THE REACTION OF CHLORINE ATOMS, Cl(3 ^2P_J), WITH NITRIC ACID IN THE GAS PHASE

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Summary

A kinetic investigation is presented of the reaction between ground state chlorine atoms, Cl(3 ^2P_J), with a Boltzmann equilibrium in the $J = 3/2$ and $J = 1/2$ ($E = 881$ cm^{-1}) spin–orbit levels, and nitric acid vapour. Atomic chlorine was generated by the repetitive pulsed irradiation of molecular chlorine in the visible region of the spectrum in a flow system kinetically equivalent to a static system and monitored by time-resolved resonance absorption in the vacuum UV at $\lambda = 138.79$ nm (Cl((3p)^4(4s), $^2P_{5/2}$) $\leftarrow$ Cl((3p)^5, $^2P_{3/2}$)). The absolute second-order rate constant for the reaction with methane, used here as kinetic standard, yielded k(Cl + CH$_4$) = (1.03 ± 0.22) × 10^{-13} cm^3 molecule^{-1} s^{-1} (room temperature; error, 2σ) which is in good agreement with previous measurements of this quantity obtained by a variety of methods. The reaction rate constant with nitric acid was found to be k(Cl + HNO$_3$) = (3.4 ± 1.6) × 10^{-14} cm^3 molecule $^{-1}$ s^{-1} (room temperature; error, 2σ). This is compared with previous rate data derived from flow discharge with mass spectrometric measurements.

1. Introduction

The role of catalytic cycles that lead to the decomposition of stratospheric ozone by pollutants is a matter of current kinetic interest. The recent review by Thrush [1] gives a concise account of such effects by hydrogen species (HO$_x$), nitrogen oxides (NO$_x$) and chlorine compounds (ClX) on the ozone decomposition, including the interaction between these competing cycles. This manuscript is concerned with the direct kinetic study of ground state chlorine atoms, Cl((3p)^5, ^2P_J), a species which, of course, arises from the photolysis of chlorofluorocarbons and which then

plays a major role in the removal of ozone [2, 3]. In particular, we describe a kinetic investigation of a reaction which is involved in the connection between the NO_x and ClX cycles

$$Cl(3\ ^2P_J) + HNO_3 \rightarrow HCl + NO_3 \tag{1}$$

The compilation of kinetic data for chlorine species in general, by Watson [4], indicates the large number of investigations that have been carried out on atomic chlorine, including those by direct monitoring of the atom via resonance absorption and resonance fluorescence spectroscopy, and constitutes a review of relevant kinetic methods as well as of the rate data. For reaction (1), two studies have been reported hitherto which have employed similar methods [5, 6]. Both investigations have used discharge flow with mass spectrometric techniques in which chlorine atoms, titrated with NOCl, were generated in excess concentration and the rate dependence of reaction (1) determined by mass spectrometric measurement on HNO_3 in the pseudo first-order regime. For T = 295 K, Leu and DeMore [5] reported k_1 = $(6.8 \pm 3.4) \times 10^{-15}$ and Poulet $et\ al.$ [6] an extrapolated rate constant of $k_1 = 7 \times 10^{-18}$, consistent with their upper limit of $k_1 < 2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. There is clearly much disagreement from these two similar measurements, and further the slow rates reported for both studies indicate that k_1 was derived from monitoring small differences in mass spectrometric peaks, initially due to HNO_3. In the present investigation we undertook a kinetic study of reaction (1) by monitoring atomic chlorine using time-resolved atomic resonance absorption spectroscopy in the vacuum UV. To the best of our knowledge, no other study of reaction (1) by monitoring $Cl(3\ ^2P_J)$ directly as a function of time has been reported hitherto.

2. Experimental details

The experimental arrangement for time-resolved resonance absorption studies of $Cl(3\ ^2P_J)$ in the vacuum UV was essentially that described hitherto [7] which utilized a modification of the earlier system employed by Fletcher and Husain [8, 9], with further marginal modification, primarily concerned with the coaxial reactor–lamp assembly and the wavelength regions of photolysis used. $Cl(3\ ^2P_J)$ was generated by the repetitive pulsed irradiation (E = 123 J; repetition rate, 0.2 Hz) of low pressures of molecular chlorine (p_{Cl_2} = 2 N m^{-2}, typically) in the presence of excess helium buffer gas. Two wavelength regions of photolysis were employed by changing the material of the common wall of the coaxial vessel–lamp assembly, namely high purity (Spectrosil) quartz, limiting the low wavelength cut-off to $\lambda \approx 165$ nm (for the measurements with CH_4), and Pyrex glass, limiting the low wavelength cut-off to $\lambda \approx 300$ nm (for the measurements with HNO_3). In kinetic terms, the overall apparatus was a slow flow system, kinetically equivalent to a static system [7 - 9]. After irradiation, $Cl(3\ ^2P_J)$ was monitored in absorption at λ = 138.79 nm ($(3p)^4(4s)$, $^2P_{5/2} \leftarrow (3p)^5$, $^2P_{3/2}$) [10] by attenuation
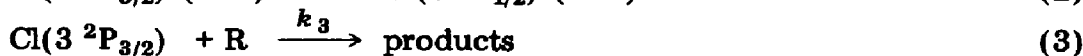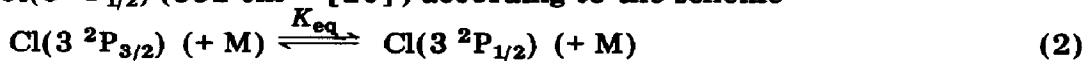
of the emission from a microwave-powered resonance source employing a flow system of Cl_2 in helium [7, 11]. The resulting photoelectric output signal at this wavelength (solar-blind photomultiplier tube, EMR 541G-0818), representing the time variation of the decay of atomic chlorine, was amplified without distortion [12] and captured in a transient recorder (Biomation 610) interfaced to a 200 point signal averager (Data Laboratories DL 102A). Kinetic results for the decay of atomic chlorine presented in this paper generally represent the averaged results of 16 individual experiments on a given flowing reactant mixture. The contents of the signal averager were transferred onto paper tape (Data Dynamics punch 1133) in binary code for computerized analysis (University of Cambridge, IBM 370/165).

2.1. Materials

In view of the controversy concerning rate data for $Cl(3\ ^2P_J)$ with HNO_3 (see Section 1), the preparation of the reactant materials is presented here. Cylinder Cl_2 (Matheson) was trapped at liquid nitrogen temperature (77 K), thoroughly degassed by many freeze-pump-thaw cycles and fractionally distilled from a CO_2-acetone slush (195 K) to 77 K. The absence of special care with this fractional distillation results in significant attenuation of the signals at $\lambda = 138.79$ nm from the spectroscopic source by trace impurities. Cylinder helium (Gold Label; Matheson, 99.999%, "ultrahigh purity") for the preparation of the reactant mixtures and for use in the flow system was passed through a molecular sieve at 77 K before use. Cylinder CH_4 (British Oxygen Co., Grade X, spectroscopically pure) was used directly. HNO_3 was prepared by the action of 70% nitric acid (AnalaR) with about twice its volume of concentrated sulphuric acid (AnalaR) under vacuum. The resulting HNO_3, trapped at 77 K, was then distilled a number of times from ice temperature (273 K) to 77 K. The resulting colourless liquid exhibited a vapour pressure of 14.1 Torr (1 Torr = 133 N m^{-2}) at 273 K as measured on a glass Bourdon gauge. A vapour pressure of 14.4 Torr at this temperature is given in ref. 13, and this drops sharply to 5.5 Torr for 90% HNO_3 (aqueous). The liquid was subjected to several freeze-pump-thaw cycles before use.

3. Results and discussion

The rate data reported in this investigation for the reaction of atomic chlorine refer to the kinetic effect of the two spin-orbit levels $Cl(3\ ^2P_{3/2})$ and $Cl(3\ ^2P_{1/2})$ (881 cm^{-1} [10]) according to the scheme

$$Cl(3\ ^2P_{3/2})\ (+ M) \overset{K_{eq}}{\rightleftharpoons} Cl(3\ ^2P_{1/2})\ (+ M) \tag{2}$$

$$Cl(3\ ^2P_{3/2})\ + R \xrightarrow{k_3} products \tag{3}$$

$$Cl(3\ ^2P_{1/2})\ + R \xrightarrow{k_4} products \tag{4}$$

If the Boltzmann equilibrium (2) is maintained through collisions, both spin–orbit levels will demonstrate identical kinetics, leading to an effective second-order rate constant k_R for either the $^2P_{3/2}$ or $^2P_{1/2}$ level of magnitude $k_R = (k_3 + k_4 K_{eq})/(1 + K_{eq})$. Measurements of the various second-order rate constants reported hitherto for atomic chlorine have not generally addressed themselves to quantification of the specific contributions by the spin–orbit levels, k_3 and k_4 [4]. Fletcher and Husain [8, 9] have carried out kinetic measurements of the spin–orbit relaxation of $Cl(3\ ^2P_{1/2})$ with a number of collision partners by generating the $^2P_{1/2}$ state photochemically in a non-Boltzmann concentration and monitoring the decay of this state on a short time scale after which equilibrium is eventually achieved. These relaxation measurements show that previous data, as might be expected, describe the effect of a Boltzmann-averaged system. Recently, Ravishankara and Wine [14] have attributed the small curvature in the Arrhenius plot for the reaction of $Cl(3\ ^2P) + CH_4$, obtained by monitoring chlorine atoms by atomic resonance fluorescence after laser flash photolysis, to the disturbance of the Boltzmann equilibrium (2). For the present experiments, Fletcher and Husain's data [8, 9] clearly indicate that the chlorine atom is monitored in these studies on time scales which are extremely long by comparison with those for spin–orbit relaxation.

Figure 1(a) gives an example of the computerized output for the digitized time variation of the transmitted light intensity I_{tr} at $\lambda = 138.79$ nm,
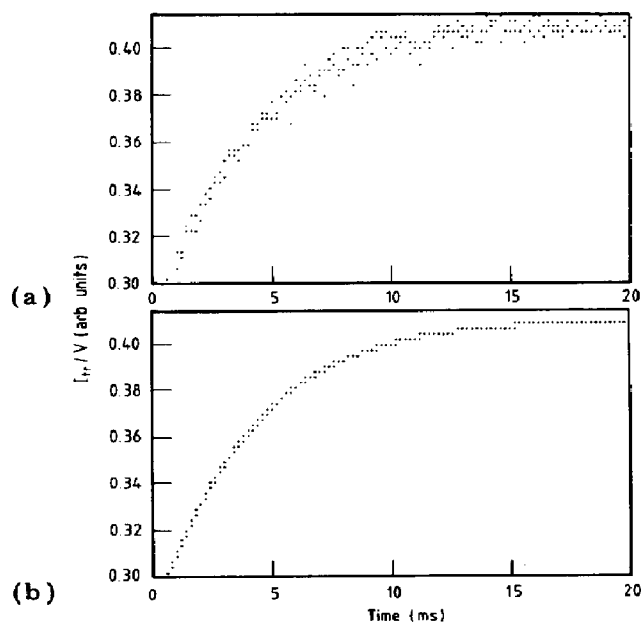

Fig. 1. Digitized time variation of the transmitted light intensity I_{tr} at $\lambda = 138.79$ nm $(Cl((3p)^4(4s),\ ^4P_{5/2}) \rightarrow Cl((3p)^5,\ ^2P_{3/2}))$, indicating the decay of $Cl(3\ ^2P_J)$ after the pulsed irradiation of molecular chlorine in the presence of helium ($p_{Cl_2} = 2.2$ N m^{-2}; $p_{total\ with\ He} = 1.75$ kN m^{-2}; $E = 123$ J; repetition rate, 0.2 Hz; sweep rate, 100 μs per channel; average of 16 individual experiments): (a) raw data; (b) computer-fitted curve of the form $I_{tr} = I_0 \exp\{-A \exp(-k't)\}$.

indicating the decay of atomic chlorine after the pulsed irradiation of Cl_2 in the presence of helium buffer gas using a Pyrex reaction vessel ($\lambda > 300$ nm). Employing the collisional relaxation rate data for $Cl(3\ ^2P_{1/2})$ of Fletcher and Husain of $k_{Cl_2} = (4.5 \pm 0.4) \times 10^{-11}$ and $k_{He} = (3.8 \pm 0.6) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} [8, 9], we see that, for the conditions of Fig. 1(a), the collisional relaxation time of $\tau_e' = 39\ \mu$s is short compared with the time scale over which the chlorine atom is monitored. The kinetic contribution from the spontaneous emission of $Cl(3\ ^2P_{1/2}) \rightarrow Cl(3\ ^2P_{3/2}) + h\nu$ (881 cm^{-1}) is, of course, negligible ($A_{nm} = 0.012$ s^{-1} [15 - 18]). Figure 1(b) shows the curve obtained from computerized fitting of the data in Fig. 1(a) to the form $I_{tr} = I_0 \exp\{-A \exp(-k't)\}$, using the numerical procedure described by Patterson [19], in order to obtain the overall first-order rate coefficient k' for the decay of chlorine atoms in a given experiment. This procedure implies the use of the standard Beer–Lambert law rather than a modified law of the form $I_{tr} = I_0 \exp\{-(\epsilon cl)^\gamma\}$ [20]. This approach is justified in this investigation by employing the rate constant for the reaction between $Cl(3\ ^2P_J) + CH_4$ as a kinetic standard (see later). Figure 2 gives an example of the atomic decay in the presence of HNO_3. Thus, in general, k' can be determined from data of the type given in Figs. 1 and 2 for the decay of $Cl(3\ ^2P_J)$ in the presence of added gases R and we may then apply the form $k' = K + k_R[R]$.
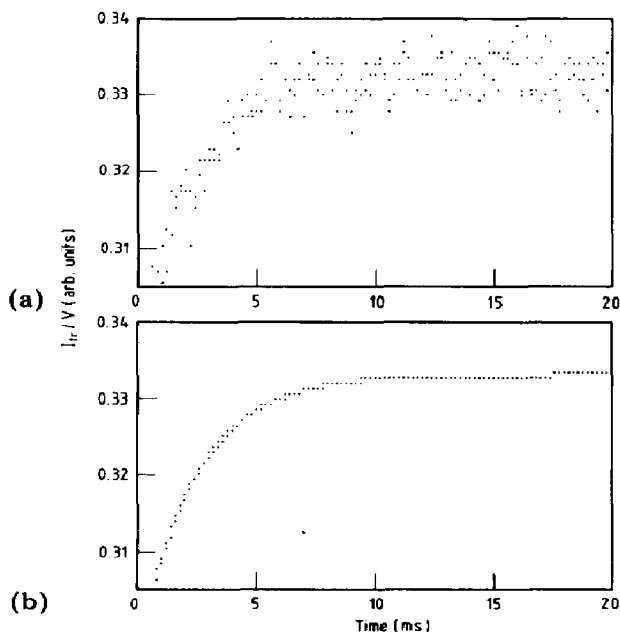

Fig. 2. Digitized time variation of the transmitted light intensity I_{tr} at $\lambda = 138.79$ nm $(Cl((3p)^4(4s),\ ^4P_{5/2}) \rightarrow Cl((3p)^5,\ ^2P_{3/2}))$, indicating the decay of $Cl(3\ ^2P_J)$ after the pulsed irradiation of molecular chlorine in the presence of helium and HNO_3 ($p_{Cl_2} = 2.5$ N m^{-2}; $p_{HNO_3} = 10.7$ N m^{-2}; $p_{total\ with\ He} = 2.09$ kN m^{-2}; $E = 123$ J; repetition rate, 0.2 Hz; sweep rate, 100 μs per channel; average of 16 individual experiments): (a) raw data; (b) computer-fitted curve of the form $I_{tr} = I_0 \exp\{-A \exp(-k't)\}$.

3.1. Cl + CH$_4$

The rate of reaction between Cl(3 ^{2}P$_J$) + CH$_4$ was measured here to provide a kinetic standard as the rate constant is well established [21]. k' was determined over the approximate concentration range [CH$_4$] = 0 - 7 × 10^{15} molecules cm^{-3} and was corrected for diffusional loss in a similar way to our earlier measurement of the diffusion coefficient (D_{12}(Cl(3 ^{2}P$_J$) in helium) = 0.43 ± 0.01 cm^2 s^{-1} at 1 atm [7]). Thus, employing the standard form $k' = K + k_{CH_4}$ [CH$_4$], we obtain k_{CH_4} = (1.03 ± 0.22) × 10^{-13} cm^3 molecule^{-1} s^{-1} (2σ) (room temperature). This may be compared with the "preferred value" of k_{CH_4} = 1.04 × 10^{-13} [21] and the recent value of Ravishankara and Wine [14] of k_{CH_4} = (0.98 ± 0.045) × 10^{-13} cm^3 molecule^{-1} s^{-1} (2σ) (298 K), clearly justifying the use of the standard Beer–Lambert law for the measured resonance absorption.

3.2. Cl + HNO$_3$

Figure 3 shows the variation in k' for the decay of Cl(3 ^{2}P$_J$) in the presence of HNO$_3$. The upper limit of the concentration of HNO$_3$ that
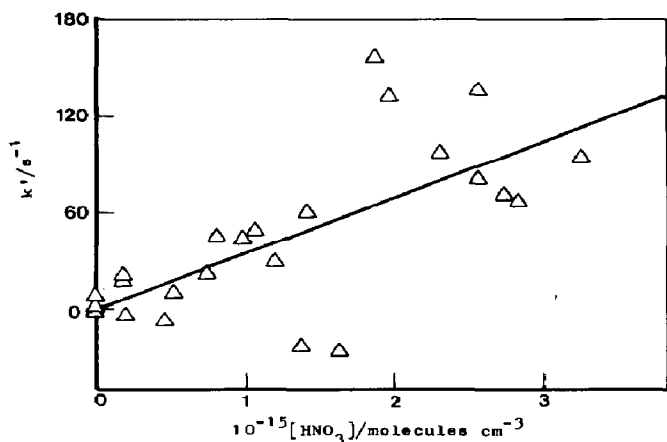

Fig. 3. Plot of pseudo first-order rate coefficients k' for the decay of Cl(3 ^{2}P$_J$) in the presence of HNO$_3$.

could be employed was determined by the degree of attenuation of the resonance transition at λ = 138.79 nm from the spectroscopic source due to the vacuum UV continuum of the reactant. The data are scattered primarily because of this attenuation but give rise to a clear rate of k_1 = (3.4 ± 1.6) × 10^{-14} cm^3 molecule^{-1} s^{-1} (room temperature; 2σ). This result is an order of magnitude higher than that reported by Leu and DeMore [5] and, of course, must be contrasted with the upper limit reported by Poulet et al. [6] who attribute the difference between their value of k_1 and that of Leu and DeMore to the effect of physical adsorption of HNO$_3$. It is difficult to envisage such effects as giving rise to rates which differ by at least two orders of magnitude and certainly, in the present system, repetitive pulsing on a continuous-flow system and a rough inspection of the extent of attenuation of the atomic chlorine resonance transition by the vacuum UV

continuum of HNO_3 indicate that such adsorption effects could not account for the qualitative difference in rates obtained in this investigation and those derived from the mass spectrometric studies [5, 6]. Further, the loss of HNO_3 in the present system by direct photolysis in the UV [22, 23] and kinetic complications arising from this were eliminated by restricting the photolysis to that of Cl_2 in the visible region of the spectrum through the use of Pyrex (see Section 2). The reactant purity should be noted (see Section 2). Leu and DeMore employed commercial HNO_3 of 90% purity without further purification; Poulet *et al.* [6] prepared HNO_3 but did not indicate the purity. Reaction (1) is exothermic ($\Delta H = -7.4$ kJ mol^{-1} [24]). If we attribute the difference between the magnitude of k_1 obtained in this investigation and that expected from the collision rate as entirely due to the activation, which is a sensible approximation for an atomic reaction, we obtain $E_1 = 22$ kJ mol^{-1}.

There is clearly a difference between the value of k_1 obtained by directly monitoring $Cl(3\ ^2P_J)$ as a function of time and those derived from mass spectrometric measurements on HNO_3. A further investigation by a different technique such as time-resolved resonance fluorescence on $Cl(3\ ^2P_J)$ would, in our view, further assist our understanding of reaction (1).

Acknowledgments

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