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# Elementary Reactions of the NCl Radical

Part 1.—Rate Constants for the Reactions NCl+NCl  $\rightarrow$  N<sub>2</sub>+2Cl and O+NCl  $\rightarrow$  NO+Cl

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A kinetic study of the NCl radical at 295 K has been carried out in a discharge-flow system using mass-spectrometric detection with molecular-beam sampling. NCl radicals were generated by the reaction of Cl atoms with  $N_3$ Cl:

$$Cl+N_{3}Cl \rightarrow N_{3}+Cl_{2}$$

$$Cl+N_{3} \rightarrow NCl(b^{1}\Sigma^{+}), (a^{1}\Delta), (X^{3}\Sigma^{-})+N_{2}$$

Metastable excited-state  $(a^{1}\Delta)$ ,  $(b^{1}\Sigma^{+})$  NCl radicals were shown to react with Cl<sub>2</sub> to produce NCl<sub>2</sub> radicals:

$$NCl^* + Cl_2 \rightarrow NCl_2 + Cl_2$$

The rate constants (295 K) for the following reactions of ground-state  $(X^{3}\Sigma^{-})$  NCl radicals have been measured:

NCl+NCl → N<sub>2</sub>+2Cl;  $k_{295} = (8.1 \pm 1.8) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}(2\sigma)$ O+NCl → NO+Cl;  $k_{295} = (1.2 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}(2\sigma)$ .

The unequivocal identification of the NCl radical was first reported by Milligan<sup>1</sup> using infrared absorption spectroscopy. The radical was formed in matrix isolation following the u.v. photolysis of N<sub>3</sub>Cl. The value for  $\omega_e^r$  of 825 cm<sup>-1</sup> agreed well with the value of 827 cm<sup>-1</sup> that was obtained by Colin and Jones,<sup>2</sup> who observed NCl ( $b^1 \Sigma^+ - X^3 \Sigma^-$ ) emission accompanying a discharge in N<sub>2</sub> + Cl<sub>2</sub> mixtures. Combourieu *et al.*<sup>3</sup> detected the NCl radical as a product of the reaction between Cl atoms and N<sub>3</sub>Cl in a discharge-flow system. These workers used mass-spectrometric detection as in the present work. However, their technique differed in several important ways, discussed below, from that of the present work. They also detected the N<sub>3</sub> and NCl<sub>2</sub> radicals as products. Low electron energies (*ca.* 20 eV) were used in order to discriminate between the NCl<sup>+</sup> fragment from NCl<sub>2</sub> and NCl itself. Two channels for the initial step were considered:

$$Cl + N_3Cl \rightarrow N_3 + Cl_2; \qquad \Delta H_{298}^{\ominus} = -96 \text{ kJ mol}^{-1}$$
(1)

$$Cl + N_3Cl \rightarrow NCl_2 + N_2; \quad \Delta H_{298}^{\ominus} = -267 \text{ kJ mol}^{-1}.$$
 (1')

At short reaction times an increase in the signal at m/e = 42 (N<sub>3</sub><sup>+</sup>) was observed using [N<sub>3</sub>Cl]<sub>0</sub>>[Cl]<sub>0</sub> which was ascribed to the production of N<sub>3</sub> radicals *via* reaction (1). With an excess of Cl atoms over N<sub>3</sub>Cl no increase in signal was observed, from which it was concluded that the N<sub>3</sub> radical was unstable in the presence of Cl atoms (discussed below). The alternative route [reaction (1')] was rejected since the NCl<sub>2</sub> radicals were not observed in the initial stages of the reaction using an

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excess of N<sub>3</sub>Cl over Cl atoms; NCl<sub>2</sub> radicals were observed at short reaction times using an excess of Cl atoms over N<sub>3</sub>Cl but the signal was dependent on the amount of Cl<sub>2</sub> present, which provided further proof that the NCl<sub>2</sub> radicals were produced via secondary processes. Clarke and Clyne<sup>4</sup> had earlier identified the  $N_3$  radical using the less sensitive u.v. absorption spectrophotometry technique in the  $Cl + N_3Cl$ reaction system and also concluded that the initial step was reaction (1). The rate constant  $k_1$  was determined by Combourieu *et al.*<sup>3</sup> as  $k_1 = 2.3 \times 10^{-11}$  exp (-4600/*RT*), giving  $k_1^{298} = (3.7 \pm 0.6) \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>.

As mentioned above, the  $N_3$  radicals formed in reaction (1) were rapidly removed in the presence of Cl atoms. In the study of Combourieu *et al.*<sup>3</sup> the removal of the N<sub>3</sub> radicals was concurrent with the formation of NCl radicals which were detected at m/e = 49. Clark and Clyne<sup>5</sup> observed intense red chemiluminescence in the  $Cl+N_3Cl$  system, which was identified as emission from the forbidden  $b^{1}\Sigma^{+}-X^{3}\Sigma^{-}$  transition of the NCl radical. Piper et al.<sup>6</sup> also observed this emission in the reaction of Cl atoms with  $N_3$  radicals which were generated by the thermal decomposition of  $NaN_3$ . These observations are consistent with reaction (2):

Cl+N<sub>3</sub> → NCl<sup>\*</sup>+N<sub>2</sub>; 
$$\Delta H_{298}^{\ominus} = -260 \text{ kJ mol}^{-1}$$
. (2)

Recently, Coombe and Pritt<sup>7</sup> have detected an emission spectrum near 1076 nm in the F+Cl<sub>2</sub>+HN<sub>3</sub> system which also showed intense NCl  $(b^{1}\Sigma^{+}-X^{3}\Sigma^{-})$ chemiluminescence. The spectrum has been assigned to the forbidden  $a^{-1}\Delta - X^{-3}\Sigma^{-1}$ transition of the NCl radical. An identical emission spectrum was observed in this laboratory<sup>8</sup> from the  $Cl + N_3Cl$  reaction system. The rate constant of reaction (2) was derived by Jourdain *et al.*<sup>9</sup> using a computer analysis of the data of Combourieu *et al.*<sup>3</sup> as  $k_2^{298} = (1^{+0.5}_{-0.25}) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at 298 K.

It has been proposed<sup>3</sup> that the source of the NCl<sub>2</sub> radical in the Cl+N<sub>3</sub>Cl reaction system is the reaction  $NCl + Cl_2 \rightarrow NCl_2 + Cl (Cl_2 \text{ present from the } Cl_2 + He microwave discharge). However, Piper<sup>10</sup> believes that the <math>NCl + Cl_2$  reaction is energetically feasible only for excited state NCl radicals, e.g. NCl  $(b^{1}\Sigma^{+})$ . For ground-state NCl radicals Piper<sup>10</sup> argues that the reaction is endothermic and would show an appreciable activation energy. Thus at 298 K the reaction would be too slow to explain the rate of formation of the NCl<sub>2</sub> radicals. This conclusion has been disputed by Jourdain *et al.*,<sup>11</sup> who maintain the reaction to be exothermic, but a fuller analysis by MacRobert<sup>12</sup> has shown the available thermodynamic data to be inconclusive.

In the present work this problem has been investigated by monitoring the kinetics of NCl<sub>2</sub> radicals in the  $Cl+N_3Cl$  reaction system with the addition of quenching agents of NCl<sup>\*</sup> such as O<sub>2</sub>.

### **EXPERIMENTAL**

Details of the apparatus and technique have been given elsewhere.<sup>13</sup> In summary, a Pyrex discharge-flow system was linked via a two-stage molecular-beam sampling system to a quadrupole mass spectrometer (V.G. Micromass Q8). The main difference from the previous work<sup>13</sup> was in the design of the flow tube, where a movable injector was used instead of fixed-point injectors. The injector was made of 6 mm diameter Teflon tubing which slid past the O-ring seal with minimal friction. Typical mass-flow conditions were 400  $\mu$  mol s<sup>-1</sup> of helium carrier gas at 1 Torr<sup>+</sup> pressure, which was measured with a capacitance manometer (M.K.S. Baratron, model 222). Reagent flows (e.g. NO diluted in He) were measured by a mass flowmeter (Hastings, model H5-M).

 $\pm 1 \text{ Torr} = 101 \ 325 / 760 \text{ Pa}.$ 

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Oxygen and chlorine atoms were generated in side-arms by microwave discharge (2.45 GHz). The walls of the chlorine atom discharge were treated with H<sub>3</sub>PO<sub>4</sub> to minimize atom recombination. The walls of the flow tube were left untreated and the first-order wall loss of Cl atoms was typically  $10 \text{ s}^{-1}$  ( $\gamma \approx 5 \times 10^{-4}$ ). The presence of the Teflon injector did not affect the rate of decay. The Cl atom concentration was measured using the rapid reaction, Cl+CINO  $\rightarrow$  Cl<sub>2</sub>+NO. An excess of ClNO was added and the removal of ClNO by Cl was monitored at the m/e = 49 (NCl<sup>+</sup>) peak. It was most important in the present work to ensure that impurities from the Cl<sub>2</sub>+He discharge such as O atoms, NO and ClO radicals were kept to negligible concentrations,  $<10^{11}$  cm<sup>-3</sup>. As is described in this work and elsewhere<sup>14</sup> all these species react rapidly with NCl radicals.

#### REAGENTS

Helium and oxygen were obtained from B.O.C. and chlorine from Matheson or B.D.H. The chlorine was degassed at 77 K and kept in a reservoir at 196 K, which provided a convenient vapour pressure of 52 Torr. Nitrosyl chloride was prepared by mixing chlorine with excess nitric oxide. The residual NO was pumped away at 196 K but also removed some ClNO.

Chlorine azide  $(N_3Cl)$  was prepared by a variant of the method used by Spencer<sup>15</sup> to prepare bromine azide. A mixture of chlorine and helium was passed over *ca*. 0.5 g of sodium azide suspended on glass wool in a tube 15 cm in length and 12 mm i.d. The tube was heated to *ca*. 400 K, which gave a higher yield than at 298 K. Some workers have found that the yield could be increased if the NaN<sub>3</sub> was moistened with H<sub>2</sub>O. However, with this method some HN<sub>3</sub> impurity is also produced. At higher temperatures near 600 K, the NaN<sub>3</sub> began to decompose and a high yield of N<sub>3</sub>Cl could be maintained only for a short time. N<sub>3</sub>Cl is highly explosive and cannot be prepared at partial pressures >*ca*. 20 Torr without a strong risk of spontaneous ignition. It will invariably explode when allowed to vaporize after being condensed in a trap. Therefore the N<sub>3</sub>Cl was prepared *in situ* and passed directly into the flow system, so that the partial pressure of N<sub>3</sub>Cl in the oven never exceeded 100 mTorr. The yield of the reaction, which can be written as

$$Cl_2(g) + NaN_3(s) \rightarrow NaCl(s) + N_3Cl(g)$$

yield = 
$$[N_3Cl]_{formed}/[Cl_2]_{into over}$$

was usually ca. 50%, and steady production of N<sub>3</sub>Cl could be maintained for several hours. The initial yield may have been higher because N<sub>3</sub>Cl does decompose at these temperatures.<sup>3</sup> The yield was fairly sensitive to the flow conditions. It was highest when the He flowrate was ca. 10  $\mu$  mol s<sup>-1</sup> and the Cl<sub>2</sub> flowrate <0.1  $\mu$  mol s<sup>-1</sup>, although it was not significantly reduced at much higher Cl<sub>2</sub> flowrates. The He flow also prevented back-diffusion of other reagents present in the flow tube into the oven, and therefore the He flow was never switched off when the oven was in use. The Cl<sub>2</sub> flow could be switched on and off repeatedly without any marked deterioration in the yield.

In conclusion, this technique is ideal for use in a discharge-flow system and has many advantages over the techniques used by other workers. Fluorine and bromine azide can also be prepared in the same way though with lower yields. The production of N<sub>3</sub>F seemed to require a higher He flowrate through the oven. Iodine azide, N<sub>3</sub>I, cannot be prepared by this method because it would condense immediately after leaving the oven, and this would lead to an explosion. The preparation and reactions of the halogen azides have been reviewed by Dehnicke.<sup>16</sup> The value for the heat of formation of N<sub>3</sub>Cl(g) has been reported<sup>17</sup> as  $\Delta H_{298}^{\ominus} = 390 \pm 8$  kJ mol<sup>-1</sup>.

#### DETECTION OF N<sub>3</sub>Cl AND CALIBRATION OF [N<sub>3</sub>Cl]

The mass spectrum of N<sub>3</sub>Cl does not exhibit a parent peak at m/e = 67. Therefore the fragment peaks at m/e = 42 (N<sub>3</sub><sup>+</sup>) and m/e = 49, 51 (NCl<sup>+</sup>) were used to detect N<sub>3</sub>Cl. The sensitivity of the m/e = 42 peak was several times greater than that for the m/e = 49 peak.

 $[N_3Cl]$  was calibrated using the production of NO on addition of a large concentration of oxygen atoms (*ca.*  $10^{14}$  cm<sup>-3</sup>), which resulted in a stoichiometric conversion of N<sub>3</sub>Cl to NO. The reaction was slow and was highly dependent on the concentration of the unreacted  $Cl_2$  present from the NaN<sub>3</sub> oven. The mechanism of the reaction may be written

$$O+Cl_{2} \rightarrow ClO+Cl; \qquad k_{298} = 4.2 \times 10^{-14} \text{ cm}^{3} \text{ s}^{-1}, {}^{18}$$
$$O+N_{3}Cl \rightarrow N_{3}+ClO; \qquad \Delta H_{298}^{\ominus} = -121 \text{ kJ mol}^{-1}$$
$$O+ClO \rightarrow Cl+O_{2}$$
$$Cl+N_{3}Cl \rightarrow N_{3}+Cl_{2}.$$

The O atoms react with the  $Cl_2$  and the CIO radicals to form Cl atoms, which then react rapidly with the N<sub>3</sub>Cl. From the data it is not clear whether the  $O+N_3Cl \rightarrow ClO+N_3$  reaction actually occurs. The rate constant certainly cannot be significantly larger than that for the  $O+Cl_2$  reaction. A further study using low initial N<sub>3</sub>Cl and Cl<sub>2</sub> concentrations (<10<sup>12</sup> cm<sup>-3</sup>) to minimise the extent of the secondary Cl+N<sub>3</sub>Cl reaction is needed.

The N<sub>3</sub> radicals react rapidly with the O and Cl atoms:  $O+N_3 \rightarrow NO+N_2$ ,<sup>6</sup> Cl+ N<sub>3</sub>  $\rightarrow NCl+N_2$ .<sup>3</sup> The NCl radicals that are formed in the Cl+N<sub>3</sub> reaction react rapidly with O atoms to form NO. The rate of removal of the N<sub>3</sub> and NCl radicals was such that the extent of recombination or disproportionation of the radicals was negligible and the ClO concentration was too low to have any effect. Therefore it is clear the O+N<sub>3</sub>Cl/Cl<sub>2</sub> reaction can be used to calibrate the N<sub>3</sub>Cl concentration, with [N<sub>3</sub>Cl]<sub>removed</sub> = [NO]<sub>formed</sub>. A plot of the change in the N<sub>3</sub>Cl signal at m/e = 49 as a function of the concentration of NO produced on the addition of O atoms was linear. The amount of N<sub>3</sub>Cl formed in the oven was in close agreement with the amount of Cl<sub>2</sub> that was removed in the oven.

#### RESULTS

The NCl and NCl<sub>2</sub> radicals were observed downstream from the Cl+N<sub>3</sub>Cl reaction zone. The signal at m/e = 86 was used to detect NCl<sub>2</sub> instead of the more intense signal at m/e = 84 owing to the high background signal at the latter mass peak. A search for more chlorinated molecules such as NCl<sub>3</sub> or N<sub>2</sub>Cl<sub>3</sub>, which would have produced fragment NCl<sub>2</sub><sup>+</sup> signals, proved fruitless. Therefore the NCl<sub>2</sub><sup>+</sup> signal resulted only from NCl<sub>2</sub> radicals. However, the signals at m/e = 49, 51 were composed of both NCl<sup>+</sup> from the NCl itself and the NCl<sup>+</sup> fragment from NCl<sub>2</sub>. This was clearly shown by the change in the time dependence of the m/e = 49 signal on the reduction of the electron energy from 30 to 15 eV. At 15 eV the relative contribution from the fragment NCl<sup>+</sup> was much lower. The complete removal of N<sub>3</sub>Cl, which also contributes to the m/e = 49, 51 peaks, by the excess of Cl atoms was shown by the absence of a signal at m/e = 42. However, the systematic detection of NCl radicals using low electron energies was impractical due to the reduced sensitivity.

The kinetic behaviour of the signals at m/e = 49 and m/e = 86 could not be compared at short reaction times due to interference at m/e = 49 from unreacted N<sub>3</sub>Cl. Although N<sub>3</sub>Cl may also be detected at m/e = 42 (N<sup>+</sup><sub>3</sub>) there was interference at short reaction times from the N<sub>3</sub> radical itself.

### MECHANISM OF THE PRODUCTION OF $NCl_2$ radicals

As mentioned in the introduction it has been speculated<sup>6</sup> that metastable excited state NCl<sup>\*</sup> radicals may react with Cl<sub>2</sub> (present from the Cl<sub>2</sub>+He discharge and the Cl+N<sub>3</sub>Cl  $\rightarrow$  Cl<sub>2</sub>+N<sub>3</sub> reaction) to produce NCl<sub>2</sub> radicals whereas ground-state NCl ( $X^{3}\Sigma^{-}$ ) radicals are unreactive towards Cl<sub>2</sub>. The identity of the precursor to

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the NCl<sub>2</sub> radicals was tested in this work by monitoring changes in the NCl<sub>2</sub> signal on addition of NCl<sup>\*</sup> quenchers such as  $O_2$ , NO and  $Cl_2$ .

### ADDITION OF Cl<sub>2</sub>

The NCl<sub>2</sub> signal at m/e = 86 was observed to increase if Cl<sub>2</sub> was added through an inlet near the Cl+N<sub>3</sub>Cl reaction zone. However, if Cl<sub>2</sub> was added further downstream after all the N<sub>3</sub>Cl and N<sub>3</sub> had reacted, the NCl<sub>2</sub> signal was not affected. The m/e = 49 signal also increased on addition of Cl<sub>2</sub>, in accord with the increased contribution of the fragment NCl<sup>+</sup> from the NCl<sub>2</sub> radicals (electron energy 30 eV). Note that the absolute effect of Cl<sub>2</sub> on the signal is difficult to quantify owing to the presence of undissociated Cl<sub>2</sub> from the Cl<sub>2</sub> + He discharge.

### ADDITION OF $O_2$ AND NO

The experiments with the addition of  $O_2$  and NO proved to be very significant, particularly in the case of  $O_2$ . For the addition of an amount of  $O_2$  equal to that of the Cl<sub>2</sub> present from the Cl<sub>2</sub>+He discharge, the NCl<sub>2</sub> signal was reduced by a factor of ten. This dramatic reduction in the NCl<sub>2</sub> signal was observed for addition of  $O_2$  at the Cl+N<sub>3</sub>Cl mixing point. As for addition of Cl<sub>2</sub>, there was no effect on the NCl<sub>2</sub> signal if  $O_2$  was added at long reaction times, which demonstrates that NCl<sub>2</sub> radicals are unreactive towards  $O_2$ . Thus addition of  $O_2$  must result in the removal of a short-lived precursor to NCl<sub>2</sub>.

The addition of NO also caused a large decrease in the NCl<sub>2</sub> signal when added at the Cl+N<sub>3</sub>Cl mixing point. However, NO is known to react rapidly with both N<sub>3</sub> and NCl radicals<sup>14,19</sup> and these species are likely to be involved in the reaction(s) leading to NCl<sub>2</sub> formation; but with O<sub>2</sub> there was no evidence of chemical interaction: no N<sub>2</sub>O, NO<sub>2</sub> or NO was formed, the expected products of reactions such as N<sub>3</sub>+O<sub>2</sub> or NCl+O<sub>2</sub>.

The absence of a chemical interaction with  $O_2$  shows that the  $O_2$  removed the NCl<sub>2</sub> precursor by a physical process. These observations confirm Piper's suggestion<sup>10</sup> that excited state NCl<sup>\*</sup> radicals are the precursors to the NCl<sub>2</sub> radicals. The addition of  $O_2$  quenches the NCl<sup>\*</sup> radicals and suppresses NCl<sub>2</sub> formation:

$$NCl^* + Cl_2 \rightarrow NCl_2 + Cl$$
$$NCl^* + O_2 \rightarrow NCl + O_2.$$

Direct evidence of the quenching of the NCl  $(b^{1}\Sigma^{+})$  and  $(a^{1}\Delta)$  states by O<sub>2</sub> leading to the production of excited-state singlet O<sub>2</sub> has been obtained recently and will be described in more detail in a later paper.<sup>20</sup>

With the removal of NCl<sub>2</sub> radicals from the system the signal that was still observed at m/e = 49 was due only to NCl radicals (after the complete removal of N<sub>3</sub>Cl). The addition of large concentrations of  $O_2 > 5 \times 10^{14}$  cm<sup>-3</sup>, suppressed the NCl<sub>2</sub> concentration by two orders of magnitude<sup>20</sup> so that [NCl<sub>2</sub>] « [NCl]. Therefore the kinetics of ground-state  $X^{3}\Sigma^{-}$  radicals could be studied specifically without interference from NCl<sub>2</sub> radicals, merely by the addition of  $O_2$ .

NCl+NCl 
$$\rightarrow$$
 N<sub>2</sub>+2Cl;  $\Delta H_{298}^{\ominus} = -300 \text{ kJ mol}^{-1}$ . (3)

The kinetics of the bimolecular disproportionation of ground-state  $(X^{3}\Sigma^{-})$  NCl radicals were studied in the presence of a large excess of O<sub>2</sub> so that [NCl<sub>3</sub>]  $\gg$  [NCl<sub>2</sub>]<sub>0</sub>.

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FIG. 1.—Kinetics of the NCl+NCl  $\rightarrow$  N<sub>2</sub>+2Cl reaction at 295 K: (a) time dependence of reciprocals of NCl signal; (b) time dependence of [NCl]<sup>-1</sup> using the O+NCl  $\rightarrow$  NO+Cl reaction to determine [NCl].

The concentration of the NCl radical was determined using reaction (4)

$$O + NCl \rightarrow NO + Cl$$
 (4)

for which the rate constant is  $k_4^{295} = 1.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  [see section on reaction (4)]. With an excess of O atoms therefore,  $[\text{NCI}]_0 = [\text{NO}]_{\text{formed}}$ . The O atom concentration was *ca*.  $3 \times 10^{13} \text{ cm}^{-3}$ . Thus complete removal (>99%) of NCl occurred within 1.5 ms and the NCl concentration was effectively 'frozen' in terms of the NO produced. In the time between the O atom addition and the sampling pinhole, negligible conversion of NO to NO<sub>2</sub> occurred (<5%), through the reaction NO+ClO  $\rightarrow$  NO<sub>2</sub>+Cl. The ClO radicals were formed *via* the reaction O+Cl<sub>2</sub>  $\rightarrow$  ClO+Cl. Note that the O atoms substantially removed any ClO or NO<sub>2</sub> that was formed.

The kinetics of reaction (3) are described by the equations

$$-d[NCl]/dt = 2k_3[NCl]^2$$
$$\frac{1}{[NCl]} - \frac{1}{[NCl]_0} = 2k_3t.$$

Fig. 1(a) shows two linear decay plots of  $(NCl \text{ signal})^{-1}$  as a function of time. The plots are parallel thus demonstrating that the kinetics of NCl conform to the above equation. The rate constant  $k_3$  was obtained by the following method. The N<sub>3</sub>Cl

injector was initially placed *ca.* 7 cm upstream from the point of the O atom addition, so that reactions (1) and (2) went to completion. The NO yield was measured and the injector was then withdrawn a further x cm. Thus [NCI] was measured at a series of reaction times. The duration of each experiment was a few minutes so that the effects of any drift in the NCl or NO signals or any variation in the N<sub>3</sub>Cl yield from the NaN<sub>3</sub> oven were small. The NO signal was calibrated after each experimental run. The precise position at which NCl was converted to NO was uncertain by  $\pm 1$  cm, as complete mixing of the oxygen atoms introduced from a side-arm occurred over a distance of 1-2 cm, as observed from the intensity distribution of the air afterglow,  $O+NO+M \rightarrow NO_2^2+M$ , on addition of NO. The error in the contact time between the injector and the O-atom addition point was therefore subject to an error of *ca.*  $\pm 1.5$  ms.

Fig. 1(b) shows plots of  $[NCl]^{-1}$  as a function of time. The decay plots are linear over reaction times of up to 25 ms, and no significant variation in the gradient occurs with different values of  $[NCl]_0$ . The following initial conditions were used:

$$[Cl]_0 \ge 1 \times 10^{14} \text{ cm}^{-3}, [N_3Cl] < 5 \times 10^{13} \text{ cm}^{-3} \text{ and } [O_2] \ge 5 \times 10^{14} \text{ cm}^{-3}.$$

The origin t = 0 corresponds to a Cl+N<sub>3</sub>Cl reaction time of ca. 12 ms. According to the results of Combourieu et al.<sup>3</sup> and Jourdain et al.<sup>9</sup> this is sufficient time to allow reactions (1) and (2) to go to 99% completion at the above concentrations. The complete removal of N<sub>3</sub> was deduced from the lack of any variation in the gradients of the plots when the value of [Cl] was increased from  $1.0 \times 10^{14}$  to  $1.6 \times 10^{14}$  cm<sup>-3</sup>. The decay of [Cl] over the maximum reaction time used was ca. 15% and did not affect the results. The linearity of the plots at long reaction times indicates the absence of first-order processes such as NCl wall removal.

Table 1 lists the 14 data points. The initial NCl concentration was in the range  $1.8 \times 10^{12} \leq [\text{NCl}]_0/\text{cm}^{-3} \leq 1.0 \times 10^{13}$ . There was no significant trend in the values of  $k_3$  with [NCl]<sub>0</sub>, thus demonstrating overall second-order behaviour. The mean of the 14 data points gives

$$k_3 = (8.1 \pm 1.8) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$
 at 295 K(2 $\sigma$ ).

No change in the results was found when  $[O_2]$  was increased, which confirmed the negligible effect of the residual NCl<sub>2</sub> present.

## RATE CONSTANT FOR THE REACTION $O+NCl \rightarrow NO+Cl; \quad \Delta H^{\ominus}_{298} = -326 \text{ kJ mol}^{-1}.$ (4)

Reaction (4) was studied by adding an excess of O  $({}^{3}P)$  atoms to a flow of ground-state NCl radicals. The rate of removal of the NCl was monitored at m/e = 49. A large concentration of O<sub>2</sub> was present (>5×10<sup>14</sup> cm<sup>-3</sup>) to prevent the formation of NCl<sub>2</sub> radicals. The reaction was found to be very rapid as expected for an atom+radical reaction and consequently it proved difficult to obtain the desirable pseudo-first-order conditions for which

$$\ln \left( [\text{NCl}]_0 / [\text{NCl}] \right) = k_4 [\text{O}]_{\text{mean}} t.$$

Low initial stoichiometries  $[O]_0/[NCl]_0$  had to be employed, which required large corrections to obtain  $[O]_{mean}$ . Therefore the results presented are subject to relatively large errors. In the experiments to be described, the value of t was held

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run	$[NCl]_0/10^{12} \text{ cm}^3$	$k_3/10^{-12} \mathrm{cm}^3 \mathrm{s}^{-1}$	
1	5.2	7.4	
2	5.5	7.3	
3	6.9	6.3	
4	4.2	7.1	
5	3.1	8.3	
6	5.0	8.4	
7	3.9	9.1	
8	1.8	8.2	
9	2.8	8.7	
10	2.2	10.0	
11	7.5	8.3	
12	9.7	7.8	
13	10.0	7.9	
14	9.1	8.1	

TABLE 1.—RATE CONSTANT FOR REACTION (3)

constant (according to the fixed position of the O<sub>2</sub> discharge) and the value of  $[O]_0$  was varied. The O (<sup>3</sup>P) atoms were generated in a O<sub>2</sub>+He discharge. Note that the alternative source, N+NO  $\rightarrow$  O+N<sub>2</sub>, could not be used since NO reacts with NCl radicals.<sup>14</sup> For the same reason it was important that the Cl<sub>2</sub>+He and O<sub>2</sub>+He discharges did not produce impurity NO.

The value of  $[O]_0$  was calibrated by measuring the removal of  $NO_2$  on addition of the O atoms

$$O + NO_2 \rightarrow NO + O_2$$
.

The calibration was performed in the presence of  $Cl_2$  to scavenge any impurity H atoms from the  $O_2$ +He discharge. The extent of wall removal of the O atoms over the reaction time of 10 ms was small at <5%. The removal of O atoms by the reaction  $O+O_2+M \rightarrow O_3+M$  was negligible. However, the O atoms were removed by  $Cl_2$  and ClO radicals, according to the reactions:  $O+Cl_2 \rightarrow ClO+Cl$ ,  $O+ClO \rightarrow Cl+O_2$ . Thus it was important to keep  $[Cl_2]$  as low as possible. In fact this did not pose a serious problem since conversion of N<sub>3</sub>Cl to NCl could take place over 30 ms and thus relatively low [Cl] and hence  $[Cl_2]$  could be used. Over the reaction time of 10 ms less than 10% of the O atoms were consumed by these reactions.

The NCl signal at m/e = 49 was calibrated using reaction (4). An excess of O atoms was added with  $[O] \approx 1 \times 10^{13}$  cm<sup>-3</sup>, and the formation of NO was monitored so that  $[NCl] = [NO]_{produced}$ . In order to obtain adequate NO signals, the values of [NCl] were *ca*.  $(1-2) \times 10^{12}$  cm<sup>-3</sup>. However, in the absence of O atoms, a small amount of NCl was removed by reaction (3) between the O-atom discharge and the sampling pinhole. Thus the observed NCl signal (in the absence of O atoms) did not correspond to [NCl] determined at the O<sub>2</sub> discharge. Therefore [NCl] (+O atoms) was corrected downwards to allow for the removal of NCl using the value of  $k_3$  determined in this work.

Table 2 lists the initial concentrations. The typical value of  $[NCl]_0$  was ca.  $4 \times 10^{11}$  cm<sup>-3</sup>. At such a concentration the correction required for NCl disproportionation was negligible. Similarly no correction to [NCl] (+O atoms) was necessary

run	$[NCl]_0/10^{11} \text{ cm}^{-3}$	$[O]_0/10^{12}  \mathrm{cm}^{-3}$	[NCl] <sub>0</sub> /[NCl]	$k_4/10^{-10} \mathrm{cm}^3 \mathrm{s}^{-1}$
1	5.4	3.3	15.0	0.97
2	3.5	2.1	6.4	1.0
3	3.9	1.0	4.3	1.8
4	5.0	2.0	11.0	1.4
5	3.6	1.1	3.2	1.3
6	4.3	1.5	4.7	1.2
7	5.0	2.2	6.1	0.95
8	5.0	2.5	15.7	1.3

TABLE 2.—RATE CONSTANT FOR REACTION (4)

for the consumption of NCl by the NO produced in reaction (4). Although a small fraction (ca. 5%) of the m/e = 49 signal resulted from NCl<sub>2</sub> no correction was necessary since the rate constant for the O+NCl<sub>2</sub> reaction is similar to that for the O+NCl reaction.<sup>12</sup> The initial concentration of the O atoms was varied in a limited range,  $1.0 \le [O]_0/10^{12}$  cm<sup>-3</sup>  $\le 3.3$ . Large corrections were necessary to obtain  $[O]_{mean}$ , and the resulting values for  $k_4$  are dependent on the accuracy of the [NCl]\_0 calibration. The estimated errors for [NCl]\_0 are  $\pm 20\%$  and for  $[O]_0 \le \pm 20\%$ . A reaction time of  $10 \pm 1$  ms was used. The uncertainty results mainly from the diffuse mixing at the point of addition of the O atoms. The mean value for  $k_4$  was

 $k_4 = (1.2 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 295 K(2 $\sigma$ ).

Despite the limited initial stoichiometry, the above value is not expected to be in error by more than a factor of two.

### DISCUSSION

The bimolecular disproportionation of ground-state NCl ( $X^{3}\Sigma^{-}$ ) radicals has been shown to be rapid at 295 K, with a rate constant  $k = (8.1 \pm 1.8) \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> This value is in agreement with the lower limit of  $1.6 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> given by Clark and Clyne<sup>20</sup> and is within the range  $(0.5-1.0) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> given by Jourdain et al.<sup>9</sup> who used computer modelling to analyse the temporal profile of the NCl signal in the  $Cl+N_3Cl$  system. However, there are several serious faults in the mechanism which Jourdain et al.<sup>9</sup> used. First, no distinction was made between the ground and metastable excited states of the NCl radical. As shown in this work, both are present in the  $Cl+N_3Cl$  system. The kinetics of the states differ considerably: NCl\* reacts with Cl<sub>2</sub> to form NCl<sub>2</sub> radicals, NCl\* + Cl<sub>2</sub>  $\rightarrow$  NCl<sub>2</sub> + Cl, whereas ground-state NCl  $(X^{3}\Sigma^{-})$  is unreactive, NCl  $(X^{3}\Sigma^{-}) + Cl_{2} \not\rightarrow NCl_{2} + Cl_{1}$ The latter reaction is most likely endoergic with an appreciable activation energy. It is probable that the detection sensitivities for the states are different, thus the signal observed may not be proportional to the sum of the concentrations. Secondly, no attempt was apparently made to determine the concentration of NCl<sub>2</sub> present. It seems that Jourdain et al.<sup>9</sup> assumed that [NCl] » [NCl<sub>2</sub>], whereas under certain conditions they may be similar.<sup>21</sup> Nor was it adequately demonstrated that the contributions to m/e = 49 from the NCl<sub>2</sub> was entirely negligible at 20 eV. A further error arises from the regeneration of NCl via the reaction  $Cl + NCl_2 \rightarrow NCl + Cl_2$ .<sup>21</sup>

### ELEMENTARY REACTIONS OF THE NCI RADICAL

Therefore it is concluded that the value obtained by Jourdain et al.<sup>9</sup> is unreliable and the agreement with the present work is fortuitous.

The products of reaction (3) are either  $N_2 + Cl_2$  or  $N_2 + 2Cl$ . Jourdain *et al.*<sup>9</sup> assumed the former, but following the work of Cheah *et al.*<sup>22</sup> on the NF radical, the latter products are more probable. Cheah *et al.*<sup>22</sup> determined the mechanism and rate constant for the bimolecular decay of NF radicals produced in the  $H + NF_2$  reaction as

NF+NF 
$$\rightarrow$$
 N<sub>2</sub>+2F;  $k^{298} = (7.0 \pm 3.5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

The disproportionation of NF radicals is therefore an order of magnitude more rapid than for NCl radicals. They speculated that a weakly bound N-N-F species is formed initially which collisionally dissociates to  $N_2 + F$ . The production of 2Cl atoms instead of  $Cl_2$  in reaction (3) is relevant to the kinetic analysis of Combourieu et al.<sup>3</sup> In their determination of the rate constant  $k_1$  for reaction (1) they found that at lower  $[Cl]_0/[N_3Cl]_0$  ratios, with  $[Cl]_0 > [N_3Cl]_0$ , the apparent rate constant increased towards  $2k_1$ . They interpreted this effect in terms of the secondary reactions: NCl + N<sub>3</sub>Cl  $\rightarrow$  N<sub>2</sub> + N<sub>2</sub><sup>\*</sup> + Cl<sub>2</sub>, N<sub>2</sub><sup>\*</sup> + N<sub>3</sub>Cl  $\rightarrow$  2N<sub>2</sub> + NCl. However, there is no evidence in the present work to support the occurrence of these reactions. In any case, the first reaction is multicentred and the rate constant for a reaction of this type is expected to be small. Alternatively, the results of Combourieu et al. may possibly be explained by the regeneration of Cl atoms via reaction (3), for which  $[NCl]_{removed} = [Cl]_{formed}$ . The effect of the regeneration of Cl atoms on the kinetics of the  $Cl+N_3Cl$  reaction should be most significant when  $[Cl]_0$  is only slightly in excess of  $[N_3Cl]_0$ , so that a large fraction of  $[Cl]_0$  is consumed in reactions (1) and (2). This explanation though cannot be firmly established on the available data. The results of Jourdain *et al.*<sup>9</sup> for the rate constant of N<sub>3</sub> recombination-disproportionation, namely  $(5-8) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> (298 K), may also be in error as a result of the regeneration of Cl atoms which then remove  $N_3$  via reaction (2).

The rate constant (295 K) for reaction (4),  $O + NCI \rightarrow NO + CI$ , has been measured as  $(1.2 \pm 0.6) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. The rate constant is slightly larger than that found for the  $N + NCI \rightarrow N_2 + CI$  reaction,  $k^{295} = 6 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.<sup>12</sup> As expected for atom + radical reactions, the rate constants are large. Reaction (4) has been used to calibrate NCl concentrations in terms of the NO produced. Piper *et al.*<sup>6</sup> have used the similar reaction of N<sub>3</sub> radicals with O atoms,  $O + N_3 \rightarrow NO + N_2$ , to calibrate N<sub>3</sub> concentrations. The rate constant for this reaction was estimated<sup>6</sup> as *ca.*  $10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> at 298 K, which is a factor of ten lower than that for reaction (4). Piper *et al.*<sup>6</sup> observed emission from the NO ( $A^2\Sigma^+$ ) state whereas reaction (4) is insufficiently exoergic to excite the A state.

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