1.5	5.0 ± 0.2	
	1.5	1.0	4.8 ± 0.2	
	2.5	0.75	5.6 ± 0.6	
	4.0	0.75	6.0 ± 0.5	
	1.9	0.75	5.3 ± 0.2	4.7±0.4
halocarbon wax	0.93	1.5	3.6±0.1	
	2.5	1.5	3.8 ± 0.1	
	4.0	1.5	3.5±0.01	· · · · · ·
	1.6	0.75	3.7 ± 0.2	
	2.6	0.75	3.1±0.3	
	4 .1	0.75	4.2 ±0.1	
	1.0	0.75	3.8±0.1	3.5 ± 0.1

^{a)} In 10^{13} molecules cm⁻³. ^{b)} In 10^{12} molecules cm⁻³.

Table 2

Contribution of the impurity + OH reaction to the observed k_1

Impurity	$k_{OH+impurity}^{a}$ (cm ³ molecule ⁻¹ s ⁻¹)	Maximum % impurity present in CINO ₂	Contribution to k_1 (%)
Cl ₂	6.7×10^{-14}	≤2.5	4.8
CINO	3.2×10^{-13}	≼ 0.5	4.6
NO ₂	5.2×10^{-14}	≤1	1.5
HNO3	1.0×10^{-13}	< 0.1	0.3

^{a)} Except for OH+CINO, rate constants are recommended values from ref. [14]. That for OH+CINO is from ref. [17].

3.2. Product studies

Fig. 4 shows the mass spectrum obtained in the region m/e=45-75 when the discharge was either on, producing OH radicals, or off. The off-scale peak at m/e=46 is due to NO₂, m/e=49 and 51 are due to the two chlorine isotope ClN fragments of ClNO₂, and the peaks at 70, 72 and 74 are from impurity Cl₂ in the ClNO₂. The 52 and 54 peaks due to HOCl appear only when the discharge is on, and by analogy with the ClNO reaction, can be ascribed to the abstraction reaction (1a). In the case of the ClNO re-

action with OH, a second, dynamically more complex, reaction channel produces HONO [15-17]. If an analogous pathway exists in the CINO₂ reaction, nitric acid and atomic chlorine would be formed (reaction 1b). No signal for HNO₃ at m/e=63 was observed, although it is known to have a parent peak which is sufficiently strong to be measured. The chlorine atoms produced in (1b) are expected to react with the excess CINO₂ to give Cl₂ via the fast reaction:

$$\operatorname{Cl}+\operatorname{ClNO}_2 \xrightarrow{k_2} \operatorname{Cl}_2 + \operatorname{NO}_2.$$
 (2)



Fig. 3. Fourier transform infrared spectrum of purified CINO₂. [CINO₂]= 6.5×10^{15} molecules cm⁻³ pressurized to 760 Torr with UHP air. Inset shows region near 1800 cm⁻¹ where the ν_1 absorption of CINO is expected.



Fig. 4. Mass spectrum observed with the microwave discharge (a) on (i.e. OH present) and (b) off, at 298 K. $[NO_2] = 3.3 \times 10^{13}$ molecules cm⁻³, $[C!NO_2]_0 = 1.4 \times 10^{14}$ molecules cm⁻³, $[OH]_0 = 4 \times 10^{12}$ radicals cm⁻³; total pressure 0.50 Torr.

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 $(k_2(298 \text{ K})=5.50\times10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ [12]. As seen in fig. 4b, Cl₂ is also present as an impurity (<1%) in the unreacted ClNO₂ so that Cl₂ from reaction (2) must be measured by an increase in the existing peak height at m/e=70.

Table 3 summarizes the product studies for the OH+CINO₂ reaction in which the ratio $m/e=(\Delta 70)/52$ was measured, where $\Delta 70$ is the increase in the m/e=70 peak over that due to impurity Cl₂. In the second and third experiment, the ratio $(\Delta 70)/52$ from the OH+CINO₂ reaction was compared to that from the OH+CINO reaction carried out under the same conditions. The branching ratios for production of HOCl and Cl (and hence Cl₂) in the latter reaction has been reported to be 0.5 for each channel [15] so that measurement of the product signals for OH+CINO can be used as an internal calibration of the mass spectrometer.

Within experimental error, no significant increase in the Cl₂ peak height was observed from the OH+ClNO₂ reaction in two of the three experiments; in the third, it was very small. From these data and the corresponding values for the ratio of peak heights at $m/e=\Delta70/52$ from the OH+ClNO reaction, channel (1a) forming HOCl must account for $\geq 90\%$ of the OH+ClNO₂ reaction at 298 K. This

Experiment no.	[OH] ₀ ^{a)}	[CINO ₂] ₀ ^{b)}	[CINO]0 ^b	$(\Delta 70)/52$ $(\pm 1\sigma)$	
 1 °)	9	2.7-3.3	-	0.18±0.23	
2A °)	7	1.8-3.7	-	0.049 ± 0.039	
2B °)	7	-	0.85-2.8	$\textbf{0.58} \pm \textbf{0.06}$	
3A ^d)	4	0.76-2.9	-	-0.15 ± 0.19	
3B ^d)	4	-	1.0-1.9	0.55 ± 0.04	

Table 3 Summary of product studies of the $OH + CINO_2$ reaction

^{a)} In 10^{12} radicals cm⁻³. ^{b)} In 10^{14} molecules cm⁻³.

^{c)} Flow tube coated with boric acid. ^{d)} Flow tube coated with halocarbon wax.

is in contrast to the OH+CINO reaction where channels corresponding to (1a) and (1b),

$$OH + CINO \rightarrow HOCI + NO$$

$$\stackrel{b}{\rightarrow} HONO + CI, \qquad (3)$$

occur at equal rates: $k_3^{298} = k_{3a} + k_{3b} = (3.2 \pm 0.5)$ ×10⁻¹³ cm³ molecule⁻¹ s⁻¹ [17], with $k_{3a} = k_{3b}$ [15].

A comparison of the thermochemistry of the direct abstraction forming HOCl indicates that the exothermicities [14] are similar: $-23.0 \text{ kcal mol}^{-1}$ for (1a) and $-18.7 \text{ kcal mol}^{-1}$ for (3a). However, the rate constant for the abstraction channels differ by approximately a factor of 5, suggesting that the pre-exponential factor for the OH+CINO₂ reaction may be significantly smaller than that for the OH+CINO reaction. A lower *A*-factor for the OH+CINO₂ reaction, reflecting a more tightly bound transition state, is perhaps not surprising given the structures [25,26] of CINO₂ and CINO:



The structure of CINO provides a wider angle of approach of OH to the chlorine atom than that of CINO₂ and hence may allow for a "looser" transition state than for the CINO₂ reaction. We are currently carrying out studies of the temperature dependence of the rate constant k_1 to determine the activation energy and pre-exponential factor for the OH+CINO₂ reaction to investigate this further.

3.3. Atmospheric implications

The reaction of ClNO₂ with OH radicals may be a significant process for removal of ClNO₂ from the atmosphere if it is fast enough to compete with photolysis. The lifetime of ClNO₂ with respect to reaction with OH, defined as the time for the concentration of ClNO₂ to reach 1/e of its initial value, is given [20] by τ (ClNO₂)=1/k₁[OH]. In the troposphere, assuming an ambient daytime OH concentration of 1×10⁶ radicals cm⁻³ and k₁=3.5× 10⁻¹⁴ molecules⁻¹ cm³ s⁻¹, τ (ClNO₂)=331 days. This lifetime can be compared to the lifetime of ClNO₂ with respect to photolysis,

$$\operatorname{CINO}_2 \xrightarrow{\kappa_p} \operatorname{Cl} + \operatorname{NO}_2,$$
 (4)

calculated using available absorption cross sections and quantum yields [14] and actinic irradiance values [20]. The photolytic lifetime of ClNO₂ given by τ (ClNO₂) = 1/ k_p is about 32 h at a solar zenith angle of 86°, corresponding to dusk or dawn. Therefore, the reaction of OH with ClNO₂ appears to be too slow to compete with photolysis.

4. Summary

Using fast-flow discharge techniques, the kinetics and products of the reaction between OH and ClNO₂ have been studied at room temperature. At a total pressure of 1.05 Torr, the room temperature rate constant has been measured to be $k_1 = (3.5 \pm 0.7) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ where the uncertainty in k_1 includes possible systematic errors due to impurities and is greater than 2σ . The stable product of the reaction has been identified to be HOCI using mass spectroscopy indicating that the reaction channel (1a) forming HOCI+NO₂ accounts for $\ge 90\%$ of the reaction at 298 K. Further work is underway to elucidate the temperature and possible pressure dependences of the reaction between OH and CINO₂. These data will be used to formulate reasonable transition state models and further probe the dynamics of the reaction.

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