Mechanism of Formation of Triatomic Molecules in Atomic Combination Reactions

Part 1.—Formation of ClNO and ClCO in reactions of atomic chlorine

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The kinetics of reaction of $^2P_{\frac{3}{2}}$ ground-state chlorine atoms with nitric oxide and with carbon monoxide have been investigated at various temperatures and at total pressures near 1 mm Hg. The reaction of Cl with NO involved a simple third-order combination reaction as the primary step forming nitrosyl chloride,

$$Cl+NO+M \xrightarrow{\text{slow}} ClNO+M+38 \text{ kcal mole}^{-1}, \quad (1n)$$

$$ClNO+Cl \xrightarrow{\text{fast}} NO+Cl_2+20 \text{ kcal mole}^{-1}. \quad (2n)$$

The overall reaction can be considered as a nitric oxide-catalyzed removal of chlorine atoms, analogous to the reactions of O and H with nitric oxide. For the third bodies M=He, Ar, O_2, N_2, Cl_2 and SF_6, the values for k_{1n} at 293°K were, respectively, (3·5±0·5), (2·9±0·5), (3·9±0·5), (3·5±0·5), (3·4±0·5), and (3·5±0·5) 10^{16} cm^6 mole^{-2} sec^{-1}. Over the temperature range 270-620°K, negative Arrhenius activation energies (kcal mole^{-1}) were found for k_{1n} as follows, $E_a = (-1{\cdot}1\pm0{\cdot}1)$ [Ar], $(-0{\cdot}7\pm0{\cdot}2)$ [Cl_2], and $(-1{\cdot}2\pm0{\cdot}2)$ [SF_6].

The reaction between chlorine atoms and carbon monoxide was much slower than the nitric oxide reaction. At 195°K, the kinetics were explained on the basis of two reactions,

$$Cl+CO+M \xrightarrow{k_{1c}} ClCO+M, \quad (1c)$$

$$ClCO+Cl \xrightarrow{k_{2c}} CO+Cl_2. \quad (2c)$$

At higher temperatures the rate of removal of Cl by CO was greatly diminished, and the kinetics became more complex. Under these conditions, contribution by the thermal dissociation of ClCO is appreciable. The results are consistent with a value of about 7 kcal mole^{-1} for the heat of dissociation of the ClCO radical. The rate constant k_{1c} (for M=Ar) at 300°K was $10^{(14\cdot5\pm0\cdot3)}$ cm^6 mole^{-2} sec^{-1}, and reaction (1c) had an Arrhenius activation energy of about −2 kcal mole^{-1}.

Recently, a number of third-order reactions involving combination of an atom with a diatomic molecule have been characterized, and, in some cases, their rate constants have been measured. These include the reactions of atomic hydrogen [1] and atomic oxygen [2] with nitric oxide, $H+NO+M \rightarrow HNO+M$, $O+NO+M \rightarrow NO_2+M$, and the reactions $H+O_2+M \rightarrow HO_2+M$,[3] and $O+O_2+M \rightarrow O_3+M$.[4, 5] All these reactions have rate constants (at 300°K) lying between $10^{14\cdot3}$ and $10^{16\cdot4}$ cm^6 mole^{-2} sec^{-1}, and have small negative activation energies.

In this work, the reactions of Cl with nitric oxide [17] and carbon monoxide have been characterized as third-order reactions of this type. The radical ClCO, which has been detected in an argon matrix at 20°K by infra-red absorption spectroscopy,[6] was formed in this work in the primary step of the reaction between carbon monoxide and

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chlorine atoms. The radical ClCO was extensively dissociated at room temperatures and above, on account of its much lower heat of dissociation [D°_{298}(Cl—CO) = 6 kcal mole^{-1}],[7, 8] as compared to those of other triatomic molecules studied in this way (e.g., D°_{298}(Cl—NO) = 38 kcal mole^{-1}).[9, 19]

EXPERIMENTAL

Two discharge-flow systems of the type described previously[10] were used. Chlorine atoms in a large excess of argon or helium carrier gas were generated by passing a mixture of chlorine (0·02-1 %) and the dry carrier gas through either a 17 Mc/sec radiofrequency or a 2450 Mc/sec microwave discharge. The quartz discharge tubes were coated with metaphosphoric acid to inhibit heterogeneous recombination of atoms within the discharge. From the discharge, atoms (~0·01-0·5 % of total pressure) flowed at 1-5 mm Hg total pressure through a 28 mm int. diam. Pyrex flow-tube with four inlet jets at equal intervals along its length. Linear velocities were between 50 and 500 cm sec^{-1}.

Nitrosyl chloride affected the surface of an untreated Pyrex tube so that the rate of the heterogeneous recombination of chlorine atoms was greatly accelerated, as was found previously.[25] Accordingly, the surface of the flow tube was coated with phosphoric acid,[11] and this recombination was then very slow at temperatures down to 273°K. Below 273°K, the surface recombination coefficient of chlorine atoms increased markedly with decreasing temperature; accordingly, the surface was first poisoned with phosphoric acid as before, and then allowed to remain at room temperature in contact with a stream of oxygen atoms for several hours. This treatment appeared to reduce the activity of the surface towards chlorine atom recombination. The absence of any detectable heterogeneous removal of chlorine atoms at 300°K and under our kinetic conditions was then checked, and the reaction tube was then cooled to 195°K, maintaining the chlorine atom stream for several hours. The rate of their heterogeneous removal at 195°K fell gradually with continued exposure to the atomic stream, until a constant value was obtained.

The total pressure in the system was measured with an oil manometer or McLeod gauge. Concentrations of carrier gas, and of added reagents were measured with calibrated capillary flow-meters designed to obey the Poiseuille equation for the gases used. Flows were controlled with Edwards LB1B fine-control needle valves, and were maintained with a high through-put mechanical pump. Argon, helium, oxygen and nitrogen were taken from cylinders (B.O.C. Ltd.), after careful drying. Chlorine and sulphur hexafluoride were the dried I.C.I. Ltd. products. In some experiments, redistilled chlorine was used, but no difference in the reactions studied could be detected. Nitric oxide was prepared from the reaction of $NaNO_2$ with acidified KI, and the product was purified in the usual way. Nitrosyl chloride was prepared by reacting excess pure nitric oxide with redistilled dry chlorine; it was stored as the solid to avoid photodecomposition. Carbon monoxide was prepared by reacting degassed sulphuric and formic acids.

For experiments below room temperature, the flow tube was immersed in a trough containing an appropriate constant-temperature bath, and for studies above room temperature, an electric furnace was wound on to the exterior of the flow tube. On account of the low atom concentrations used, and the slowness of reactions studied in this work, the temperature rise in the flowing gas due to exothermicity of the reaction is negligible.

Streams of atomic chlorine in SF_6 were produced by adding an excess of sulphur hexafluoride to the products of a discharge in a mixture of chlorine and argon. Pure chlorine was passed through the discharge in order to obtain flows of atomic chlorine in Cl_2 carrier gas. Atomic chlorine in an oxygen carrier gas was generated by addition of Cl_2 to the products of a discharge in O_2 according to the overall stoichiometry $2O+Cl_2 \rightarrow O_2+2Cl$ as found previously.[12] A slow reaction between Cl and O_2 occurs when these reactants are mixed, but since this reaction is first-order in [Cl], its occurrence does not affect the kinetics of the NO+Cl reaction (see eqn. (I),). Atomic oxygen in a nitrogen carrier was produced by addition of the stoichiometric concentration of nitric oxide to a stream of partially-dissociated nitrogen, $N+NO \rightarrow N_2+O$. Chlorine atoms in N_2 were then formed by adding molecular chlorine to the atomic oxygen thus generated.

The concentrations of atomic chlorine were measured by titration with nitrosyl chloride using the red chlorine afterglow spectrum in a manner similar to that described for atomic hydrogen,[25]

$$Cl+Cl(+M)\rightarrow Cl_2(^3\Pi_{0_u+})(+M),$$

$$Cl_2(^3\Pi_{0_u+})\rightarrow Cl_2(^1\Sigma_g^+)+h\nu.$$

Relative concentrations of chlorine atoms were determined by measurements of the relative intensities of the chlorine afterglow; at constant total pressure, $\sqrt{I}$ is proportional to [Cl].[13, 14] The detectors used were R.C.A. 931-A and E.M.I. 9558-C photomultiplier cells with appropriate filters; the former cell, whose range of detection extended up to 7000 Å, was used for the NO+Cl experiments. The latter cell was sensitive up to 8500 Å, and was used in the Cl+CO studies.

The kinetics of the reactions Cl+NO and Cl+CO were studied by addition of different concentrations of the reactant (NO or CO) at each of four inlets upstream of the fixed photomultiplier cell, at which point the relative concentrations of Cl remaining were measured. Kinetic analysis shows [10] that eqn. (I) holds for constant t,

$$\ln([Cl]_i) = B-k[R]t, \tag{I}$$

where $[Cl]_i$ is the concentration of atomic chlorine remaining at the photomultiplier cell when a concentration of reactant [R] is added at the ith inlet, and B is a time-dependent constant independent of [R]. Eqn. (I) is obeyed in the presence of concurrent first-order removal of atomic chlorine even if the first-order rate constant varies along the flow tube (e.g., for wall recombination of atoms), and it also holds quite well in the presence of a slow concurrent recombination second-order in [Cl].

In the Cl+NO reaction, these conditions were closely followed, but the Cl+CO reaction was so slow that the rate of concurrent homogeneous recombination of Cl atoms via Cl+Cl+M was comparable to that of the CO+Cl reaction. The effect of this recombination was minimized by using very low concentrations of atomic chlorine, but an error of ~5 % was always present on this account in these experiments using eqn. (I). Accordingly, the rate constants given for the Cl+CO reaction are less accurate than those for the Cl+NO reaction.

RESULTS

In these kinetic investigations, the chlorine atoms are present predominantly as the ground state $^2P_{\frac{3}{2}}$; the equilibrium concentration of the upper spin-orbit state $^2P_{\frac{1}{2}}$ is 0·8 % at 300°K and 6 % at 620°K, as the energy difference between the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ states is 881 cm^{-1}.

REACTION OF Cl WITH NITRIC OXIDE

Addition of nitric oxide to a stream of chlorine atoms at 0·7-3 mm Hg total pressure caused a steady removal of atoms, as indicated by the diminution of the intensity of the associated red chlorine afterglow at the point of detection. The reproducibility of the system was tested by measurements of the chlorine atom concentration at the point of detection before adding and after removing various flows of nitric oxide; no difference was observed.

A search was made for chemiluminescent emission by electronically excited ClNO, which may be formed by the radiative combination of NO with Cl, $Cl+NO+M\rightarrow ClNO+M+38$ kcal mole^{-1}, although it has been suggested that ClNO is vibrationally rather than electronically excited.[23] The high-energy (low wavelength) cut-off of the electronic emission spectrum is expected to occur at about 7900 Å. To minimize the effect of the overlapping chlorine afterglow emission, the ratio [Cl]/[NO] was made as small as possible using very low chlorine atom concentrations (~10^{-4} mm Hg). Under these conditions, no chemiluminescent emission from ClNO was detected with the E.M.I. 9558-C photomultiplier cell at wavelengths up to 8500 Å. However, investigation at longer wavelengths, where the intensity of emission is expected to be greater, was not possible with this detector.

The products of reaction were investigated by allowing known concentrations of atomic chlorine to react completely with excess nitric oxide, with subsequent trapping (at 90°K) of the reaction products. Under these conditions, $ClNO$ and Cl_2, but not nitric oxide can be condensed, and no significant amounts of any reaction product was detected by infra-red analysis of the condensate. By considering the possible errors of the product analysis, the yield of nitrosyl chloride is given by $[(ClNO_{formed}]/[Cl_{reacted})] \ll 0{\cdot}05$. It is concluded that the $Cl + NO$ reaction is a nitric-oxide catalyzed recombination of atomic chlorine.

As well as causing removal of chlorine atoms, addition of nitric oxide resulted in appreciable quenching of the chlorine afterglow when low concentrations of atomic chlorine were used. A similar but more pronounced quenching effect was caused by added oxygen and hydrogen, but not by carbon monoxide or nitrogen. The quenching effect of nitric oxide was revealed by an examination of the magnitudes of the ordinate intercepts of plots of $\frac{1}{2}$ ln [intensity of emission] against time (cf. fig. 1), i.e., when $t \rightarrow 0$. The extent of diminution of the chlorine afterglow by added nitric oxide thus found decreased with increasing [Cl], and was negligible under the conditions used for kinetic measurements on the $Cl + NO$ reaction.

Qualitatively similar quenching effects by added nitric oxide were observed with both photomultiplier cells, the E.M.I. 9558C (8500 Å > λ > 6000 Å) and R.C.A. 931A (7000 Å > λ > 6000 Å), but with both these detectors the photon sensitivity is appreciable only in the high-energy " tail " of the chlorine afterglow, the spectrum of which extends to at least 1·2 μ.[14] However, in the wavelength range used, no change of intensity distribution with wavelength was detected when the afterglow was strongly quenched with nitric oxide or oxygen. This observation strongly suggests that vibrational quenching by nitric oxide of the electronically-excited $^3\Pi_{0_u^+}$ Cl_2 molecules is absent, as the high-energy tail of the afterglow spectrum is expected to be especially sensitive to vibrational relaxation. The diminution of the afterglow spectrum by nitric oxide is therefore due to appreciable electronic quenching and this conclusion requires a modification of Bader and Ogryzlo's [14] mechanisms for the chlorine afterglow, in which only vibrational quenching is included.

The kinetics of reaction were investigated using measurements of the intensity I of the chlorine afterglow. For a given total pressure of carrier gas, $I \propto [Cl]^2$, so that $\sqrt{I}$ is proportional to [Cl]. Using this method, an RCA 931-A photomultiplier cell and Kodak Wratten filter 23A were used to measure the relative intensity of emission (7000 Å > λ > 5800 Å) at a fixed observation point downstream from the four nitric oxide inlets. By addition of various concentrations of nitric oxide at different inlets, with simultaneous measurements of the concentrations of chlorine atoms remaining at the photomultiplier cell, the kinetics of reaction were found. Fig. 1 shows a typical linear plot of ln [Cl] against reaction time t for various (constant) concentrations of added nitric oxide; in addition, no dependence of $(\partial \ln [Cl]/\partial t)_{[NO]}$ upon [Cl] could be detected. The reaction is therefore first-order in [Cl]. Fig. 2 shows a typical plot of ln [Cl] against [NO] for constant reaction times, from which it is seen that the reaction is also first-order in [NO]. The slopes of lines similar to those of fig. 2, i.e., $(-\partial \ln [Cl]/\partial [NO])_t$, are plotted against t in fig. 3. A good linear correlation with negligible intercept is obtained. The gradients of the lines of fig. 3 are equal to the apparent second-order rate constants k, in accordance with eqn. (I).

Experiments were conducted at different total pressures for all the carrier gases used. Fig. 4(*a*) shows a plot of k (measured from fig. (3)) against total pressure of argon [M]; a satisfactory linear correlation is shown, and there is no evidence for a finite

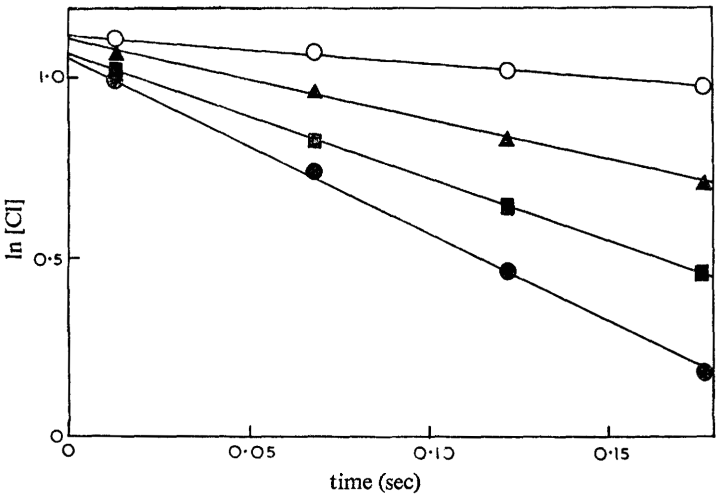

FIG. 1.—Kinetics of the reaction Cl+NO at 293°K for argon as third body; [M] = $6{\cdot}74\times10^{-8}$ (mole cm^{-3}): dependence of [Cl] upon reaction time for constant [NO]
[NO](10^{-9} mole cm^{-3}): ○, 0·34; ▲, 0·69; ■, 1·03; ●, 1·38

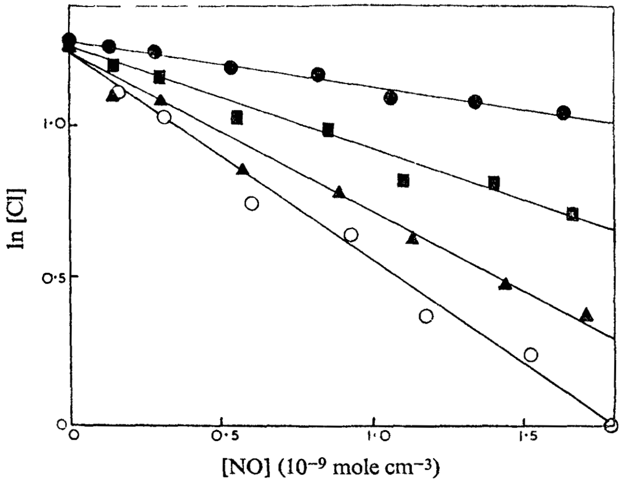

FIG. 2.—Kinetics of the reaction Cl+NO at 293°K for argon as third body; [M] = $6{\cdot}74\times10^{-8}$ (mole cm^{-3}): variation of [Cl] with [NO] for constant time *t*.
t(sec); ●, 0·013; ■, 0·068; ▲, 0·122; ○, 0·177

intercept. It is concluded that the reaction has overall third-order kinetics, with no detectable contribution by any heterogeneous process; the mechanism may be represented by the two steps;

$$Cl+NO+M \xrightarrow{\text{slow}} ClNO+M, \qquad (1n)$$

$$ClNO+Cl \xrightarrow{\text{fast}} NO+Cl_2. \qquad (2n)$$

Reaction (2*n*) is rapid at 300°K.[7] The rate constant k_{1n} can therefore be determined from the rate equation, $-\mathrm{d}\ln[Cl]/\mathrm{d}t = 2k_{1n}[NO][M]$, by measurement of the slopes of plots similar to fig. 4(*a*). Table 3 shows the values of k_{1n} found in this way for different third bodies M.

The effect of temperature upon k_{1n} was studied for argon, chlorine and sulphur hexafluoride as third bodies, and over the range 270-620°K. Fig. 5 shows the data,

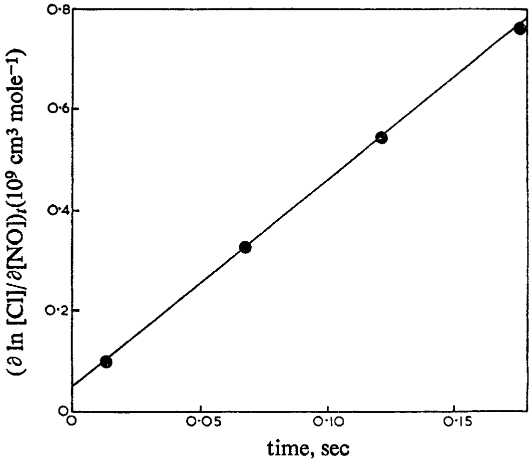

FIG. 3.—Kinetics of the reaction Cl+NO at 293°K for argon as third body; [M] = 6·74 × 10^{-8} (mole cm^{-3}): variation of $-(\partial \ln [Cl]/\partial[NO])_t$ with time *t*
The time zero is arbitrary

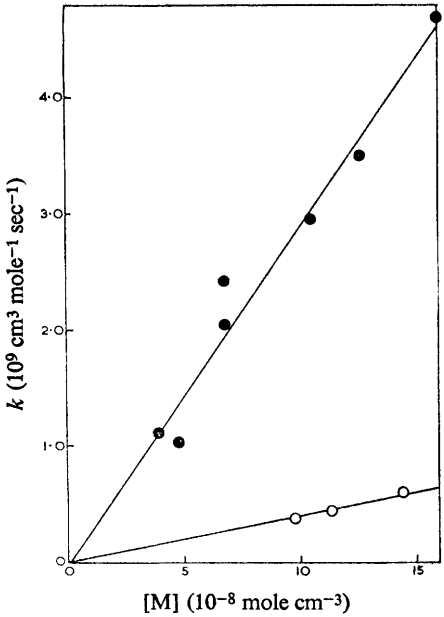

FIG. 4(*a*) and (*b*).—Kinetics of the reactions Cl+NO and Cl+CO for argon as third body: variation of *k* with [M]
(*a*) ●, Cl+NO at 293°K; (*b*) ○, Cl+CO at 195°K.

for M = Cl_2 and Ar, and in terms of the Arrhenius equation $k_{1n} = A \exp(-E_a/RT)$, the results may be represented by values for E_a of $(-1{\cdot}1 \pm 0{\cdot}1)$, $(-0{\cdot}7 \pm 0{\cdot}2)$ and $-1{\cdot}2 \pm 0{\cdot}2)$ kcal $mole^{-1}$ for Ar, Cl_2 and SF_6 respectively.

REACTION OF Cl WITH CARBON MONOXIDE

The reaction of atomic chlorine with carbon monoxide at room temperature was about 200 times slower than the Cl+NO reaction under similar conditions. Consequently, to obtain appreciable extents of reaction, higher total pressures (2-4 mm Hg) and lower linear flow velocities were used. The products of reaction condensible at 77°K were trapped and analyzed by infra-red spectroscopy. No significant concentration of products was obtained, although phosgene in very low yield could be detected, with $([COCl_2]_{\text{formed}})/([Cl]_{\text{removed}}) < 0{\cdot}004$.

Under conditions similar to those used in the Cl+NO experiments ($[Cl] \sim 0{\cdot}02$ mm Hg), the rate of homogeneous recombination of atomic chlorine, $Cl+Cl+M \rightarrow Cl_2+M$, is expected to be similar to that of the Cl+CO reaction, and consequently the approximations used to obtain eqn. (I) [10] are invalid. This difficulty was resolved by using small concentrations of atomic chlorine ($[Cl] \sim 2 \times 10^{-3}$ mm Hg) for kinetic studies, so that the homogeneous recombination is largely suppressed; the error in k_{1c} when eqn. (I) is used under these conditions is ~5 %. A second factor which might affect the measurements of reaction rates was the possible perturbation of the flow by the comparatively large concentrations of added carbon monoxide (~10 % of total pressure) necessary to cause appreciable removal of chlorine atoms. To investigate this effect, the flow of carbon monoxide was replaced by the same flow of nitrogen, which has the same density and coefficient of viscosity as carbon monoxide. Under these conditions, the concentration of Cl at the photomultiplier cell was independent of the time of contact between Cl and added nitrogen; a small time-independent dilution or quenching effect by added nitrogen was also observed. It follows that the physical effect of adding carbon monoxide to the flow can be neglected in the kinetic measurements.

The kinetics of the reaction of carbon monoxide with very small concentrations of atomic chlorine were investigated using the same method as that described for the NO+Cl reaction studies, and at 195, 300 and 373°K. A typical experiment led to about 20 % removal of the chlorine atoms initially present, whereas the extent of reaction was about ten times as great in some of the NO+Cl studies. For given initial concentrations of Cl and of CO, plots of ln [Cl] against t were linear, and for constant initial [Cl], the slopes of these plots were directly proportional to [CO] over the carbon monoxide concentration range 0·4 to $2{\cdot}0 \times 10^{-9}$ mole cm^{-3}. The reaction is consequently first-order in [CO]. But since the extents of removal of Cl are small, the linearity of the ln [Cl] against t plots cannot be taken as evidence that the reaction

TABLE 1.—VARIATION OF APPARENT SECOND-ORDER RATE CONSTANT k FOR THE Cl+CO REACTION WITH $[Cl]_0$ AT DIFFERENT TEMPERATURES

T(°K)	$[Cl]_0$(10^{-10} mole cm^{-3})	k(10^7 cm^3 $mole^{-1}$ sec^{-1})
195	3·4	22 ± 1
195	2·1	21 ± 1
195	1·7	22 ± 1
300	2·8	3·8 ± 0·3
300	2·0	3·3 ± 0·3
300	1·8	3·2 ± 0·3
300	1·5	3·1 ± 0·3
373	2·1	2·01 ± 0·15
373	1·6	0·75 ± 0·12
373	1·2	0·52 ± 0·08

is first-order in [Cl]. To investigate this point, the dependence of the apparent second-order rate constant k upon initial concentration of atomic chlorine $[\mathrm{Cl}]_0$ was examined. Table 1 shows the dependence of the apparent second-order rate constant k upon $[\mathrm{Cl}]_0$ at 195, 300 and 373°K. At the higher temperatures the second-order rate constant increased markedly with increasing $[\mathrm{Cl}]_0$. At 195°K, however, the apparent second-order rate constant was independent of $[\mathrm{Cl}]_0$.

At 195°K, but not at the higher temperatures, the reaction rate was therefore first-order in both [Cl] and [CO]. Accordingly, the dependence of the apparent second-order rate constant k upon total pressure [M] at 195°K was examined, and typical results are shown in fig. 4(*b*). This plot shows that the second-order rate constant varies linearly with [M]. The course of reaction of atomic chlorine with carbon monoxide at 195°K and 3 mm Hg total pressure can therefore be described in terms of a slow, rate-determining, third-order reaction (1*c*) followed by rapid removal of ClCO radicals (2*c*):

$$\mathrm{Cl+CO+M} \xrightarrow{\text{slow}} \mathrm{ClCO+M}, \qquad (1c)$$

$$\mathrm{ClCO+Cl} \xrightarrow{\text{fast}} \mathrm{CO+Cl_2}. \qquad (2c)$$

The mechanism of reaction under these conditions is therefore identical to that of the Cl+NO reaction. The more complex kinetics at higher temperatures can be readily explained if the dissociation energy of ClCO into Cl+CO is small, and has a similar magnitude to the value of about 6 kcal mole^{-1}.[7, 8] At room temperatures and above, redissociation of the ClCO molecule could therefore become comparable in rate to reaction (2*c*).

On the basis of a mechanism including reaction (1*c*), (2*c*) and redissociation (−1*c*),

$$\mathrm{ClCO+M \rightarrow Cl+CO+M}, \qquad (-1c)$$

the following rate expression is obtained, assuming a steady-state concentration of ClCO,

$$-\frac{\mathrm{d[Cl]}}{\mathrm{d}t} = 2k_{1c}[\mathrm{Cl}][\mathrm{CO}][\mathrm{M}]\frac{k_{2c}[\mathrm{Cl}]}{k_{-1c}[\mathrm{M}]+k_{2c}[\mathrm{Cl}]}, \qquad (\mathrm{II})$$

i.e.,

$$-\frac{1}{2}\frac{\partial}{\partial t}\left[\frac{\partial\ \ln\ [\mathrm{Cl}]}{\partial\ [\mathrm{CO}]_t}\right]_{[\mathrm{CO}]} = k = \frac{k_{1c}k_{2c}[\mathrm{Cl}][\mathrm{M}]}{k_{-1c}[\mathrm{M}]+k_{2c}[\mathrm{Cl}]},$$

and thus, since $[\mathrm{Cl}] \cong [\mathrm{Cl}]_0$,

$$\frac{1}{k} = \frac{k_{-1c}}{k_{1c}k_{2c}}\left(\frac{1}{[\mathrm{Cl}]_0}\right)+\frac{1}{k_{1c}}\left(\frac{1}{[\mathrm{M}]}\right). \qquad (\mathrm{III})$$

In eqn. (III), k is the apparent second-order rate constant. Fig. 6 shows plots (at 195, 300 and 373°K) of $1/k$ against $1/[\mathrm{Cl}]_0$ for a constant [M] at each temperature. Satisfactory linear correlations are obtained. Values for k_{1c} at 195 and 300°K can be calculated from the intercepts of these plots. The apparent activation energy of the slopes of the plots, i.e., of the composite rate constant $(k_{-1c}/k_{1c}k_{2c})$, is about 6 kcal mole^{-1}. At 300°K the variation of intercept with [M] was examined, and a satisfactory correlation of intercept values with $[\mathrm{M}]^{-1}$ was obtained. Because of the limited range of [M] available, a quantitative dependence of k_{1c} upon [M] cannot be verified at room temperature. However, the third-body dependence has been shown for this reaction at 195°K. Table 2 shows the values found for k_{1c}, and for $(k_{-1c}/k_{1c}k_{2c})$. The values for k_{1c} at 300 and 195°K show that the primary reaction (1*c*) has a small negative temperature coefficient, which can be expressed as an Arrhenius activation energy of about −2 kcal mole^{-1}.

TABLE 2.—VALUES FOR k_{1c} AND $k_{-1c}/k_{1c}k_{2c}$ AT 195, 300 AND 373°K

T(°K)	k_{1c} (cm^6 mole^{-2} sec^{-1}) (M = Ar)	($k_{-1c}/k_{1c}k_{2c}$) (mole^2 sec cm^{-6})
373	a	$1{\cdot}8 \pm 0{\cdot}4 \times 10^{-17}$
300	$(3{\cdot}3 \pm 1{\cdot}1) \times 10^{14}$	$0{\cdot}38 \pm 0{\cdot}10 \times 10^{-17}$
195	$(19 \pm 4) \times 10^{14}$	—

[a] not possible to find k_{1c} with any useful accuracy under these conditions.

DISCUSSION

This work shows that the reactions of NO and CO with Cl take place through a simple mechanism involving a third-order process as the primary step;

$$\mathrm{Cl + XO + M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ClXO + M}, \qquad (1)$$

$$\mathrm{Cl + ClXO} \xrightarrow{k_2} \mathrm{Cl_2 + XO}. \qquad (2)$$

Reaction (1) is much slower than reaction (2) in both cases, so that the steady-state concentrations of the triatomic ClXO molecules are very small, and the reactions approximate to catalyzed recombinations of chlorine atoms.

With ClCO, where the Cl—C bond energy is very small, extensive redissociation occurs, and reaction (−1) is competitive in rate with reaction (2) at ordinary temperatures. But since the Cl—N bond energy in ClNO is 38 kcal mole^{-1}, redissociation of nitrosyl chloride formed in the primary step is unobservably slow at ordinary temperatures under the conditions of the flow system.

The reaction (−1n), ClNO + M→Cl + NO + M, has been established as an important rate-determining process in investigations of the thermal decomposition of nitrosyl chloride at temperatures between 430 and 580°K,[19] 470-880°K,[21] and near 1100°K.[20] The main mode of decomposition at the lower temperatures [15, 16] is the molecular reaction $\mathrm{2ClNO \rightleftharpoons Cl_2 + 2NO}$. (In the earlier work,[19] the heterogeneous decomposition of ClNO to Cl + NO on the walls of the reaction vessel was also found to be a significant process affecting the reaction rates, but later work showed that this surface reaction can be completely removed by suitable treatment of the surface of the vessel.[21]) In our work, the absence of a finite intercept in plots such as those of fig. 4(a) shows that no rate-determining heterogeneous reaction of NO with Cl was involved under our conditions, in agreement with the work quoted.[21]

A comparison of the present data for k_{1n} with those obtained from kinetic studies of nitrosyl chloride decomposition [19-21] is of interest. The most significant comparison is with the determination of k_{1n} for M = Ar and M = $\mathrm{Cl_2}$ at 470°K.[19] These data are shown in fig. 5 together with the present values. Values for the rate constant of reaction k_{-1n} can be combined with the calculated equilibrium constant for reaction (1n) to give k_{1n}. The equilibrium constants have been calculated from the thermodynamic data recommended by Deklau and Palmer,[20] and the resulting values of k_{1n} (for M = Ar at 1137°K [20] and for M = $\mathrm{N_2}$ between 473-573°K [21]) are also shown in fig. 5. The possible errors in the equilibrium constant and the approximate nature of the shock-tube value found at 1137°K must give less weight to this value for k_{1n} than to the determinations by Ashmore and Spencer.[19]

The following points emerge from a consideration of fig. 5, and of table 2(b) of ref. (19). (A) The values of k_{1n} obtained by different techniques have similar orders of magnitude. (B) Our value of k_{1n} at 300°C for M = $\mathrm{Cl_2}$ agrees well with that determined by Ashmore and Spencer, and also with that reported by Hutton.[22] (C) The relative efficiencies of the third bodies M = $\mathrm{Cl_2}$, $\mathrm{N_2}$ and Ar are different in the present work at 300°K to those found previously at higher temperatures.[19, 21] (D) The values of k_{1n}

for M = Ar obtained from the studies of nitrosyl chloride decomposition all lie below the line ($E_A = -(1100 \pm 200)$ cal mole^{-1}) representing the variation of our values of k_{1n} (M = Ar) with temperature. The correlation with temperature of our Ar data for

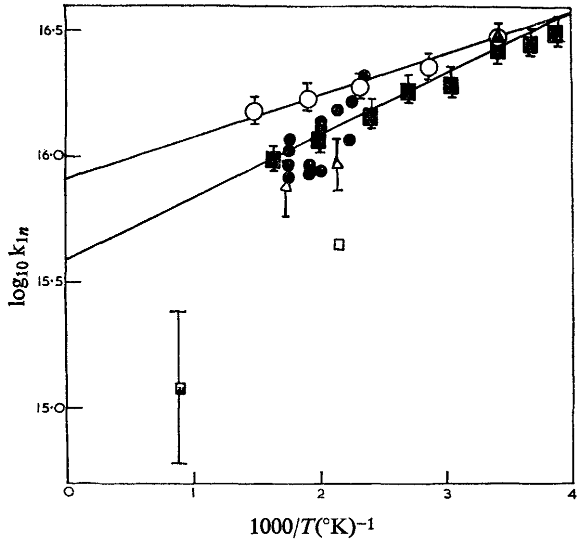

FIG. 5.—Temperature dependence of k_{1n} (cm^6 mole^{-2} sec^{-1}) for different third bodies M. The lines show the best correlation of the present results

M = N_2	M = Ar	M = Cl_2
▲, this work;	■, this work;	○, this work
△, Ashmore and Burnett.[21]	□, Ashmore and Spencer [19];	●, Ashmore and Spencer.[19]
	⬓, Deklau and Palmer.[20]	

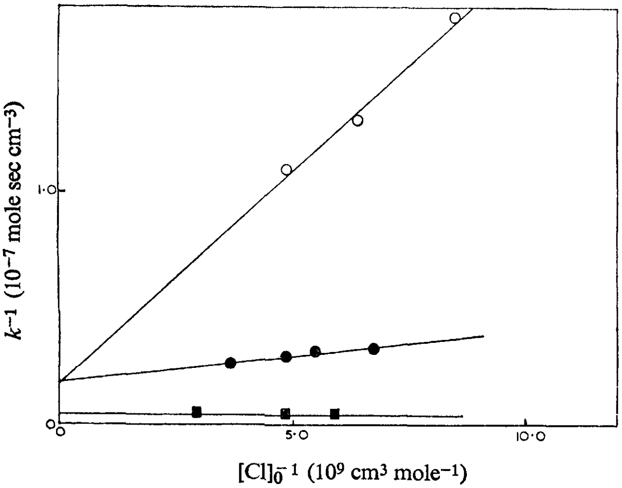

FIG. 6.—Dependence of apparent second-order rate constant k for the reaction Cl + CO upon initial concentration of chlorine atoms $[Cl]_0$, at various temperatures
■, 195°K; ●, 298°K; ○, 373°K

k_{1n} is not satisfactorily fitted by Ashmore and Spencer's value of -2600 cal mole^{-1} for the Arrhenius activation energy. However, the possible errors of the data are such that it is unreliable to combine all the results at different temperatures to give a

" best " value for the temperature coefficient of k_{1n}. In view of the larger range of $1/T$ used in our work, the present value of $-1{,}100$ cal mole^{-1} for the activation energy has greater reliability than the value of $-2{,}600$ cal mole^{-1} found previously.

Redissociation of ClNO (reaction $(-1n)$) is a significant rate-determining step in the above-mentioned studies [19-21] of the decomposition of nitrosyl chloride, but it was not observed in the present flow system experiments at lower temperatures. This situation contrasts with that of the radical ClCO formed by Cl + CO, where extensive redissociation is believed to occur in the flow system at 300°K. Bodenstein *et al.*[8] have reported a value of 5·7 kcal mole^{-1} for the Cl—C bond dissociation energy in ClCO. Recently, a careful investigation of the photochemical formation of $COCl_2$ [7] has led to a value for (k_{-1c}/k_{1c}) of $10^{-0\cdot 194}\exp(-6310/\boldsymbol{R}T)$ mole cm^{-3}, i.e., D^0(Cl—CO) = 6·3 kcal mole^{-1}. In the present work the temperature-dependence of $(k_{-1c}/k_{1c}k_{2c})$ corresponded to an activation energy of 6-7 kcal mole^{-1}. As reaction $(2c)$ has only a small activation energy (see below), our result confirms that D^0(Cl—CO) is ~6-7 kcal mole^{-1}.

From the present values of $(k_{-1c}/k_{1c}k_{2c})$ at various temperatures, the magnitude of k_{2c} can be found. The equilibrium constant for the Cl + CO reaction can be expressed in the form $k_{-1c}/k_{1c} = \exp(\Delta S^0/\boldsymbol{R})\exp(-\Delta H^0/\boldsymbol{R}T)$; ΔH^0 is about +6 kcal mole^{-1}. Burns and Dainton's [7] determination of (k_{-1c}/k_{1c}) give a value for ΔS°_{300} of about +19·0 cal mole^{-1} deg.$^{-1}$ for the reverse reaction $(1c)$, corresponding to S°_{300} = 67·8 cal mole^{-1} deg.$^{-1}$ for the ClCO radical.[19] This value for the absolute entropy of ClCO is much greater than that reported recently,[6] S°_{300} = 63·5 cal mole^{-1} deg.$^{-1}$, and also than the absolute entropies of related triatomic molecules. It seems unlikely that the value of S°_{300} for ClCO given by Jacox and Milligan [6] can be incorrect by more than about 2 cal/mole deg., since the absolute entropy is insensitive to variations in the bond lengths and angle, which were the only unknown parameters in that work.[6] Thus, there seem to be good grounds for accepting the value for ΔS°_{300} = +23·3 cal mole^{-1} deg.$^{-1}$ from Jacox and Milligan's work.[6] However, if one also accepts Burns and Dainton's [7] value for ΔH°_{300} of +6·3 kcal mole^{-1}, the value found from our work at 300°K for the equilibrium constant k_{-1c}/k_{1c} is much greater than that determined by Burns and Dainton,[7] on account of the different ΔS°_{300} values. Evidence for the correctness of Burns and Dainton's value for k_{-1c}/k_{1c} at 300°K derives from the fact that this value is used [7] to obtain k_{2n};

$$\mathrm{Cl+NOCl}\xrightarrow{k_{2n}}\mathrm{Cl_2+NO},$$

$k_{2n} = 10^{13\cdot 06}\exp(-1060/\boldsymbol{R}T)$ cm^3 mole^{-1} sec^{-1}. The latter value is consistent with work using reaction $(2n)$ as a titration reaction for chlorine atoms,[13, 14, 24] whereas if the values ΔS°_{300} = +23·3 cal mole^{-1} deg.$^{-1}$ and ΔH°_{300} = +6·3 kcal mole^{-1} are used to derive k_{2n}, a much lower value for k_{2n} is obtained from Burns and Dainton's [7] work. Such a value for k_{2n} is not consistent with the present and other work relating to k_{2n}.

The solution to this problem could be that Burns and Dainton's value for k_{1c}/k_{1c} at 300°K is correct, but that their temperature dependence of this equilibrium constant is slightly in error. In other words, if we accept both Burns and Dainton's [7] value for k_{-1c}/k_{1c} at 300°K and the value ΔS°_{300} = +23·3 cal mole^{-1} deg.$^{-1}$, then ΔH°_{300} would have to be increased arithmetically by about 1 kcal mole^{-1}. On this basis, and taking ΔH°_{300} = +7·6 kcal mole^{-1} to give exactly Burns and Dainton's value for (k_{-1}/k_{1c}) at 300°K, our values for $(k_{-1c}/k_{1c}k_{2c})$ give $k_{2c} = 10^{12\cdot 8\pm 0\cdot 2}$ and $10^{13\cdot 0\pm 0\cdot 2}$ mc^3 mole^{-1} sec^{-1} at 300 and 373°K respectively. These are to be compared with the values for k_{2c} of $10^{14\cdot 0}$ and $10^{14\cdot 1}$ cm^3 mole^{-1} sec^{-1} found at 300° and 373°K by Burns and Dainton.[7]

Finally, we compare the magnitudes of the third-order rate constants k_2 with those previously found for combination reactions of an atom with a diatomic molecule; table 3 shows the data.

TABLE 3.—VALUES OF THIRD-ORDER RATE CONSTANTS FOR REACTIONS OF THE TYPE

$$A+BC+M \rightarrow ABC+M$$

reaction	ref.	k_1(10^{16} cm^6 $mole^{-2}$ sec^{-1}) at 293°K						Arrhenius activation energy for M=Ar (kcal $mole^{-1}$)
		M=Ar	He	O_2	N_2	Cl_2	SF_6	
Cl+NO+M	this work	2·9±0·5	3·5±0·5	3·9±0·5	3·5±0·5	3·4±0·5	3·5±0·5	−1·1±0·2
O+NO+M	2	2·7	1·8	2·1	3·3	—	5·6	−1·8±0·4
	18	2·7±0·3	1·8±0·3	2·7±0·3	3·1±0·4	—	—	—
H+NO+M	1	0·87±0·15	0·66±0·10	—	—	—	—	−0·6±0·2
Cl+CO+M	this work	0·03±0·01	—	—	—	—	—	∼−2
$O+O_2+M$	4	—	—	0·027	—	—	—	
	5	0·019±0·002	—	—	—	—	—	−1·8±0·4
$H+O_2+M$	3	2·1±0·3	—	—	—	—	—	∼−1

The close similarity of the rate constants near 300°K and their dependences on M for the Cl+NO+M and O+NO+M reactions is evident. On the other hand, the rate constant for Cl+CO+M is more similar in magnitude to that for the reaction $O+O_2+M$, than to those for the reactions Cl+NO+M, O+NO+M, H+NO+M and $H+O_2+M$. There is a rough correlation of the larger rate constants with the more exothermic reactions, and vice versa, as has been suggested by Thrush for reactions of this type. However, the reaction Cl+NO+M which is only slightly more exothermic than the reaction $O+O_2+M$, is much faster than that reaction, so the correlation of rate constants and exothermicities must be regarded with caution.

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