# Reaction between Chlorine Dioxide and Nitric Oxide

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The reaction between chlorine dioxide and nitric oxide has been studied in a fast-flow system at total pressures near 1 mm Hg and at  $294^{\circ}$ K. Under conditions when atomic chlorine is removed heterogeneously, the mechanism of the reaction is described by

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$$NO + OCIO \rightarrow NO_2 + CIO$$
 (1)

$$NO+CIO \xrightarrow{k_2} NO_2+CI$$
 (2)

$$k_{w}$$
  
2Cl+wall $\rightarrow$ Cl<sub>2</sub> (w)

with  $k_2/k_1 = (0.30 \pm 0.05)$ , and  $k_1 \ge 5 \times 10^{11}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup>. For systems in which  $k_w$  is small, chlorine atoms produced in reaction (2) remove further chlorine dioxide according to the fast reaction,

$$Cl + OClO \rightarrow ClO + ClO$$
 (3)

The rate constant  $k_1$  is large for a molecular reaction of low exothermicity.

The reactions of chlorine dioxide with oxygen, chlorine and bromine atoms occur rapidly <sup>1-3</sup> at room temperature, and produce the CIO radical in stoichiometric amounts. The reaction with atomic chlorine is a particularly efficient source of CIO, and was used in a determination of the kinetics of CIO radical decay over a range of temperature.<sup>3</sup> In the present work, further data on the formation and reactions of CIO have been obtained by an investigation of the reaction between nitric oxide and chlorine dioxide,

$$NO + OCIO \rightarrow NO_2 + CIO.$$
 (1)

Although this reaction is exothermic by only 14 kcal mole<sup>-1</sup>, its rate constant at room temperature is similar in magnitude to those found for exothermic atom + diatomic molecule abstraction reactions. No work on reaction (1) has been previously published. The analogous reaction between nitric oxide and ozone, however,

$$NO+O_3 \rightarrow (NO_2, NO_2^*)+O_2$$
,

has been extensively studied,<sup>4-6</sup> and produces both ground and electronically excited  $NO_2$ .

### EXPERIMENTAL

The reaction between nitric oxide and chlorine dioxide was studied in a fast-flow system using the  $4 \times 2$  cm cross-section quartz tube described previously.<sup>1</sup> Concentrations of CIO and OCIO were determined by application of Beer's law to measurements of their intensities of absorption of ultra-violet light at 2776 and 3515 Å respectively. At these wavelengths, the apparent extinction coefficients were both accurately known for the constant slit widths (~0.2 mm) used. The optical system, consisting of a stabilized-output deuterium

continuous source, a multiple-reflection mirror system giving a total absorption path length of 20 cm, an Optica CF 4 monochromator, and an R.C.A. 1P 28 photomultiplier cell, could be moved along the length of the quartz tube.

The reaction was studied in an argon carrier at total pressures  $P_T$  near 1 mm Hg. The reagents were prepared by the methods described previously,<sup>1</sup> and were rapidly mixed at a multi-perforated glass inlet jet. Known flows  $F_i$  of nitric oxide and argon were introduced from calibrated capillary flowmeters, and use was made of the relationship,  $p_i = F_i P_T / \Sigma F_i$ , for conversion from flow rates to concentrations ( $p_i$ ). In some of the runs, chlorine atoms were rapidly removed from the reacting mixture by means of a plug of freshly cleaned nickel wire.

The chemiluminescent emission spectrum associated with the reaction was recorded on Kodak 2475 emulsion ( $\lambda \leq 7100$  Å). An f/1.5 Bass-Kessler plane-grating spectrograph was mounted with its collimating axis perpendicular to the axis of the flow-tube, and the recording was made in the second-order with a slit width of 0.4 mm.

### **RESULTS AND DISCUSSION**

Nitric oxide was added in increasing amounts to a constant flow of chlorine dioxide in an argon carrier at 1.40 mm Hg total pressure. The chlorine dioxide was rapidly removed close to the inlet jet (contact time ~5 msec), and with sufficiently large amounts of added nitric oxide, the OCIO band absorption system could not be detected. Under these conditions, the banded absorption spectrum of the ClO radical was observed with high intensity. Following a second-order rate law,<sup>1, 3</sup> [ClO] decayed from a maximum value that occurred just past the point of nitric oxide addition. At the same time, a red chemiluminescence was visible along the flow-tube. Spectrographic recording of the emission ( $\lambda \leq 7100$  Å) showed bands only of the system,<sup>2,7</sup> Cl<sub>2</sub>( ${}^{3}\Pi_{out} \rightarrow {}^{5}\pi_{g}^{+}$ ).

Typical quantitative data are shown in fig. 1, in which the variations of [OCIO] and [CIO], measured 8 msec after the NO+OCIO mixing point, are presented as functions of the initial concentration of added nitric oxide,  $[NO]_0$ . As  $[NO]_0$  was increased from zero, there was, within the limits of experimental error, a 1 : 1 stoichiometric fall in the concentration of OCIO, and a corresponding 1 : 1 rise in [CIO]. The increase in the CIO radical concentration continued until sufficient nitric oxide had been added to remove all the chlorine dioxide initially present; in a preliminary experiment with a flow of discharged chlorine, it had been verified that the flow-tube surface was inactive for Cl atom recombination. The addition of still larger concentrations of NO then caused a reduction in [CIO].

The products of complete reaction, obtained under conditions of a slight initial excess of OClO were collected in a trap at 77°K. After warming, analysis by infra-red absorption of the gas mixture showed nitrogen dioxide as the only major product. No evidence was found for the nitrosyl chloride band at  $2135 \text{ cm}^{-1}$ . Chlorine, which is certainly also a product of the reaction, does not have an infra-red active fundamental.

The reaction between NO and OCIO was too rapid for its rate to be measurable. However, by working under conditions of the highest linear flow speed obtainable, it was possible to set a lower limit on the rate constant of the primary step. With equal initial concentrations of NO and OCIO  $(7 \times 10^{-10} \text{ mole cm}^{-3})$ , the absorbance by OCIO was barely detectable after 2 msec. From this observation, it was estimated that the bimolecular rate constant for the primary reaction between NO and OCIO was  $\ge 5 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ .

The results can be understood in terms of the rapid primary reaction,

$$NO + OClO \rightarrow NO_2 + ClO; \quad \Delta H^{\circ}_{298} = -14 \text{ kcal mole}^{-1}, \tag{1}$$

## REACTION OF $ClO_2$ with NO

Consideration of this reaction alone can explain the 1:1 stoichiometries for

However, from the similarly fast removal of ClO under conditions of high  $[NO]_0$ , the reaction,

$$NO + ClO \rightarrow NO_2 + Cl; \quad \Delta H_{298}^\circ = -9 \text{ kcal mole}^{-1}, \tag{2}$$

also has a high rate constant. Direct evidence for this conclusion has been obtained <sup>1, 3</sup> from experiments in which NO was added to a flow of ClO radicals in a titration reaction for the estimation of ClO concentrations. If  $k_1$  and  $k_2$  are of the same order of magnitude, there results an apparent inconsistency in the experimental observations, since with increasing [NO]<sub>0</sub>, one would expect



FIG. 1.—Stoichiometry of the reaction between nitric oxide and chlorine dioxide. Variation of [OCIO] and [CIO] with [NO]<sub>0</sub> added to constant [OCIO]<sub>0</sub>. △, [CIO]; ○, [OCIO].

a departure from the 1 : 1 stoichiometries mentioned above. In this case, the increasing  $[ClO]_{produced}$  formed in reaction (1) can compete more and more effectively with OClO for NO in reaction (2). However, the reaction,<sup>3</sup>

k,

$$Cl + OClO \rightarrow ClO + ClO; \quad \Delta H_{298}^{\circ} = -5 \text{ kcal mole}^{-1},$$
 (3)

is also very rapid  $(k_3 \ge 5 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \text{ at } 294^\circ\text{K})$ . Reactions (2) and (3) together are equivalent stoichiometrically to reaction (1), so that even if ClO does compete with OCIO for NO, the overall stoichiometry is not affected, in agreement with the experimental result. The two possible paths for removal of OCIO could not therefore be distinguished. However, from the value of  $k_1/k_2$  (see later), it appears that the lower limit for the rate constant determined above does relate predominantly to reaction (1). The fall-off in the stoichiometry for [ClO]<sub>produced</sub> at high [NO]<sub>0</sub> is due to a small amount of ClO decay between the reaction zone and observation point;

$$ClO + ClO \rightarrow products.$$
 (4)

Since  $k_4 = 1.2 \times 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  (ref. (3)), this effect is only significant at the highest [ClO]. The apparently incomplete removal of OClO at high [NO]<sub>0</sub> is

probably due to a small loss of atomic chlorine via surface recombination (the absorbances were corrected for absorption due to  $NO_2$ ).

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Although it was not possible to determine accurately either  $k_1$  or  $k_2$ , their ratio was found with good precision using a competitive method. For this experiment, a 10 m length of freshly cleaned nickel wire was packed around the rapid mixing jet, and in the region immediately downstream. With this arrangement, chlorine atoms formed in reaction (2) were known to be rapidly removed on the wire, and the system was not complicated by the otherwise possible occurrence of reaction (3). Chlorine dioxide was added at different concentrations to a constant concentration of nitric oxide and measurements of the concentrations of CIO and OCIO were made 5 cm



FIG. 2.—The variations of [OCIO] and [CIO] with [OCIO]<sub>0</sub> after constant reaction time (20 msec).  $[NO]_0 = 13.9 \times 10^{10} \text{ mole cm}^{-3}$ .  $\triangle$ ,[CIO];  $\bigcirc$ ,[OCIO]; ---[CIO] after correction for decay between the reaction zone and observation point.

(20 msec) downstream from the mixing point. The total pressure (argon) was 1.34 mm Hg. The variations of [OCIO] and [CIO] with the added OCIO concentration, [OCIO]<sub>0</sub>, are shown for one of the runs in fig. 2. CIO and OCIO were only detected in the reaction products when  $[OCIO]_0 > \frac{1}{2}[NO]_0$ , in agreement with the proposed scheme involving reactions (1) and (2) only. If chlorine atoms formed in reaction (2) were not removed efficiently by the nickel wire, CIO formed in the scheme, (1)+(2)+(3) would increase linearly with  $[OCIO]_0$  for  $[OCIO]_0 > \frac{1}{2}[NO]_0$ , and would attain a constant value equal to  $[NO]_0$  when  $[OCIO]_0 = [NO]_0$ . Furthermore, OCIO would not be detected until  $[OCIO]_0 > [NO]_0$ . Since the experimental data (fig. 2) did not show this behaviour, it was possible to infer that  $\gamma$ , the surface recombination efficiency for CI atoms on a nickel wire, is so large ( $\gamma \ge 5 \times 10^{-2}$ ) that reaction (3) was effectively eliminated. When the method was previously applied <sup>1</sup> in a similar determination of the ratio of the rate constants for O+OCIO and O+CIO, it was not possible to make use of the nickel wire technique owing to rapid heterogeneous recombination of O-atoms. For this reason, reaction (3)

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could not be neglected completely and the result was subject to greater error than in the present case. In the NO+OCIO system, the results were analyzed on the basis that reaction (3) could be excluded, which implies that the relative CIO and OCIO product concentrations are related to the magnitude of  $k_2/k_1$ . In fig. 2, the CIO concentrations have been corrected (broken curve) for the small amount of decay which occurred between the mixing and observation points. The corrected curve rises asymptotically to a value near the constant initial nitric oxide concentration, indicating the expected result that with  $[OCIO]_0 \ge [CIO]$ , reaction (1) occurs predominantly.



Fig. 3.—Determination of  $k_2/k_1$ . Plots of [ClO]/[OClO] against [OClO]/[OClO]\_0.  $\bigcirc$ ,  $\triangle$ , expt points; - - - calc. curves for (a)  $k_2/k_1 = 0.25$  and (b)  $k_2/k_1 = 0.35$ .

Thus with the assumption that only reactions (1) and (2) control the ClO and OClO concentrations, it follows that

$$-d[OClO]/dt = k_1[NO][OClO],-d[ClO]/dt = k_2[NO][ClO]-k_1[NO][OClO].$$

Therefore,

$$-d[ClO]/d[OClO] = (k_1[OClO] - k_2[ClO])/k_1[OClO].$$

Integration using the boundary condition, [ClO] = 0 when  $[OClO] = [OClO]_0$ , gives the equation,

$$\frac{[\text{CiO}]}{[\text{OCIO}]} = \frac{k_1}{k_1 - k_2} \left\{ 1 - \left( \frac{[\text{OCiO}]}{[\text{OCiO}]_0} \right)^{(k_2/k_1 - 1)} \right\}.$$

In fig. 3, calculated curves of [CIO]/[OCIO] as a function of [OCIO]/[OCIO]<sub>0</sub> are plotted from this equation for  $k_2/k_1 = 0.25$  and 0.35. The data from fig. 2 and a second similar run are also shown, and lie entirely in the region defined by the two curves. In this way, the result  $k_2/k_1 = (0.30 \pm 0.05)$  was obtained at 294°K. Using the lower limit found for the rate constant for removal of chlorine dioxide by nitric oxide, the results,  $k_1 \ge 5 \times 10^{11}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> and  $k_2 \ge 1.5 \times 10^{11}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> were obtained at 294°K.

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The value of  $k_1$  is high for a reaction of low exothermicity between two polyatomic molecules. In fact, it seems likely that reaction (1) is the fastest known reaction between two stable molecules at room temperature. For the similar O-atom abstraction reaction between nitric oxide and ozone.

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$$NO + O_3 \rightarrow NO_2 + O_2; \quad \Delta H_{298}^\circ = -48 \text{ kcal mole}^{-1},$$
 (5)

Clough and Thrush <sup>6</sup> obtained the result,  $k_5 = 4.3 \times 10^{11} \exp(-2330/RT) \text{ cm}^3$ mole<sup>-1</sup> sec<sup>-1</sup>, giving a rate constant at room temperature of about 10<sup>10</sup> cm<sup>3</sup> mole<sup>-1</sup>  $sec^{-1}$ . Since reactions (1) and (5) are both allowed by the spin-correlation rule<sup>8</sup>,<sup>8</sup> they would be expected to have similar pre-exponential factors. This would imply that reaction (1) between NO and OCIO has little or zero activation energy. The conclusion of a higher activation energy for the reaction of NO with ozone compared to that with chlorine dioxide is difficult to reconcile with any obvious parameters. For a series of O+diatomic molecule abstraction reactions, Clyne and Coxon<sup>3</sup> found some evidence for a correlation of the activation energy with heat of reaction. In the present case, reaction (5) is considerably more exothermic than reaction (1), and on this basis would thus be expected to have a lower activation energy, contrary to the observation above. Even if the activation energies correlate with the energy required to break the O-ClO and O-O<sub>2</sub> bonds, the same difficulty still arises since  $D^{\circ}(O-ClO) \cong 60 \text{ kcal mole}^{-1}$  and  $D^{\circ}(O-O_2) \cong 25 \text{ kcal mole}^{-1}$ . However, the pre-exponential factor of reaction (1) may be anomalously high. From both the stoichiometries and the product analyses, any reaction between NO and OCIO proceeding via a triangular transition state to give ClNO and  $O_2$  as products, is much less efficient than via (1), indicating a higher activation energy for this path.

Finally, the observed chemiluminescent emission from  $Cl_2({}^{3}\Pi_{ou}+)$  probably has two distinct origins. First, atomic chlorine is produced in large concentrations by reaction (2), and gives rise <sup>2, 7</sup> to the red and near infra-red chlorine afterglow emission spectrum,

$$Cl+Cl(+M) \rightarrow Cl_2({}^{3}\Pi_{ou^+}, v' \leq 14)(+M)$$
$$Cl_2({}^{3}\Pi_{ou^+}) \rightarrow Cl_2({}^{1}\Sigma_{q}^+) + hv.$$

However, an alternative explanation is provided by the finding <sup>3</sup> that the  ${}^{3}\Pi_{ou^{+}}$  state of chlorine is also populated in the ClO radical decay reaction. The resulting emission is intense, and although closely similar to the chlorine afterglow spectrum, has a red-shifted intensity distribution. It is likely that under most conditions, there would be an appreciable contribution to the overall emission from both sources. Unlike the case of NO+O<sub>3</sub>, no emission is expected from the  ${}^{2}B_{1}$  excited state of NO<sub>2</sub> in the present system. Since reaction (1) is only 14 kcal mole<sup>-1</sup> exothermic, it is not possible in this step to excite NO<sub>2</sub>( ${}^{2}B_{1}$ ), which is estimated <sup>6</sup> to lie approximately 44 kcal mole<sup>-1</sup> above ground-state NO<sub>2</sub>( ${}^{2}A_{1}$ ).

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