Photoemissive and Recombination Reactions of Atomic Chlorine

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The red glow emitted from partially dissociated chlorine has been shown to occur via the termolecular reaction,

$$Cl+Cl^*+Cl_2 \xrightarrow{k_{14}} Cl_2^*+Cl_2$$

followed by the emission process,

$$Cl_2^* \xrightarrow{k_{15}} Cl_2 + h_{\nu}.$$

From measurement of the absolute quantum yield of emission, and quenching of the emission by Cl_2 , $k_{14} = 0.94 \times 10^{15}$ cm⁶ mole⁻² sec⁻¹, and the radiative lifetime of $Cl_2^* = 1/k_{15} \ge 3 \times 10^{-7}$ sec. Addition of argon to the chlorine gave the reaction rate for

$$Cl+Cl^*+Ar \xrightarrow{k_{18}} Cl_2^*+Ar$$

as $k_{18} = 2.35 \times 10^{14} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$.

Rates of recombination of chlorine atoms were investigated using the red emission to measure atom concentrations; the process occurs via the two consecutive reactions:

$$Cl+Cl_{2} \stackrel{k_{9}}{\rightleftharpoons} Cl_{3}$$
$$\underset{k_{-9}}{\overset{k_{10}}{\longrightarrow}} Cl_{2}+Cl_{2}.$$

 $k_9 = 9.09 \times 10^7$ cm³ mole⁻¹ sec⁻¹, $k_{-9} \le 7.6 \times 10^5$ sec⁻¹, and under experimental conditions [Cl₃] > 1.2×10^{-5} [Cl]. Recombination of chlorine atoms with argon as third body has given the overall termolecular rate constant for the reaction,

$$Cl+Cl+Ar \xrightarrow{k_{23}} Cl_2+Ar$$

as $4.25 \pm 0.8 \times 10^{15}$ cm⁶ mole⁻² sec⁻¹.

The kinetics of halogen atom reactions have recently been reviewed,¹ and although competitive experiments have provided much data on relative rate constants, little is known of the absolute values. Measurements of absolute rates require a knowledge of both the absolute atom concentration and the rates of the atom recombinations which terminate the reaction chain. With the exception of iodine, only limited data are available on the mechanism and rates of recombination of the halogen atoms, and even for iodine, ambiguity still exists as to the true reaction path.²

The study of chlorine atom recombination reported here was undertaken first, to develop a method of monitoring the atom concentration and secondly, to measure the absolute rates of recombination of chlorine in an effort to establish the detailed mechanism of the recombination process.

The Wrede-Harteck diffusion gauge ³ and the isothermal probe ^{4, 5} have been used to measure chlorine atom concentrations, but both are limited by virtue of their

non-selectivity to chlorine atoms. When gaseous chlorine is passed through an electrodeless discharge, a red glow is emitted from the partially dissociated gas. The dependence of the intensity of this red emission on the chlorine atom concentration was investigated, and used in the measurement of chlorine atom reaction rates.

EXPERIMENTAL

The apparatus was similar to that described by Kaufman.⁶ The reaction cell was a Pyrex tube, 2.9 cm int. diam. and 150 cm long, fitted with B.10 ground joints to allow the injection of the reactant gases. All ground joints were sealed with P.T.F.E. sleeves. The cell was evacuated via a 121. ballast flask and liquid nitrogen traps. A large stopcock between the ballast flask and the traps enabled the gas flow rate and pressure in the reaction cell to be regulated. A 7 mm int. diam. quartz tube, carrying external aluminium electrodes coupled to a 350 W, 19 Mc/sec transmitter, served as the discharge tube for the dissociation of molecular chlorine, and was sealed into the upstream end of the reaction cell. 10 cm downstream from the point of injection of the chlorine, a multi-perforated jet allowed the injection of nitrosyl chloride gas.

As all available pressure measuring devices were either susceptible to attack by chlorine, or too insensitive in the 0.1 torr range, pressures were measured on a specially constructed McLeod gauge filled with concentrated sulphuric acid. This was calibrated against a standard mercury-filled McLeod gauge. Rapid first-order recombination of chlorine atoms on the walls of the reaction cell was prevented by poisoning the surface with sulphuric acid solution.⁷

PREPARATION AND PURIFICATION OF GASES

Chlorine obtained from I.C.I. Ltd. as 99.99 % pure was used without further purification. Nitrosyl chloride was prepared by the reaction of nitric oxide with molecular chlorine. It was condensed and purified by selective vaporization of the nitric oxide and chlorine impurities, and stored at liquid nitrogen temperature. In later work, nitrosyl chloride from the Matheson Chemical Company was used. Argon was obtained from B.O.C. and purified by passing first through tightly packed copper foil at 900°C and then through a trap at -80° C. Nitrogen dioxide obtained from the Matheson Chemical Co. was used without further purification.

GAS FLOW RATES

The chlorine flow was metered by measurement of the pressure head produced on a sulphuric acid manometer across a capillary. The flow was regulated by two stainless steel needle valves, and the system calibrated by expansion of the gas into an evacuated vessel of known volume. The argon flow rate was metered on a conventional flowmeter, calibrated by the soap bubble method.⁸ Nitrosyl chloride and nitrogen dioxide flow rates were measured by recording the rate of fall of pressure in a closed vessel of $6\cdot21$ capacity. In the measurement of the NO₂ flow rate correction was made for N₂O₄ formation.⁹

PHOTOMETRIC MEASUREMENTS

Measurements of the glow intensities at different positions along the length of the reaction cell were made using an E.M.I. 6094 photomultiplier. This movable photomultiplier viewed a length of approximately 0.5 cm of the reaction cell corresponding to a time resolution of 1-15 msec, depending on gas flow rates. Preliminary experiments established that no scattered light from the discharge was detected by the photomultiplier.

Emission spectra of the glows occurring in the reaction cell were recorded by a Jarrell-Ash monochromator, type 82,000, with 50 μ slits, giving a resolution of 5 Å. An E.M.I. 9558 red-sensitive photomultiplier was used as detector in the spectroscopy experiments, and the spectra were displayed on a Honeywell-Brown 0-10 mV pen recorder.

CHEMICAL TITRATION OF CHLORINE ATOMS

Nitrosyl chloride reacts rapidly with chlorine atoms by the reaction,7

$$NOCl + Cl \rightarrow NO + Cl_2.$$
(1)

This gas phase titration of atomic chlorine was used to measure absolute chlorine atom concentrations.

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RESULTS

The object of the preliminary experiments was to establish that the observed red glow was associated with atomic chlorine. A catalytic probe consisting of 10 cm of silver wire was positioned in the reaction cell 5 cm downstream from the nitrosyl chloride injector. The addition of excess nitrosyl chloride led to a sharp extinction of the red glow at the point of mixing, and no heat release was measured on the probe. On decreasing the nitrosyl chloride flow rate a point was reached at which the red glow persisted weakly beyond the titration point, and, at the same time heat was released on the probe. This release of heat has been used previously to detect chlorine atoms $^{5, 6}$ and the inference is therefore that the red glow is due to the presence of atomic chlorine.

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FIG. 1.—The Deslandres table for the $Cl_2({}^{3}\Pi_{ou}^{*}) - Cl_2({}^{1}\Sigma_{\theta}^{*})$ transition bands; \bigcirc , observed in adsorption by Kuhn; \bullet , observed in emission by Kitagawa; \times , observed in emission, this work.

The spectrum of the glow was recorded, and consisted of a large number of bands degraded towards the red. Analysis of the spectrum enabled 31 of the bands to be identified with those previously observed by Kuhn ¹⁰ from absorption measurements on chlorine and by Kitagawa,¹¹ from the emission spectrum of a hydrogen-chlorine flame. Using the Elliott formula ¹² to calculate the wave numbers of the chlorine band-heads, 10 new bands were identified. The Deslandres table showing the comparison of our observations with those of other authors is shown in fig. 1. Several other bands of an unidentified progression were observed extending to longer wavelengths. Similar bands have been observed ¹³ but have not been associated with any

specific progression. The conclusion from the above results is that the red emission arises from excited chlorine molecules in the ${}^{3}\Pi_{0^{\mu}}^{+}$ state, their formation being dependent on the presence of atomic chlorine.

DEPENDENCE OF THE EMISSION INTENSITY ON THE CONCENTRATION OF ATOMIC CHLORINE

The flow rate of molecular chlorine into the reaction cell was maintained constant and the atom concentration varied by detuning the transmitter. The atom concentration for each setting of the transmitter was measured by titration with nitrosyl chloride to the extinction of the red glow, which was determined by a photomultiplier placed 10 cm downstream of the point of titration. The nitrosyl chloride flow was then cut off and the intensity of the glow measured at the nitrosyl chloride



FIG. 2.—A typical plot of the variation of emission intensity I with the square of the chlorine concentration, at 293°K and 1.45 torr total pressure.

injection point. The experiment was repeated at several pressures in the range 0.2-2.5 torr. Small corrections were made to the results to allow for changes in the chlorine molecule concentration due to dissociation, and the corrected results (fig. 2) showed that the observed light intensity was proportional to the square of the atom concentration over the range of pressures studied.

DEPENDENCE OF THE EMISSION INTENSITY UPON THE CHLORINE MOLECULE CONCENTRATION

The chlorine molecule concentration in the reaction cell was varied, the chlorine atom concentration and emission intensity being determined at each pressure. A plot of $I/[Cl]^2$ against $[Cl_2]$ shown in fig. 3 illustrates that the intensity is dependent on the molecular chlorine concentration below 2 torr, but above 2 torr is pressure independent. The dependence of the red glow intensity is thus rigidly defined, and was used for the determination of recombination rates of chlorine atoms.

RATE OF RECOMBINATION OF ATOMIC CHLORINE

The intensity of the red glow was measured at several positions along the reaction cell, and since the intensity is proportional to the square of the atom concentration the relative atom concentrations were obtained. The absolute value of the atom concentration at one position was found by nitrosyl chloride titration, and thus the relative concentrations were converted to absolute values at all positions.



FIG. 3.—The dependence of $I/[C1]^2$ on the molecular chlorine concentration.

The mechanism of removal of the chlorine atoms has been postulated as 5

$$Cl+Cl+Cl_2 \xrightarrow{k_2} Cl_2 + Cl_2, \qquad (2)$$

$$Cl + wall \rightarrow \frac{1}{2}Cl_2, \qquad (3)$$

yielding the kinetic expression

$$-\frac{d[Cl]}{dt} = 2k_2[Cl]^2[Cl_2] + k_3[Cl].$$
(4)

The wall recombination constant k_3 was obtained from experiments at very low pressures and low atom concentrations where $k_3[Cl] \gg k_2[Cl]^2[Cl_2]$, and the atoms recombine by a first order process. The experimental value of $k_3 = 0.7 \text{ sec}^{-1}$, corresponds to a wall recombination efficiency $\gamma = 3.5 \times 10^{-5}$.

At higher pressures and high atom concentrations, $k_2[Cl]^2[Cl_2] \gg k_3[Cl]$, and under these conditions eqn. (4) requires that a plot of 1/[Cl] against time is a straight line of slope $2k_2[Cl_2]$. Experimental plots of these variables were, however, non-linear.

Decays of the chlorine atom concentrations with time were plotted, and the slopes of the tangents to these curves gave values of -d[Cl]/dt for several values of [Cl]. By substitution in eqn. (4), k_2 was determined as a function of [Cl]. Fig. 4 shows that k_2 decreases with [Cl] independently of total pressure.

MEASUREMENT OF THE QUANTUM YIELD OF THE CHLORINE EMISSION

The absolute quantum yield of the chlorine emission process was determined by comparison with the "air afterglow" emission, the quantum yield of which is known.^{15, 16} The intensity emitted in a spectral band of 5 Å width at 6,200 Å from the chlorine molecule + atom mixture was measured and compared with the emission from the nitric oxide + atomic oxygen mixture at the same wavelength and under identical geometrical conditions. The concentrations of molecular chlorine and nitric oxide were determined from their flow rates, the concentration of chlorine atoms as described above and the concentration of oxygen atoms by titration with nitrogen dioxide to extinction of the air afterglow.



FIG. 4.—Experimental values of k₂ at pressures (torr): ○, 2.03; ○, 1.65; ①, 1.21; ○, 0.91;
O, 0.66; ①, 0.58; ①, 0.33; ×, values obtained by Bader and Ogryzlo by an independent method divided by two for comparison).

The spectral sensitivity of the E.M.I. 9558 photomultiplier was measured as a function of wavelength in the region 5000-8000 Å by calibration against a tungsten strip lamp of known colour temperature. Correction for wavelength sensitivity of the photomultiplier produced the true intensity distribution of the chlorine emission spectrum with wavelength. The measured emission from the chlorine was situated entirely between 5200 and 8000 Å, but the upper spectral limit was somewhat indefinite due to the lack of sensitivity of the photomultiplier in that region. The spectral intensity distribution of the air afterglow obtained by Clyne and Thrush 16 was used.

Measurement of the spectral intensity distributions of the two emission processes gave

fraction of the total chlorine emission intensity in a 5 Å band at 6,200 Å fraction of the total air afterglow emission intensity in a 5 Å band at 6,200 Å = 3.31and

observed intensity of the red chlorine glow at 6,200 Å (I'_{Cl}) = observed intensity of the air afterglow at 6,200 Å (I'_0)

> 3.31 (total number of quanta emitted from the red chlorine glow (I_{Cl})) total number of quanta emitted from the air afterglow (I_0)

As the molecular chlorine pressure was >2 torr, $I_{C1} = k_5[C1]^2$ and since $I_0 = k_6$ [O][NO], then

$$\frac{I_{\rm Cl}'}{I_0'} = \frac{3.31k_5[{\rm Cl}]^2}{k_6[{\rm O}][{\rm NO}]},\tag{7}$$

where k_5 and k_6 are the rate constants of the respective pseudo-bimolecular reaction processes.

By substitution of the known values in the above equation we obtain

 $k_5 = 4 + 2 \times 10^5 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$.

This enables the results of fig. 3 to be expressed in absolute terms, and the plot of $1/[Cl]^2$ against $[Cl_2]$ at very low molecular chlorine concentrations gives the rate constant of the light emitting reaction,

$$Cl + Cl + Cl_2 \xrightarrow{k_8} Cl_2 + Cl_2 + h\nu$$
(8)

as

 $k_8 = 1.5 \times 10^{13} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1} \text{ at } 20^\circ \text{C}.$

DEPENDENCE OF THE INTENSITY OF THE CHLORINE EMISSION ON ARGON CONCENTRATION

Argon was added at various flow rates to the chlorine before passage through the The partial pressure of the molecular chlorine was within 10 % of 0.2 discharge. torr throughout the whole of the experiment, i.e., within the limits of experimental error the component of the emission due to the chlorine molecules was proportional to $[Cl]^2[Cl_2]$. The linear dependence of $I/[Cl_2]$ upon $[Ar]/[Cl_2]$ is illustrated in fig. 5.

DISCUSSION

MECHANISM OF ATOM RECOMBINATION

Reaction (2) for the termolecular recombination of chlorine atoms may be interpreted in terms of two consecutive bimolecular reactions :

$$Cl + Cl_{2} \underset{k=9}{\overset{k_{9}}{\rightleftharpoons}} Cl_{3} \tag{9}$$

$$Cl_3 + Cl \rightarrow Cl_2 + Cl_2.$$
(10)

With the inclusion of the wall recombination reaction (3) and assuming a stationary state of [Cl₃], the recombination rate is given by

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$$\frac{-d[Ci]}{dt} = \frac{2k_9k_{10}[Ci]^2[Ci_2]}{k_{-9} + k_{10}[Ci]} + k_3[Ci].$$
(11)

Comparison of eqn. (4) and (11) gives

$$k_2 = k_9 k_{10} / (k_{-9} + k_{10} [\text{Cl}])$$
(12)

which may be expressed as

$$\frac{1}{k_2} = \frac{[Cl]}{k_9} + \frac{k_{-9}}{k_9 k_{10}}.$$
 (12a)

 $1/k_2$ is plotted as a function of [Cl] in fig. 6; the slope of the line yields $1/k_9$ and the intercept k_{-9}/k_9k_{10} . From fig. 6, $k_9 = 9.09 \times 10^7$ cm³ mole⁻¹ sec⁻¹, and $k_9k_{10}/k_{-9} = 2.04 \times 10^{16}$ cm⁶ mole⁻² sec⁻¹. A maximum value of k_{10} was obtained by assuming that reaction (10) is unit collisionally efficient; thus $k_{10} \le 1.7 \times 10^{14}$ cm³ mole⁻¹ sec⁻¹, and $k_{-9} \le 7.6 \times 10^5$ sec⁻¹.



FIG. 5.—The variation of I/[Cl]²[Cl₂] with [Ar]/[Cl₂].

Reactions (9) and (-9) and (10) give

$$[Cl_3] = k_9[Cl][Cl_2]/(k_{-9} + k_{10}[Cl]).$$
(13)

At low atom concentrations $(k_{10}[Cl] \ll k_{-9})$,

$$[Cl_3]/[Cl] = k_9[Cl_2]/k_{-9}, \qquad (13a)$$

and at a total pressure of 2 torr, $[Cl_3] \ge 1.2 \times 10^{-5}[Cl]$. Attempts to detect absorption by Cl₃ in the wavelength region 2,200-8,000 Å were unsuccessful.

The value obtained for the overall termolecular recombination rate constant at low chlorine atom concentrations is in good agreement with results of Bader and Ogryzlo,⁵ but is almost two orders of magnitude greater than those of Linnett and Booth.⁴

MECHANISM OF THE EMISSION REACTION

The observed linear dependence of the emission intensity I on [Cl]² under all experimental conditions rules out the possibility of the emission arising as a secondary

process associated with the main mechanism of the atom recombination. If the emission arose from some reaction of the intermediate Cl_3 radical, then on increasing the atom concentration, the intensity of emission would change from a second- to a first-order dependence on [Cl]. Nevertheless, since the emission spectrum has structure, and since the emission intensity at low pressures is pressure dependent, then it cannot arise from the direct radiative recombination of two atoms, but must be produced by an overall termolecular reaction.



FIG. 6.—The dependence of the reciprocal of the termolecular rate constant, $1/k_2$, on the atomic chlorine concentration, cf. fig. 4.

The simplified potential energy diagram of molecular chlorine is shown in fig. 7.¹⁴ The structured emission spectrum arises from molecules in ${}^{3}\Pi_{0u}^{+}$ state formed by recombination of two chlorine atoms. This glow spectrum shows bands emitted from levels up to v' = 13 corresponding to an upper state energy of 56.9 kcal mole⁻¹, but the limit is somewhat indefinite due to the weak emission intensities from the higher vibrational levels. Two alternative mechanisms for the formation of $Cl_{2^{3}}[\Pi_{0u}^{+}]$ may be written :

(1)
$$\operatorname{Cl}[{}^{2}P_{\frac{3}{2}}] + \operatorname{Cl}[{}^{2}P_{\frac{3}{2}}] + \operatorname{Cl}_{2}[{}^{1}\Sigma_{g}^{+}] \rightarrow \operatorname{Cl}_{2}[{}^{1}\Pi_{1u}] + \operatorname{Cl}_{2}[{}^{1}\Sigma_{g}^{+}].$$

 $Cl_2(1\Pi_{1u})$ is a repulsive state and hence dissociates within one vibration. If (1) is the true mechanism then the intersystem crossing

$$\operatorname{Cl}_{2}[^{1}\Pi_{1u}] \rightarrow \operatorname{Cl}_{2}[^{3}\Pi_{0u}^{+}]$$

must occur at a rate comparable with the vibrational frequency.

(2) The formation of $Cl_2(3\Pi_{0u}^+)$ via

$$\operatorname{Cl}[{}^{2}P_{\frac{3}{2}}] + \operatorname{Cl}[{}^{2}P_{\frac{1}{2}}] + \operatorname{Cl}_{2}[{}^{1}\Sigma_{g}^{+}] \rightarrow \operatorname{Cl}_{2}[{}^{3}\Pi_{0u}^{+}] + \operatorname{Cl}_{2}[{}^{1}\Sigma_{g}^{+}]$$

is a fully allowed process expected to have a high efficiency. The lifetime of $Cl(3\Pi_{0u}^+)$ is thought to be between 3×10^{-7} to 5×10^{-6} (see later), and the absence of emission

bands from levels above v' = 13, may be due to the intersystem crossing,

$$\operatorname{Cl}_{2}[^{3}\Pi_{0u}^{+}] \rightarrow \operatorname{Cl}_{2}[^{1}\Pi_{1u}]$$

occurring within this time. The energy of excitation of $Cl({}^{2}P_{3/2})$ to $Cl({}^{2}P_{1/2})$ is 2.5 kcal (g atom),⁻¹ and in thermal equilibrium at 20°C, the concentration of $Cl({}^{2}P_{1/2})$ is 1.6 % that of $Cl({}^{2}P_{3/2})$.



FIG. 7.--The simplified potential energy diagram of molecular chlorine.

If mechanism (2) is adopted then denoting $Cl(^2P_{3/2})$ by Cl, $Cl(^2P_{1/2})$ by Cl^* , $Cl_2(^{1}\Sigma_{g}^+)$ by Cl_2 and $Cl_2(^{3}\Pi_{0u}^+)$ by Cl_2^* , we may write :

$$Cl+Cl^*+Cl_2^{k_{14}} + Cl_2^* + Cl_2, \qquad (14)$$

and in addition,

$$\operatorname{Cl}_{2}^{*} \rightarrow \operatorname{Cl}_{2} + hv \tag{15}$$

$$Cl_2^* + Cl_2 \rightarrow Cl_2 + Cl_2.$$
(16)

Then for a stationary state of $[Cl_2^*]$,

$$I = k_{15}[Cl_2^*] = \frac{k_{14}k_{15}[Cl][Cl^*][Cl_2]}{k_{15} + k_{16}[Cl_2]},$$
(17)

and at low pressures where $k_{15} \ge k_{16}[Cl_2]$,

$$I = k_{14}[Cl][Cl^*][Cl_2], (17a)$$

and at higher pressures where $k_{16}[Cl_2] \gg k_{15}$,

$$I = k_{14}k_{15}[\text{Cl}][\text{Cl}^*]/k_{16}$$
(17b)

Since, at thermal equilibrium, [Cl*] is proportional to [Cl], the proposed mechanism gives a good explanation of the experimental results shown in fig. 3, and k_8 [Cl]²

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 $[Cl_2] = k_{14}[Cl^*][Cl_2]$, therefore $k_{14} = 0.94 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$. The collision rate of the termolecular reaction (14) is of the order of $10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$; therefore, within experimental error, reaction (14) occurs on every termolecular collision. From the value of the absolute quantum yield of emission and the high pressure results of fig. 3, $k_{15}/k_{16} = 2.7 \times 10^{-8} \text{ cm}^3 \text{ mole}^{-1}$.

The quenching of Cl_2^* by Cl_2 (reaction (16)) is analogous to the quenching of I_2 $({}^{3}\Pi_{0\mu}^{+})$ by $I_{2}({}^{1}\Sigma_{a}^{+})$ which has been postulated to be unit collisionally efficient.¹⁷ By this analogy we may obtain an upper limit to the rate of reaction (16) of unit collisional efficiency, i.e., $k_{16} \leq 10^{14}$ cm³ mole⁻¹ sec⁻¹, giving the lifetime of $Cl_2(^{3}\Pi_{0u}^{+}) =$ $1/k_{15} \ge 3 \times 10^{-7}$ sec¹. The lifetimes of fully allowed electronic transitions are usually of the order of 10^{-8} sec, but since the emission from Cl_2^* is not a fully allowed process by virtue of the change in spin multiplicity on emission, the lifetime of Cl_2^* would be expected to be somewhat longer than 10^{-8} sec. Three values have been proposed for the lifetime of $I_2(3\Pi_{0\mu}^+)$; they are $10^{-8} \sec^1$, $3 \times 10^{-7} \sec^1$ and 1.6×10^{-6} sec1,18,19,17 and by analogy the value determined for chlorine appears reasonable. Furthermore, Briggs and Norrish ²⁶ have observed absorption from ${}^{3}\Pi_{0u}^{+}$ state chlorine by flash photolysis, and found that its intensity closely follows the intensity of the photolysis flash, indicating a lifetime of the $3\Pi_{0u}^+$ state of much less than 50 μ sec and probably less than 5 μ sec under their experimental conditions. The satisfactory interpretation of the emission process by the above mechanism shows that the populations of the atomic states of the chlorine atom (at least, the ${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$ states) are in thermal equilibrium.

We may now interpret the dependence of the intensity of the chlorine emission upon the concentration of added argon. If reactions (14), (15) and (16) are written as before, and in addition,

$$Cl+Cl^*+Ar \rightarrow Cl_2^*+Ar, \qquad (18)$$

then kinetic analysis yields

$$I = \frac{k_{15}[\text{Cl}][\text{Cl}^*](k_{14}[\text{Cl}_2] + k_{18}[\text{Ar}])}{k_{15} + k_{16}[\text{Cl}_2]},$$
(19)

and under the experimental conditions, $k_{15} \gg k_{16}$ [Cl₂],

$$\frac{I}{[CI][CI^*][CI_2]} = k_{14} + k_{18} \frac{[Ar]}{[CI_2]}.$$
(19a)

The plot of this expression in fig. 5 shows that the relationship holds. The intercept k_{14} may be used to calibrate the plot in absolute terms, and from the gradient $k_{18} = 2.35 \times 10^{14}$ cm⁶ mole⁻² sec⁻¹. The third-body efficiency of chlorine for the photo-emissive recombination is thus 4 times that of argon.

RECOMBINATION OF ATOMIC CHLORINE IN THE PRESENCE OF ARGON

Argon was added at several known flow rates to chlorine before passage through the discharge, and the intensity of the red emission measured at several positions along the reaction cell to obtain decay rates for chlorine atoms. Taking reactions (3,) (9), (-9) and (10) as before and, in addition,

$$Cl + Ar \underset{k_{-20}}{\overset{k_{20}}{\approx}} ClAr \tag{20}$$

$$ClAr + Cl \rightarrow Cl_2 + Ar$$
(21)

the rate expression,

$$\frac{-d[Cl]}{dt} = \frac{2k_9k_{10}[Cl]^2[Cl_2]}{k_{-9} + k_{10}[Cl]} + \frac{2k_{20}k_{21}[Cl]^2[Ar]}{k_{-20} + k_{21}[Cl]} + k_3[Cl],$$
(22)

is obtained.

The value of $k_{20}k_{21}/(k_{-20}+k_{21}$ [Cl]) was determined from these experiments as $3\cdot5-5\times10^{15}$ cm⁶ mole⁻² sec⁻¹, but results were not obtained for a sufficient range of [Cl] to enable the relative importances of k_{-20} and k_{21} to be established. The overall termolecular rate of constant for the reaction,

$$Cl+Cl+Ar \rightarrow Cl_2+Ar,$$
 (23)

of $4.25 \pm 0.8 \times 10^{15}$ cm⁶ mole⁻² sec⁻¹ determined agrees well with Bader and Orgyzlo's value ⁷ of 4×10^{15} cm⁶ mole⁻² sec⁻¹ obtained using a different technique to monitor atom concentrations.

Most detailed experiments on halogen atom recombination have been performed with iodine,²⁰⁻²⁵ and although it is generally accepted that the recombination of atomic iodine occurs by two consecutive bimolecular reactions rather than by a direct termolecular reaction, the detailed mechanisms of these reaction have not been established.² The mechanism of chlorine atom recombination now postulated leads to an identification of the two reactions, and furthermore a genuine three-body radiative recombination of chlorine atoms has been observed, with a measured rate of about one thousandth of the radiationless recombination rate. The self consistency of these results is illustrated by the correlation of the experimental data with mechanistic predictions, and by the realistic order of magnitude of the value calculated for the lifetime of the $Cl_2 (3\Pi_{0\mu}^{+})$ on the basis of the proposed mechanisms.

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