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Infrared Spectroscopic Investigation of the Reaction between $SOCl_2$ and NO_2

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FT-IR spectroscopy has been used to explore the gas-phase reaction between NO_2 and $SOCl_2$. This reaction occurs in several stages. The initial products are NOCl, NO_2Cl, and SO_2. Standard kinetic plots indicated that this initial reaction is first order in $SOCl_2$ and second order in NO_2. Upon standing, a white solid containing at least three different compounds formed. These products and the reactions leading to their formation are also discussed.

Introduction

The reaction between NO_2 and $SOCl_2$ was first investigated by Stopperka and Grove.[1] They found that a 4:1 mole ratio of NO_2 and $SOCl_2$ produced $(NO)_2S_2O_7$, NOCl, NO_2Cl, and traces of SO_2Cl_2 after 3 days in a stainless-steel bomb at temperatures above 345 K. Since the products obtained for this reaction were the same as the products obtained from the reaction between SO_2Cl_2 and NO_2 under similar conditions, they speculated that the first step in the reaction between $SOCl_2$ and NO_2 was the formation of SO_2Cl_2. Apparently, no further investigation of this reaction has been done, so this investigation was undertaken to determine if more could be learned about it.

Experimental Section

A home-built stainless-steel infrared cell, which has been described in detail previously,[2] served as the reaction vessel. Briefly, it was constructed from an MDC Manufacturing Co., Inc., four-way cross stainless-steel vacuum flange. Two opposing ends of this flange were capped with KBr windows. One of the remaining legs was attached to the vacuum system. The cell could be isolated from the vacuum system during the reaction by a brass bellows valve. A thermocouple vacuum gauge was used to monitor the total pressure in the system. The fourth leg of the cell was attached to a glass vessel containing $SOCl_2$ or SO_2Cl_2 and to a gas cylinder containing NO_2. Presently, this cell can only be used at room temperature ($\sim$295 K).

To operate, the cell was evacuated and placed in the sample beam of a Nicolet MX-1 Fourier transform infrared spectrometer. The valve was closed, and NO_2 (Matheson) and $SOCl_2$ (Eastman) were added to the cell in varying mole ratios at a total pressure of 0.1–1.0 mbar. For most experiments the infrared spectrum of the reaction mixture was taken by using 30-s scans at 90-s intervals. The concentrations of NO_2 and $SOCl_2$ in the cell were determined from Beer's law plots, which were made by measuring the spectrum of the pure gas at several known pressures. Since these pressures were 1 mbar or less, concentrations were computed from the ideal gas law. The monomer–dimer equilibrium constant for $N_2O_4 \rightleftarrows 2NO_2$ was used to obtain the partial pressure of NO_2 in the cell. No equilibrium corrections were made for $SOCl_2$.

The infrared spectra reported here have 1-cm^{-1} resolution, the maximum available with the MX-1. These spectra represent 16 repetitive scans of the instrument. Band positions were measured at the band maximum with the peak-locating program in the spectrometer, which is calibrated with atmospheric CO_2 and is accurate to ± 0.20 cm^{-1} when not corrected for systematic errors.

Results

The spectrum shown in Figure 1 is typical of those obtained by mixing NO_2 and $SOCl_2$ at room temperature. Usually, all of the limiting reagent had reacted during the first hour, and bands that could readily be assigned to SO_2, SO_2Cl_2, NO_2Cl, and NOCl were clearly visible in the spectrum. Since it was possible that the Nernst glower could have photolyzed the mixture, separate experiments were done in the dark and while photolyzing the reaction mixture with a xenon solar lamp. No obvious differences were observed under either set of conditions, indicating that this is a thermal reaction.

The stoichiometry of the reaction was established by measuring the relative decrease in the concentration of NO_2 and $SOCl_2$ with time (see Figures 2 and 3). Although there is some uncertainty in these measurements due to the presence of secondary reaction products and the NO_2/N_2O_4 equilibrium, the ratio of moles of NO_2 reacted per mole of $SOCl_2$ reacted, equaled 2 within experimental error, indicating that the initial reaction is

$$SOCl_2 + 2NO_2 \rightleftarrows SO_2 + NOCl + NO_2Cl$$

The kinetic expression for this reaction was established from the same data used to obtain the stoichiometry by using standard integrated rate equation plots[3] (see Figures 2–4). The reaction is first order in $SOCl_2$ and second order in NO_2. No attempt was made to establish an accurate value for the rate constant for this reaction because (1) the thermocouple gauge used to measure the pressure was not calibrated, (2) the various equilibria affected the concentrations in the reaction mixture, and (3) temperature-dependent studies could not be done with the present apparatus, so this number would have little meaning or value.

Since Stopperka and Grove had suggested that the first step of this reaction was the formation of SO_2Cl_2, the experiment was repeated with SO_2Cl_2 used in place of the $SOCl_2$. However, consistent with previous reports,[1,4–7] little reaction had occurred after 8 h, which shows that the formation of SO_2Cl_2 is not the first step in the reaction between $SOCl_2$ and NO_2 at room temperature. The SO_2Cl_2 formed probably results from a secondary reaction such as

$$SOCl_2 + NO_2 \rightleftarrows SO_2Cl_2 + NO$$

or, as reported previously,[8] from

$$2SOCl_2 \rightleftarrows SO_2Cl_2 + SCl_2$$

and it apparently plays no role in the main reaction sequence. The NO that would be formed by the first of these reactions is reported to react rapidly with NO_2Cl to form NO_2 and NOCl,[9] so it is likely that the NO formed from this reaction would not be observed. Experiments done here with NO added to the reaction mixture confirmed that this was the case.

Several weak bands (Figure 5) were also observed that could arise either from minor reaction products or from reaction intermediates. However, it is not possible to make definite assignments for these molecules.

Stopperka and Grove reported that solid products were also obtained after 96 h. The reactions leading to the formation

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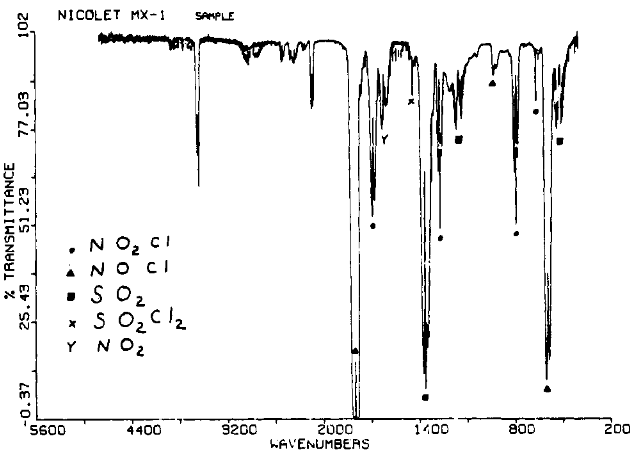


Figure 1. Typical IR spectrum of the reaction between NO_2 and $SOCl_2$ after 12 h.

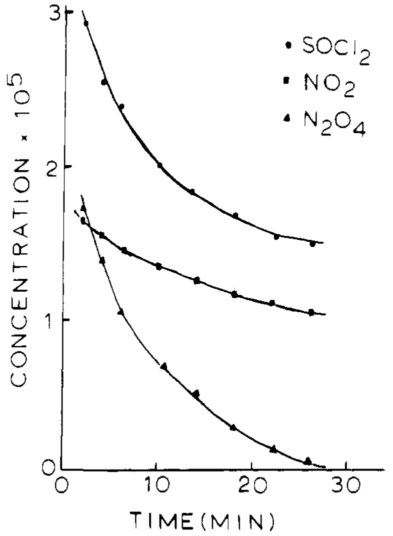


Figure 2. Concentration changes of NO_2, N_2O_4, and $SOCl_2$ with time.

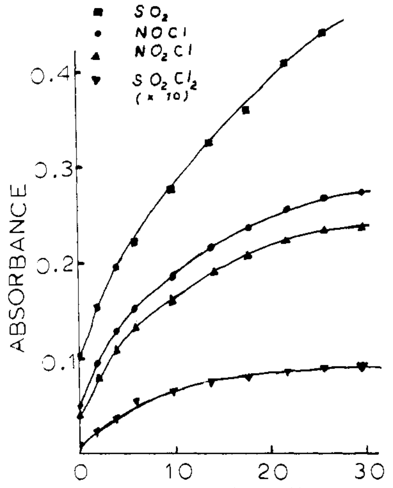


Figure 3. Absorbance changes for NOCl, NO_2Cl, SO_2, and SO_2Cl_2 (×10) with time.

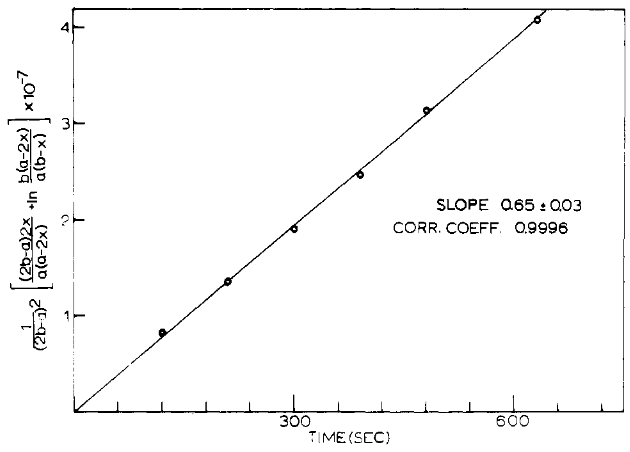


Figure 4. Plot of $(1/(2b-a)^2)[(2b-a)2x/(a(a-2x))+\ln(b(a-2x)/(a(b-x)))]$ vs. time in seconds. b = initial concentration of $SOCl_2$, a = the initial concentration of NO_2, and x = decrease in the concentration of $SOCl_2$. The linear relationship shows the reaction is first order in $SOCl_2$ and second order in NO_2. The slope equals the rate constant.

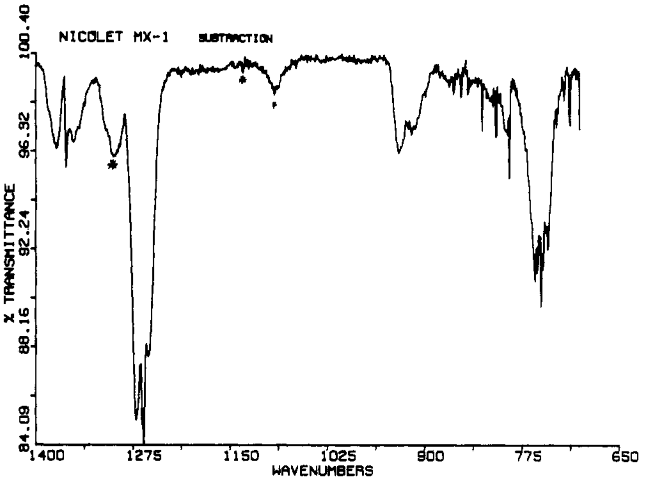


Figure 5. Infrared spectrum of the weak gas-phase bands (*) observed after 96 h. The 1090-cm^{-1} band could be observed after less than 10 min, but the other bands were masked by stronger SO_2 and NO_2Cl bands.

Table I. Observed Main-Product Gas-Phase IR Bands from the Reaction between NO_2 and $SOCl_2$

band, cm^{-1}	assgnt	band, cm^{-1}	assgnt
525	SO_2	652	NO_2Cl
1150		792	
1360		1267	
592	NOCl	1318	
1798		1684	
		1211	SO_2Cl_2
		1437	

of these solid products were investigated by filling the cell with varying ratios of $SOCl_2$ and NO_2 (always in excess) and observing the changes in the infrared spectrum at approximately 12-h intervals over the course of 4–6 days. The results of a typical experiment are as follows. By 24 h, nearly all of the NO_2Cl formed during the initial reaction had reacted, the concentrations of NO_2 and SO_2 had decreased markedly, and NO was clearly present. In addition, bands at 1064, 1046, 997, and 833 cm^{-1}, which arose from solid products plated on the windows, were also visible. By 48 h, the NO_2Cl had reappeared in the spectrum, and the solid product bands had increased in intensity. The 1046-cm^{-1} band had increased at a faster rate than the others, showing that there were at least two different solid products formed. The concentration of NO had markedly decreased and the concentrations of NO_2, SO_2, and SO_2Cl_2 continued to decrease. These trends continued for the next 72 h, at which time the remaining gases were pumped from the cell and the spectrum of the solid residue was taken (see Figure 6). The bands observed and the assignments for each are given in Tables I and II.

The cell developed a leak during one experiment and allowed slightly moist air to slowly enter the reaction vessel. While

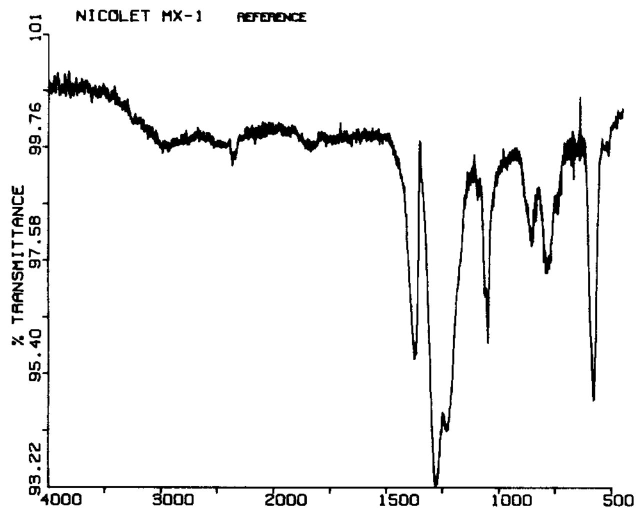


Figure 6. Solid product bands observed for the reaction between NO_2 and $SOCl_2$ after 96 h.

Table II. Observed IR Bands for the Solid Products Formed from the Reaction between $SOCl_2$ and NO_2

band, cm^{-1}	assgnt	band, cm^{-1}	assgnt
510	$S_2O_7^{2-}$	1060	$S_2O_6Cl^-$
577	NO_2^+, $ClSO_3^-$	1094	$S_2O_7^{2-}$
740	$S_2O_7^{2-}$	1235	$S_2O_6Cl^-$
780	$S_2O_6Cl^-$	1275	SO_3Cl^-
854	$S_2O_6Cl^-$	1364	$S_2O_7^{2-}$
1027	$S_2O_6Cl^-$	2325	NO^+
1046	SO_3Cl^-	2358	NO_2^+

Table III. Observed IR Bands of the Solid Products Formed from the Reaction between $SOCl_2$, NO_2, and H_2O

band, cm^{-1}	assgnt	band, cm^{-1}	assgnt
441	HSO_4^-	1090	$S_2O_7^{2-}$
459	HSO_4^-	1169	HSO_4^-
579	NO_2^+, HSO_4^-, SO_3Cl^-	1201	HSO_4^-, SO_3Cl^-
593	HSO_4^-, HS_2O_7	1231	$HS_2O_7^-$
602	HSO_4^-	1283	HSO_4^-
662	HSO_4^-	1324	HSO_4^-
695		1569	
802	$HS_2O_7^-$	1747	
814	$HS_2O_7^-$	1928	
850	HSO_4^-	2206	NO^+
882	HSO_4^-	2415	NO_2^+
1024	HSO_4^-	2485	HSO_4^-
1055	HSO_4^-, $ClSO_3^-$	2924	HSO_4^-, $HS_2O_7^-$
1071	$HS_2O_7^-$	2963	HSO_4^-, $HS_2O_7^-$

the general pattern followed by the gaseous species was similar to that observed in the anhydrous experiments, the solid products produced formed faster with H_2O present and clearly had a different composition (see Figure 7). The solid product bands formed under these conditions and the assignments for each are given in Table III.

Discussion

The assignments for the reaction products were made by comparing the observed IR spectrum to previously reported spectra[4-20] and by observing the time when the product was first observed during the reaction sequence. Since all of the strong bands expected for each molecule were observed, the main gas-phase products could be assigned with certainty. The assignments made for the solid product bands are less certain. Several of these species have very similar IR frequencies, and the bands from these species were often blended, which unfortunately, masked the bands needed to confirm the assignments.

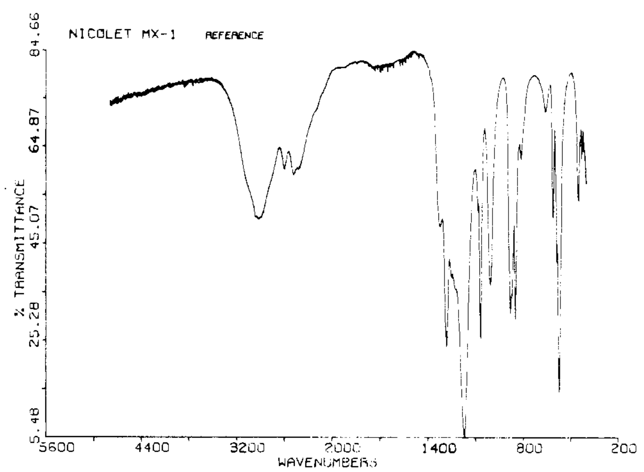
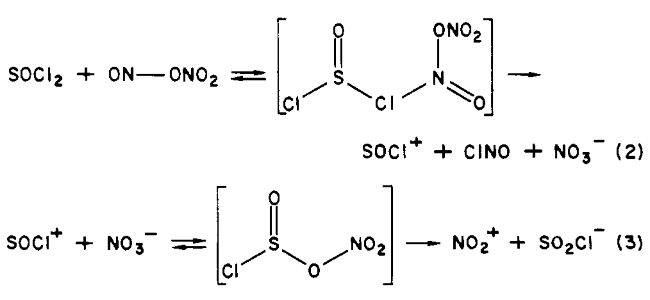


Figure 7. Solid product bands formed after 96 h from the reaction between $SOCl_2$, NO_2, and H_2O.

Since the reaction is second order in NO_2, the dimer N_2O_4 is most likely involved in the reaction mechanism. Three isomers of this molecule have been identified.[21,22] There is little direct evidence to indicate which of these is the reactive form in the gas phase, but a great deal of circumstantial evidence, including this work, indicates that the oxygen-bridged form [$ON-ONO_2$] is the reactive species.[23] consequently, the first step in the mechanism for the initial gas-phase reaction is proposed to be the formation of isomeric N_2O_4. Since this molecule can dissociate into either radicals (NO and NO_3) or ions (NO^+ and NO_3^-) and it is possible to transfer either chloride atoms or ions from $SOCl_2$ to these species, the reaction could occur through an ionic mechanism, a radical mechanism, or some combination of the two. In either case, it is likely that the reaction occurs via a "sticky collision" mechanism such as (1)-(4), where the circled plus sign indicates a positive ion or radical and the circled minus sign indicates a negative ion or radical. The intermediates shown in steps 2 and 3 of this

$$2NO_2 \rightleftharpoons ON{-}ONO_2 \qquad (1)$$



$$SO_2Cl^- + NO_2^+ \longrightarrow SO_2 + ClNO_2 \qquad (4)$$

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mechanism need not dissociate and probably would not dissociate if the steps involved the transfer of an ion. The small amount of SO_2Cl_2 forms from steps such as (5)–(7).

$$2SOCl_2 \rightleftarrows SO_2Cl_2 + SCl_2 \tag{5}$$

$$SOCl_2 + NO_3 \rightleftarrows SO_2Cl_2 + NO_2 \tag{6}$$

$$\begin{gathered} SO_2Cl + ClX \rightleftarrows SO_2Cl_2 + X \\ X = NO,\ NO_2,\ SOCl,\ \text{or } SO \end{gathered} \tag{7}$$

Stopperka and Grove[1] observed that similar reaction products were formed from the reaction between any sulfur oxychloride and NO_2. This work indicates that this occurs because the products of the initial reaction (SO_2, NO_2Cl, NOCl, and the excess NO_2) were the same. Of the possible reactions between these compounds, only SO_2 and NO_2 are reported to react under the conditions used here.[24–29] Because of the importance of this reaction to atmospheric chemistry, it has been reasonably well characterized. The first step in the reaction is the slow formation of SO_3 and NO. The SO_3 then rapidly reacts with SO_2 and NO_2 to form solid $(NO)_2S_2O_7$. In addition, SO_3 is known to react with NO_2Cl, NOCl, and N_2O_5 in solution to form $NO_2S_2O_6Cl$, $NOSO_3Cl$, and $(NO)_2S_2O_6Cl$ and $(NO_2)_2S_2O_7$, respectively.[29–34] The chlorinated solids will further react with N_2O_5 to form $(NO_2)_2S_nO_{3n+1}$, where $2 \leq n \leq 4$.[34]

A mechanistic type reaction scheme for the solid products observed here, and based upon this previous work, has been developed. It is

$$NO_2 + SO_2 \rightleftarrows SO_3 + NO \tag{8}$$

$$2SO_3 + NO_2Cl \rightarrow NO_2^+S_2O_6Cl^-(s) \tag{9}$$

$$NOCl + SO_3 \rightarrow NO^+SO_3Cl^-(s) \tag{10}$$

$$NO^+SO_3Cl^- + SO_3 \rightarrow NO^+S_2O_6Cl^-(s) \tag{11}$$

$$2NO_2 + SO_3 + SO_2 \rightarrow (NO^+)_2S_2O_7^{2-}(s) \tag{12}$$

$$NO^+S_2O_6Cl^- + N_2O_4 \rightarrow NO_2Cl + (NO^+)_2S_2O_7^{2-}(s) \tag{13}$$

$$NO_2^+S_2O_6Cl^- + N_2O_4 \rightarrow NOCl + (NO_2^+)_2S_2O_7^{2-}(s) \tag{14}$$

plus other similar reactions. Reaction 9 could occur in steps such as

$$SO_3 + NO_2Cl \rightarrow NO_2^+SO_3Cl^-(s) \tag{9a}$$

$$NO_2^+SO_3Cl^- + SO_3 \rightarrow NO_2^+S_2O_6Cl^-(s) \tag{9b}$$

Reaction 12 could occur in steps such as

$$NO_2 + SO_3 \rightleftarrows NO^+SO_4^- \tag{12a}$$

$$NO^+SO_4^- + SO_2 \rightarrow NO^+S_2O_6^{-*} \tag{12b}$$

$$NO^+S_2O_6^{-*} + NO_2 \rightarrow (NO^+)_2S_2O_7^{2-}(s) \tag{12c}$$

In the preceding equations (s) indicates stable solid products, * indicates unstable reaction intermediates, and (9a), (9b), and (12a)–(12c) give proposed "sticky collision" type mechanisms to form the products reported previously.

Clearly, steps 9–12 can occur concurrently, albeit at different rates. The experimental observations support this reaction sequence. By 24 h, NO has appeared in the spectrum, and solid product bands, which are assigned as SO_3Cl^- and $S_2O_6Cl^-$, were clearly observed. Canosa et al.[28] reported that a solid product (probably $(NO)_2S_2O_7$) formed within 20 h of mixing NO_2 and SO_2 at room temperature, so it is likely that this compound is also present, but it was not observed. Since nearly all of the NO_2Cl had reacted within the first 24 h, little $NO_2S_2O_6Cl$ would be expected to form during the next 24 h, and the bands assigned to SO_3Cl^- did increase in intensity relative to the $S_2O_6Cl^-$ bands during this period. The reappearance of NO_2Cl in the spectrum shows that reactions such as (13) must occur.

Water is known to increase the rate of reaction between NO_2 and SO_2 and to change the product distribution.[26–29,35–38] The main product found previously when water is present was $NOHSO_4$, which was also the main product found here with water present. Water could enter into the mechanism of this reaction in several places. It reacts with NO_xCl to form HNO_x, which can then further react to form products. For example, HNO_3 is known to react with SO_3 to form $NO_2HS_2O_7$.[29] Water also reacts with SO_3 to form H_2SO_4, which reacts with NO_xCl to form NO_xHSO_4 and HCl. It could also enter the reaction through the mechanism discussed by Canosa et al.[28] Finally, water reacts with the solid products SO_3Cl^- and $S_2O_7^{2-}$ to form HSO_4^- and with $S_2O_6Cl^-$ to form $HS_2O_7^-$. This was confirmed by allowing the solids formed from the anhydrous experiments to stand in moist air for approximately 4 h. The amount of HSO_4^- increased, confirming that this anion will form from the reaction between the solid products and water.

Conclusion

$SOCl_2$ is found to react with NO_2 to form NOCl, NO_2Cl, and SO_2. These products will then further react to form a variety of solid products. Kinetic data have been collected which indicate that the initial reaction is first order in $SOCl_2$ and second order in NO_2. The chemistry of the secondary reactions has been partially explored. However, there are still many reactions occurring that are not completely understood.

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Registry No. $SOCl_2$, 7719-09-7; NO_2, 10102-44-0.

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