Elementary Reactions of the NCl Radical
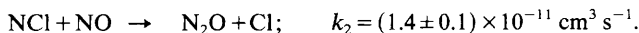
Part 2.—Kinetics of the NCl+ClO and NCl+NO Reactions

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The reaction kinetics of ground-state $NCl(X\,^3\Sigma^-)$ radicals have been studied in a discharge–flow system at 295 K. The time-resolved decay of NCl in the presence of an excess of $ClO(X\,^2\Pi)$ and $NO(X\,^2\Pi)$ was followed using molecular-beam mass spectrometry and compared with those for analogous radical–radical reactions.

$$NCl+ClO \rightarrow ClNO+Cl; \qquad k_1 = (2.3 \pm 0.2) \times 10^{-11}\ cm^3\ s^{-1}$$

$$NCl+NO \rightarrow N_2O+Cl; \qquad k_2 = (1.4 \pm 0.1) \times 10^{-11}\ cm^3\ s^{-1}.$$

Observations supporting the indicated reaction products are discussed. These are the first determinations of the rate constants for the above reactions. The values determined are compared with those for analogous radical–radical reactions.

The kinetics of nitrogen halide radicals (NF, NCl and NBr) have been studied in several laboratories recently.[1-3] Interest has focused mainly on the properties of the metastable $^1\Delta$ and $^1\Sigma^+$ excited states of these radicals, which undergo energy-transfer processes similar to those known for the analogous $^1\Delta_g$, $^1\Sigma_g^+$ states of O_2. Efficient means of producing both ground- and excited-state nitrogen halide radicals have been developed using either photolysis or chemical reactions, and chemiluminescence resulting from the weak spin-forbidden transitions from the singlet states to the ground $X\,^3\Sigma^-$ state has been observed in several cases.[3,4] Sensitive detection of the ground state itself is more problematic, and correspondingly less attention has been paid to the ground-state kinetics. Laser-induced fluorescence appears to be impractical at present as no suitable allowed transitions to upper triplet states have yet been identified for any of the nitrogen radicals. However, mass spectrometry has recently been employed in the detection of NCl radicals with molecular-beam sampling from a discharge–flow system in Part 1 of this work.[5] Rate constants were measured for the second-order decay of NCl radicals, $NCl+NCl \rightarrow N_2+2Cl$, and the reaction with oxygen atoms, $O+NCl \rightarrow NO+Cl$. The high sensitivity for detection of the NCl radical using mass spectrometry enables kinetic studies of rapid bimolecular reactions to be carried out. In this work we report measurements at 295 K under pseudo-first-order conditions on the radical–radical reactions

$$NCl+ClO \rightarrow ClNO+Cl; \qquad \Delta H^\circ = -196\ kJ\ mol^{-1} \tag{1}$$

and

$$NCl+NO \rightarrow N_2O+Cl; \qquad \Delta H^\circ = -153\ kJ\ mol^{-1}. \tag{2}$$

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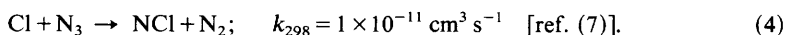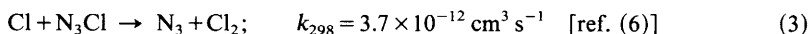
EXPERIMENTAL

A quadrupole mass spectrometer (V. G. Micromass Q8) was coupled to the discharge–flow system *via* a two-stage stainless-steel sampling system. An improved design of the sampling system incorporating larger pumping speeds and thus larger sampling pinholes resulted in a higher detection sensitivity of NCl than in the previous study.[5] A cooled shroud consisting of a liquid-N_2 reservoir attached to a copper cylinder surrounded the quadrupole analyser and had the effect of substantially reducing the intensity of the mass spectrum of the background residuals, thus aiding detection of species such as N_2O at m/e 44, where a high background signal had previously limited sensitivity. A channeltron multiplier was used and signals were analysed by ion counting. The lower limit to detection of NCl was *ca.* 3×10^9 cm^{-3} at a signal to noise ratio of 1:1.

The flow tube (Pyrex, 26 mm i.d.) incorporated a moveable PTFE injector (6 mm o.d.) for addition of reagents such as N_3Cl. Typical mass-flow conditions were 400 μmol s^{-1} of helium carrier gas at 1 Torr† 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). Errors in measurement of concentration are estimated to amount to 10%.

Chlorine and oxygen atoms were generated in side-arms by a microwave discharge (2.45 GHz). The walls of the chlorine-atom discharge tube were treated with H_3PO_4 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 s^{-1} ($\gamma \approx 5 \times 10^{-4}$, where γ is the fraction of collisions leading to recombination). The presence of the PTFE injector did not affect the chlorine-atom concentration, which was measured using the rapid titration reaction $Cl + ClNO \rightarrow Cl_2 + NO$. An excess of ClNO was added and the removal of ClNO by Cl was monitored at the m/e 49 (NCl$^+$) fragment peak since the parent ClNO peak intensity was too weak. It was most important in the present work to ensure that impurities from the $Cl_2 + He$ discharge such as O atoms, NO and ClO were kept to negligible concentrations ($< 10^{11}$ cm^{-3}).

### GENERATION AND CALIBRATION OF THE NCl RADICAL

Details of the generation, detection and calibration of NCl have been described in Part 1.[5] The rapid reaction of an excess of Cl atoms with chloride azide (N_3Cl) was used to generate NCl:

$$Cl + N_3Cl \rightarrow N_3 + Cl_2; \qquad k_{298} = 3.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \quad [\text{ref. (6)}] \tag{3}$$

$$Cl + N_3 \rightarrow NCl + N_2; \qquad k_{298} = 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \quad [\text{ref. (7)}]. \tag{4}$$

With $[Cl] \approx 1 \times 10^{14}$ cm^{-3} an excess of Cl atoms was mixed with the N_3Cl and O_2 flows *ca.* 20 ms upstream from the reaction zone, thus allowing complete formation of NCl. Removal of NCl on the walls of the flow tube was negligible. Addition of O_2 (*ca.* 5×10^{14} cm^{-3}) quenches the initially formed metastable excited $a\,^1\Delta$ and $b\,^1\Sigma^+$ states of NCl[8] and suppresses the rapid reaction of excited NCl with Cl_2:

$$NCl(a\,^1\Delta, b\,^1\Sigma^+) + Cl_2 \rightarrow NCl_2 + Cl. \tag{5}$$
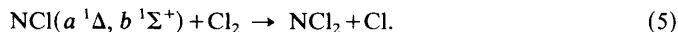
The reaction of ground-state NCl with Cl_2 is slow, with an estimated upper limit at 295 K for the rate constant as $k < 6 \times 10^{-15}$ cm^3 s^{-1},[4] and can therefore be neglected. Formation of singlet O_2 is observed concurrent with removal of NCl*[4] and has been assigned to the energy-transfer process
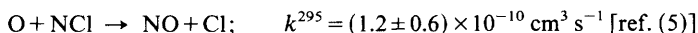
$$NCl^* + O_2 \rightarrow NCl + O_2^*.$$
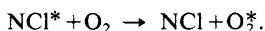
The presence of singlet O_2 is not important in this study, where the concentration of NCl generated is low, $< 5 \times 10^{11}$ cm^{-3}.

NCl radicals were detected at m/e 49, 51 in the expected 3:1 isotopic ratio from the ^{35}Cl and ^{37}Cl isotopes using an electron energy of 25 eV. The N_3Cl and NCl_2 species also contribute
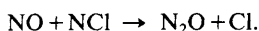
† 1 Torr $\equiv$ 101 325/760 Pa.

to these signals through fragmentation for electron energies > 16 eV. N_3Cl fragmentation was not a problem, due to complete removal of N_3Cl upstream of the reaction zone. However, the m/e 49 signal due to fragmentation of the residual NCl_2 from reaction (5) had to be taken into account. Therefore, signals were corrected for the NCl_2 contribution, which although small at *ca.* 2% of the initial signal did become important for large decays in [NCl]. The NCl_2 contribution to the m/e 49 signal was first found by adding NO, which removed the NCl radical but did not react with NCl_2. Then the NCl_2 radicals were monitored at m/e 84 and the reduction observed when O_2 was added was applied to the m/e 49 NCl_2 fragment signal. Thus the relative contributions to m/e 49 from NCl and NCl_2 in the presence of O_2 were known. The resulting logarithmic plots for the decay of [NCl] were found to be linear for decay by a factor of 50. Since NCl_2 radicals react rapidly with ClO radicals no correction was required in the case of the NCl + ClO study.

The concentration of NCl radicals was calibrated using either of the two reactions:

$$O + NCl \rightarrow NO + Cl; \qquad k^{295} = (1.2 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ [ref. (5)]}$$

or

$$NO + NCl \rightarrow N_2O + Cl.$$

In each case an excess of O atoms or NO was added which rapidly converted NCl into a stable species, NO or N_2O, whose signal was calibrated using the flowmeter. Sensitivity for detection of NO and N_2O was sufficient to determine concentrations of 5×10^{11} cm^{-3} to $\pm 10\%$ accuracy. The calibrations were performed near the sampling orifice using low concentrations of NCl (*ca.* 5×10^{11} cm^{-3}), for which corrections arising from NCl disproportionation were small:

$$NCl + NCl \rightarrow N_2 + 2Cl; \qquad k^{295} = (8.1 \pm 1.8) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \text{ [ref. (5)]}.$$
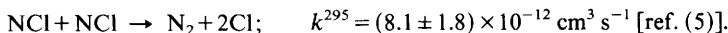
GENERATION AND CALIBRATION OF THE ClO RADICAL

$ClO(X\,^2\Pi)$ radicals were generated *via* the rapid reaction of Cl atoms with chlorine dioxide, OClO:

$$Cl + OClO \rightarrow ClO + ClO; \qquad k^{298} = (5.9 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ [ref. (9)]}.$$
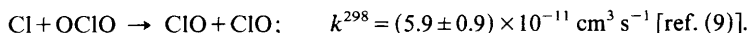
The reaction is virtually thermoneutral, $\Delta H^\circ = -6.7$ kJ mol^{-1}, and there is little initial internal excitation in the ClO radicals. The fact that both NCl and ClO could be generated by reactions involving only one atomic species, Cl atoms, greatly simplified the study of reaction (1), NCl + ClO $\rightarrow$ products. Relative flowrates of dilute OClO + He mixtures ($> 95\%$ He) were measured using a heat-capacitance flow transducer. During a run, however, the OClO flow bypassed the flow transducer since a proportion of the OClO decomposed within the heated section of the transducer. In the bypass mode the actual flowrate was larger by *ca.* 10% for the same needle-valve setting since there is a small pressure drop when the gas flows through the transducer. The correction required was found by flowing Cl_2 + He mixtures at similar flowrates and pressures through and around the flow transducer and monitoring the Cl_2^+ signal.

The absolute calibration of [ClO] was made for two preset OClO flowrates using the rapid titration reaction NO + ClO $\rightarrow$ NO$_2$ + Cl with an excess of NO present so that $[ClO]_0 = [NO_2]_{\text{formed}}$ and the NO$_2$ signal at m/e 46 was then calibrated as a function of NO$_2$ + He flowrates.

REAGENTS

Helium and oxygen were obtained from B.O.C. and chlorine (99.9% purity) 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 an excess of nitric oxide (Matheson). The residual NO was pumped away at 196 K. Chlorine azide (N_3Cl) was prepared as described in Part 1.[5] Chlorine dioxide (OClO) was prepared from moist mixtures of potassium chlorate with oxalic acid. Traces of water vapour were removed with P_2O_5. The OClO was then diluted with helium.
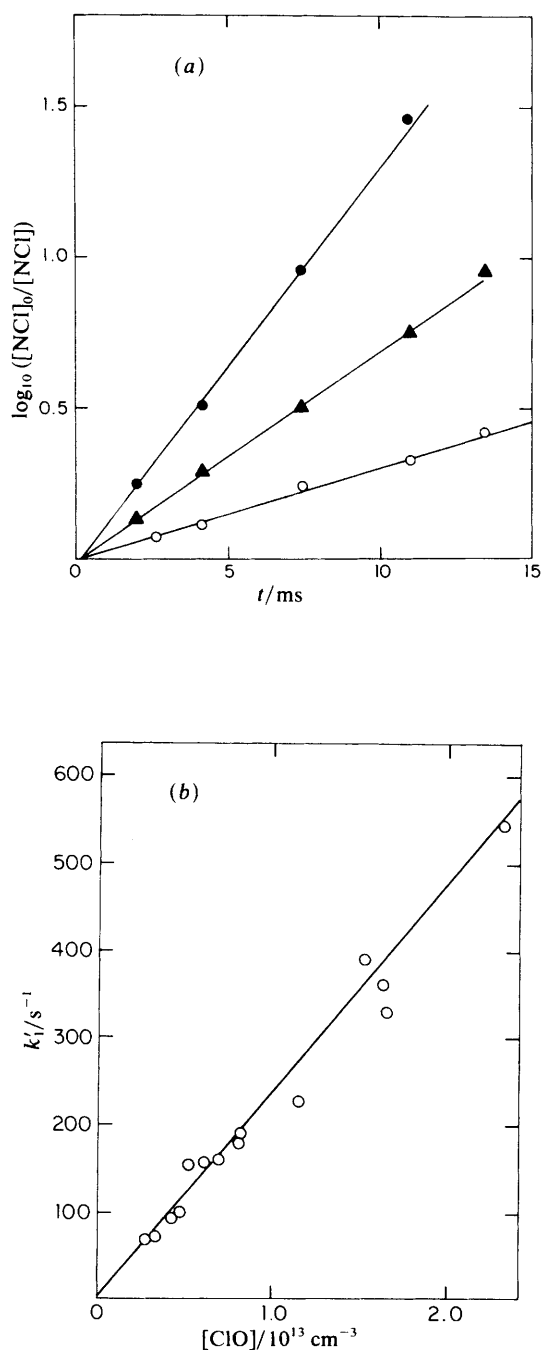
Fig. 1. Kinetics of reaction (1) at 295 K. (a) Typical first-order logarithmic decay plots of NCl in the presence of various excess concentrations of ClO (10^{13} cm^{-3}): ●, 1.63; ▲, 0.52 and ○, 0.33. (b) Summary plot for the variation of the first-order rate constants corrected for axial diffusion.

Table 1. Rate constant for $NCl + ClO$

run	$[NCl]_0/10^{11}$ cm^{-3}	$[ClO]_{mean}/10^{13}$ cm^{-3}	k_1'/s^{-1}	$k_1/10^{-11}$ cm^3 s^{-1}
1	2.8	0.52	153	2.9
2	3.7	0.70	160	2.3
3	3.6	1.65	327	2.0
4	3.7	1.53	390	2.5
5	3.5	2.33	542	2.4
6	2.5	0.81	175	2.2
7	4.0	1.15	226	2.0
8	1.8	0.29	68	2.3
9	4.0	0.62	156	2.5
10	4.3	1.63	359	2.2
11	2.8	0.43	91	2.1
12	1.8	0.33	70	2.1
13	1.1	0.81	188	2.3
14	2.1	0.47	100	2.1

$$\text{mean value} = (2.3 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} (1\sigma)$$

RESULTS

REACTION (1)

NCl radicals were generated upstream from the $NCl + ClO$ reaction zone. For ClO radical generation OClO was added through the injector, which could be positioned at a series of distances from the sampling orifice. The chlorine atom concentration was sufficiently large, $[Cl] \approx 2 \times 10^{14}$ cm^{-3}, so that the OClO completely reacted (99.9%) *via* $Cl + OClO \rightarrow 2ClO$ within the mixing time of *ca.* 1 ms. Thus the $NCl + ClO$ reaction zone essentially spanned the distance between the OClO injection point and the sampling system.

For the kinetic measurement of reaction (1), pseudo-first-order conditions were used with $[ClO]_0/[NCl]_0 > 15$, and the rate of decay of the NCl signal was monitored at m/e 49; thus

$$\ln \{[NCl]_0/[NCl]\} = k_1[ClO]t = k_1't.$$

The range of $[ClO]_0$ used was $0.3 > [ClO]_0/10^{13}$ cm$^{-3} > 2.4$, for which corrections to allow for second-order disproportionation were small, $< 2\%$. Fig. 1(a) shows typical logarithmic decay plots which are linear over at least a 20-fold decay in [NCl]. The values of k_1' derived from the gradients and corrected for axial diffusion were then plotted against the mean value of [ClO] in fig. 1(b), which shows good linear correlation. The data are listed in table 1.

The rate constant k_1 was derived as

$$k_1 = (2.3 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \quad \text{at } 295 \text{ K}(1\sigma).$$

The main products of reaction (1) are most likely $ClNO + Cl$, *i.e.* $NCl + ClO \rightarrow ClNO + Cl$, by analogy with other rapid radical–radical reactions of ClO, *e.g.* $SO + ClO \rightarrow SO_2 + Cl$[10] and $NO + ClO \rightarrow NO_2 + Cl$,[11] where the ClO oxygen atom is transferred to the other radical (see Discussion). Indirect evidence for this reaction mechanism was obtained through the detection of NO at m/e 30: in the presence of an excess of Cl atoms ClNO reacts rapidly *via* $Cl + ClNO \rightarrow Cl_2 + NO$.

Table 2. Rate constant for NCl + NO

run	$[\text{NCl}]_0/10^{11} \text{ cm}^{-3}$	$[\text{NO}]_{\text{mean}}/10^{13} \text{ cm}^{-3}$	k_2'/s^{-1}	$k_2/10^{-11} \text{ cm}^3 \text{ s}^{-1}$
1	3.3	0.71	96	1.4
2	4.3	0.67	101	1.5
3	3.7	1.68	237	1.4
4	4.0	1.70	224	1.3
5	4.4	3.10	423	1.4
6	2.9	3.10	459	1.5
7	4.0	2.62	366	1.4
8	3.0	2.40	338	1.4
9	3.3	2.46	380	1.5
10	3.1	1.33	175	1.3
11	2.0	0.95	131	1.4
12	2.0	0.42	57	1.4
13	1.3	0.41	57	1.4
14	1.4	0.29	39	1.3

mean value = $(1.4 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}(1\sigma)$

ClNO could not be detected directly owing to the low ionization cross-section for producing the ClNO^+ parent peaks at m/e 65 and 67. In addition the ionization cross-section to produce the NCl^+ ion from ClNO is significantly lower than that for the NCl radical itself. With an excess of ClO present, NO is concerted to NO_2, and this was also observed at m/e 46. The alternative atom-transfer mechanisms $\text{NCl} + \text{ClO} \rightarrow \text{NCl}_2 + \text{O}$ or $\text{N} + \text{Cl}_2\text{O} \rightarrow \text{NCl}_2 + \text{O}$ may be rejected as they are endothermic.

REACTION (2)

The kinetics of reaction (2) were studied using pseudo-first-order conditions with $[\text{NO}]_0 \gg [\text{NCl}]_0$ and the removal of NCl was monitored at m/e 49:

$$\ln ([\text{NCl}]_0/(\text{NCl})) = k_2[\text{NO}]t = k_2't.$$

Concentrations of NO in the range $0.3 \leqslant [\text{NO}]/10^{13} \text{ cm}^{-3} \leqslant 3.1$ were added at reaction time up to 17 ms. Small corrections for the residual contribution from NCl_2 were applied to the m/e 49 signal since NO does not react with NCl_2. The procedure for evaluating the corrections required is described in the Experimental section. The concentration of NCl_2 was largely suppressed by the addition of O_2 ($>5 \times 10^{14} \text{ cm}^{-3}$). Table 2 lists the 14 sets of data, with the values of k_2' corrected for axial diffusion. Examples of the NCl decay at several values of [NO] are shown in a logarithmic scale in fig. 2(a). Fig. 2(b) shows the second-order plot of k_2' against [NO] and shows good linear correlation. The value for the rate constant k_2 is derived as

$$k_2 = (1.4 \pm 0.1) \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1} \quad \text{at } 295 \text{ K}(1\sigma).$$

There are several possibilities for the products of the NCl + NO reaction:

(a) $\text{NCl} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{Cl};$ $\Delta H° = -153 \pm 30 \text{ kJ mol}^{-1}$

(b) $\rightarrow \text{N}_2 + \text{ClO};$ $\Delta H° = -258 \pm 30 \text{ kJ mol}^{-1}$

(c) $\rightarrow \text{N}_2 + \text{Cl} + \text{O};$ $\Delta H° = +8 \pm 30 \text{ kJ mol}^{-1}.$
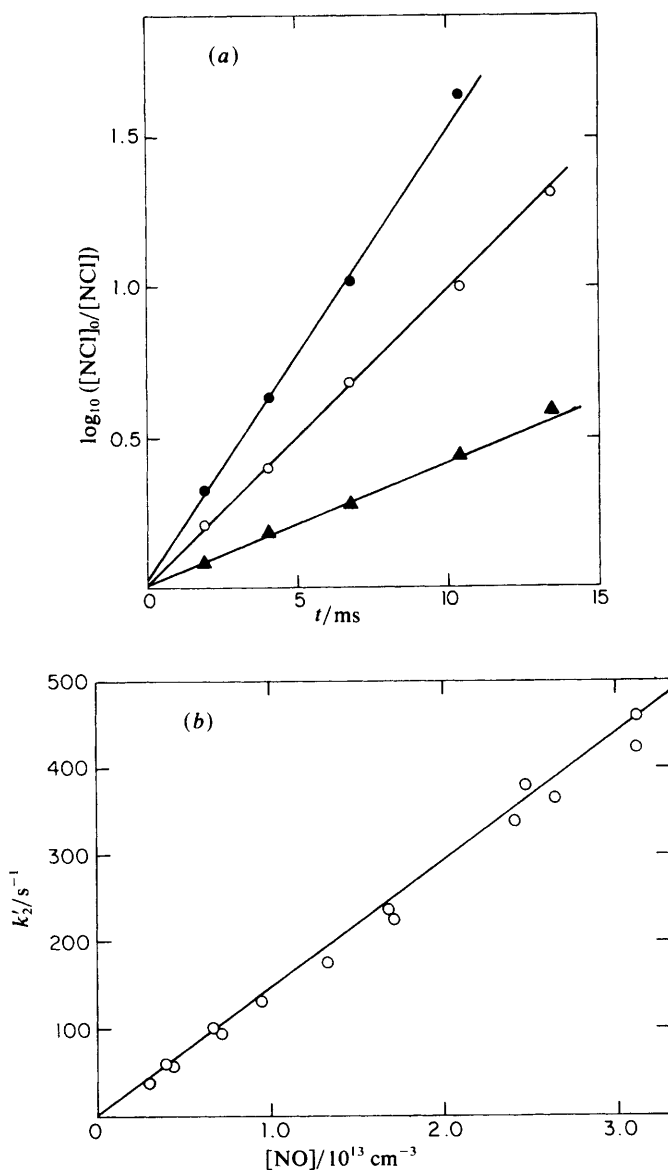
Fig. 2. Kinetics of reaction (2) at 295 K. (*a*) First-order logarithmic decay plots of NCl in the presence of excess concentrations of NO (10^{13} cm^{-3}): ●, 2.62; ○, 1.68 and ▲, 0.71. (*b*) Summary plot for the variation of the first-order rate constants corrected for axial diffusion.

The first channel (*a*) leading to $N_2O + Cl$ is the most simple in mechanistic terms, involving the transfer of a N atom from NCl to NO, whereas channels (*b*) and (*c*) involve multiple bond fission and formation. The major product observed was indeed N_2O (m/e 44), constant with channel (*a*), but there was indirect evidence for a small contribution of *ca.* 5% from channel (*b*). This conclusion was based
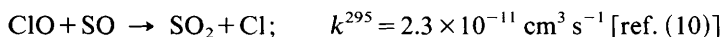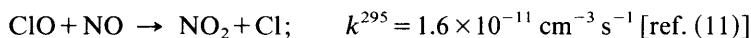
on the detection of NO_2 which may be produced in the following reaction scheme:

$$NCl + NO \rightarrow N_2 + ClO$$
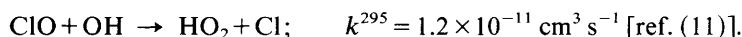
$$NO + ClO \rightarrow NO_2 + Cl.$$
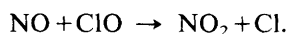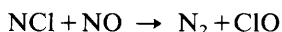
However, detection of ClO itself was not achieved because of its rapid removal by NO.

DISCUSSION

The present and previous parts of this work[5] have shown that ground-state NCl radicals undergo both rapid self-disproportionation and rapid bimolecular reactions with other radicals. No previous determinations of the rate constants for reactions (1) and (2) have been made. However, analogies may be drawn between these reactions and other radical–radical reactions. In the case of reaction (1) the kinetics and mechanistics appear similar to the following reactions:

$$ClO + NO \rightarrow NO_2 + Cl; \quad k^{295} = 1.6 \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1} \text{ [ref. (11)]}$$

$$ClO + SO \rightarrow SO_2 + Cl; \quad k^{295} = 2.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ [ref. (10)]}$$

and

$$ClO + OH \rightarrow HO_2 + Cl; \quad k^{295} = 1.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ [ref. (11)]}.$$

Comparing reaction (1) with these reactions, in each case the ClO radical transfers its O atom to the other radical and the 295 K rate constants are all very similar at *ca.* $1-2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

Reaction (2) may be compared to the reaction

$$NH + NO \rightarrow \text{products}; \quad k^{298} = 4.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ [ref. (12)]}.$$
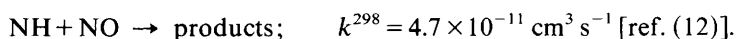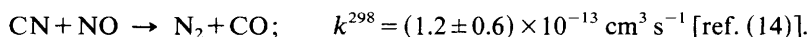
The rate constant for this reaction is almost a factor of three larger than that of reaction (2). The products of the $NH + NO$ reaction have not been detected directly, but in view of the formation of N_2O in reaction (2), the exothermic channel giving $N_2O + H$ is a strong possibility. Comparison may also be made with the reaction

$$N_3 + NO \rightarrow N_2O + N_2; \quad k^{295} = 1.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \text{ [ref. (13)]}.$$
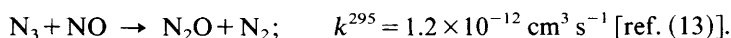
As in the case of reaction (2), this reaction also involves transfer of an N atom to NO but has an order-of-magnitude lower rate constant.

The evidence for a minor secondary channel in reaction (2), $NCl + NO \rightarrow N_2 + ClO$, albeit indirect, suggests a comparison with the reaction of $CN(X\,^2\Pi)$ radicals with NO:

$$CN + NO \rightarrow N_2 + CO; \quad k^{298} = (1.2 \pm 0.6) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \text{ [ref. (14)]}.$$

Both may occur *via* a four-centre complex which could account for the slower rate constants observed.

The removal of NCl_2 radicals by ClO, as mentioned briefly in the Experimental section, was found to be a rapid process. Although it was not quantitatively studied here, the rate constant is estimated to be $> 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 295 K. The reaction mechanism in this case is difficult to identify, but the large rate constant would imply an atom-transfer process such as

$$NCl_2 + ClO \rightarrow ONCl_2 + Cl.$$
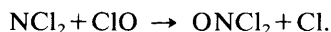
The intermediate $ONCl_2$ species may then decompose to give $NO + Cl_2$ or react further with Cl atoms:

$$Cl + ONCl_2 \rightarrow Cl_2 + ClNO.$$

It has been speculated[15] that the $ONCl_2$ species may exist as an intermediate in the third-body assisted reaction between NO and Cl_2 to give ClNO:
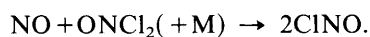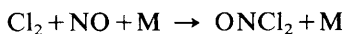
$$Cl_2 + NO + M \rightarrow ONCl_2 + M$$

$$NO + ONCl_2(+M) \rightarrow 2ClNO.$$

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