A KINETIC STUDY OF THE CHEMILUMINESCENCE IN THE Cl–NO₂–O₃ SYSTEM

W. WONGDONTRI-STUPER, R. SIMONAITIS and JULIAN HEICKLEN

Department of Chemistry and Ionosphere Research Laboratory, The Pennsylvania State University, University Park, Pa. 16802 (U.S.A.)

Summary

Cl_2 was photolyzed at 366 nm at temperatures in the range 219 - 273 K in the presence of NO_2 with added N_2 or O_2. The reaction mixture was bled continuously into a stream of ozonized oxygen; chemiluminescence was observed during the photolysis or shortly thereafter. The dark decay of the chemiluminescence was first order with a decay constant of $46.1 \exp\{-(2000 \pm 300)/T\}$ s^{-1}. During irradiation the initial relative quantum yield $\Phi_i^{rel}\{I\}$ of the chemiluminescence was independent of the absorbed intensity, the total pressure, the Cl_2 pressure and the diluent gas (N_2 or O_2). The quantum yield increased with an NO_2 pressure increase at 273 K, but was independent of the NO_2 pressure at 238 or 219 K. The identity of the species responsible for the chemiluminescence is not yet certain.

1. Introduction

Chlorine atoms are known to add readily to NO_2 [1, 2]. However, few studies of this reaction have been carried out. We have observed that, when Cl_2 is photolyzed in the presence of NO_2 at 366 nm and at temperatures below 296 K, a strong chemiluminescence in the red is observed if, during irradiation, a portion of the photolysis mixture is passed through a capillary bleed into a stream of ozonized oxygen. It is presumed that an unstable intermediate, formed from the reaction of chlorine atoms with NO_2, reacts with O_3 in a chemiluminescent reaction. In this work we present our results of a kinetic study of this chemiluminescence.

2. Experimental

The experimental procedure was essentially the same as that used to determine NO by the chemiluminescent reaction with O_3 [3]. Mixtures of Cl_2 and NO_2 with added N_2 or O_2 as carrier gases were irradiated at 366 nm

in a cylindrical quartz cell 10 cm long and 5 cm in diameter. The 366 nm line was obtained by passing the radiation from an Illumination Industries high pressure 200 W mercury arc lamp (Type 202-1003) through a Corning CS 7-37 filter. The cell contents were bled through a sampling capillary tube into the chemiluminescent chamber where they were mixed with ozonized oxygen. The chemiluminescence was viewed with an EMI 9785B photomultiplier tube after passing through a Corning CS 2-62 filter. In one experiment a Corning CS 2-64 filter was used but the results obtained were identical. Details of the chemiluminescent cell and other experimental details have been published elsewhere [3].

The chemiluminescence intensity was monitored continuously during the irradiation and also after the irradiation had been terminated. The initial rates of emission were corrected for the time constant (0.73 s) of the measurement system. However, for the dark decay of the emission the correction was negligible. The evacuation rate through the sampling capillary was $(4.3 \pm 0.2) \times 10^{-4}$ s^{-1} independent of temperature. This leads to a negligible correction for the initial emission growth rates and to a small but significant correction ($\leqslant 10\%$) for the decay of the dark rate of emission.

Actinometry was carried out by the photolysis of optically equivalent amounts of NO$_2$ in the presence of N$_2$. The NO produced was determined by the chemiluminescent reaction with O$_3$. The absorbed light intensities I_a were determined from the known quantum yield for NO formation, the value of which in this case was 2.0 [4].

Chlorine, N$_2$ and O$_2$ were purified using the methods described previously [3]. The NO$_2$ was purified by mixing with about 600 Torr O$_2$ and then repeatedly freezing at -196 °C and warming to room temperature until the blue color of N$_2$O$_3$ was absent. The NO$_2$ was then distilled over the range from -63 to -130 °C. ClONO was prepared by the method of Molina and Molina [5].

3. Results

Chemiluminescence is observed when Cl$_2$ is photolyzed at 366 nm in the presence of NO$_2$ with added N$_2$ or O$_2$, provided that the photolysis mixture is mixed with ozonized oxygen either during the photolysis or a short time after photolysis has ceased. A typical profile is shown in Fig. 1. Initially the chemiluminescence intensity grows rapidly and soon reaches a steady state value. If the irradiation is terminated the chemiluminescence intensity decays exponentially. If the irradiation is not terminated the emission intensity eventually declines as the NO$_2$ is consumed.

Chemiluminescence is observed only when both Cl$_2$ and NO$_2$ are present and only when the ozonizer is being used. In all experiments one of the carrier gases (N$_2$ or O$_2$) was also present; identical results were obtained for the two gases. In practice a very weak signal is observed when NO$_2$ is photo-
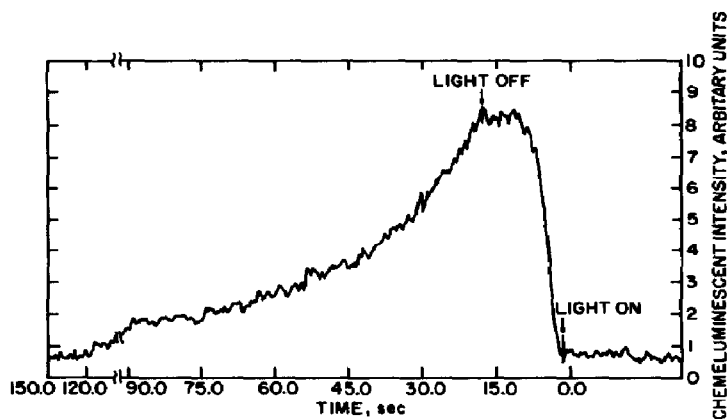
Fig. 1. A light emission profile during and after irradiation: $[NO_2]$, 102 mTorr; $[Cl_2]$, 4.01 Torr; $[O_2]$, 584 Torr; T, 273 K.

lyzed alone, because of the formation of NO. However, the contribution of the signal due to NO_2 photolysis to the total signal is negligible.

Kinetic studies were performed at temperatures of 273, 238 and 219 K respectively. Although emission could also be observed at 296 K, the intensity was too low for an accurate kinetic study to be carried out.

Relative initial emission quantum yields $\Phi_i^{rel}\{I\}$, obtained from the initial slopes of the emission profile, were normalized to a value of 2.0 for all temperatures. Values of $[Cl_2]$, $[NO_2]$ and I_a were varied over a wide range for each temperature, the respective ranges being 1 - 17 Torr, 30 - 568 mTorr and $(0.27 - 22) \times 10^{13}$ photons cm^{-3} s^{-1}. Runs were carried out both in the absence and in the presence of O_2 or N_2 at a pressure of about 500 Torr.

$\Phi_i^{rel}\{I\}$ is independent of $[Cl_2]$, I_a and the total pressure $[M]$. However, $\Phi_i^{rel}\{I\}$ increases with increasing $[NO_2]$ at 273 K to an upper limiting value, although it is independent of $[NO_2]$ at lower temperatures.

Figure 1 shows that the chemiluminescence decays when the irradiation is terminated. Typical first order plots of the dark decay are shown in Fig. 2. The plots are linear, indicating that the dark decay of the chemiluminescence follows first order kinetics. Values of the first order decay constant k were obtained from the slopes of the plots. The average values of k at each temperature are $(3.4 \pm 0.6) \times 10^{-2}$ s^{-1} at 273 K, $(8.74 \pm 1.38) \times 10^{-3}$ s^{-1} at 239 K and $(5.90 \pm 0.53) \times 10^{-3}$ s^{-1} at 219 K. From the Arrhenius plot of k shown in Fig. 3 the Arrhenius expression $k = 46.1\exp\{-(2000 \pm 300)/T\}$ s^{-1} is obtained.

The low values obtained for the pre-exponential factor and the activation energy suggest that the decay of the species responsible for the chemiluminescence is probably heterogeneous in nature. Further evidence that the surface can influence the chemiluminescence intensity comes from attempts to prepare ClONO in the reaction cell. ClONO was prepared in the reaction cell, by mixing Cl_2O and ClNO, to see if it would react with NO_2 to produce
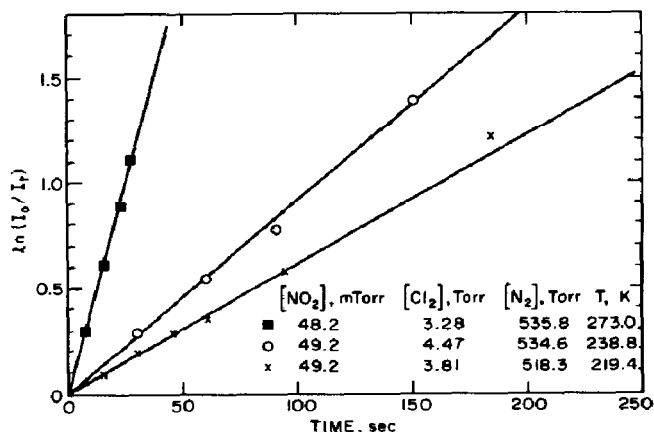
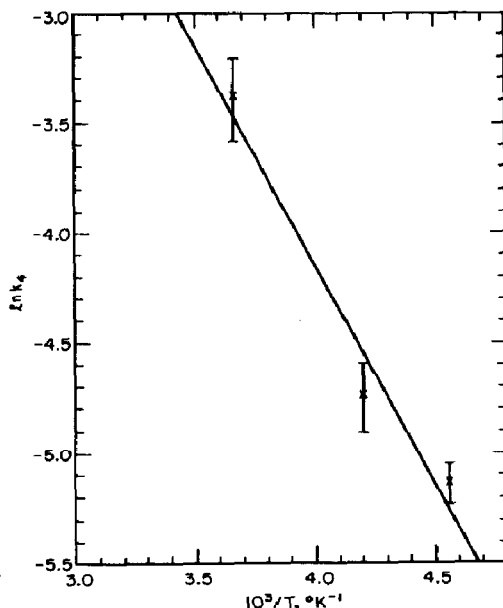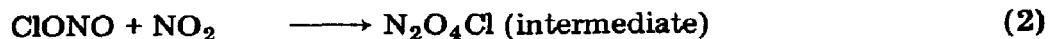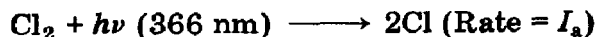Fig. 2. First order plots of the dark decay of the chemiluminescence.

Fig. 3. An Arrhenius plot of k.

the chemiluminescent species. Not only did this not occur, but the emission was completely suppressed in subsequent photochemical experiments, even in those carried out at 226 K. When the reaction cell was cleaned with cleaning solution ($K_2Cr_2O_7$–H_2SO_4) and reconditioned after this procedure, the emission intensity was restored to its original value and was reproducible.

4. Discussion

The observations indicate that an unstable compound is formed when Cl_2 is photolyzed in the presence of NO_2. In the chemiluminescence chamber this intermediate reacts with O_3 to produce the observed chemiluminescence.

The identity of the intermediate is not clear. However, a mechanism consistent with these observations is

$$Cl_2 + h\nu \text{ (366 nm)} \longrightarrow 2Cl \text{ (Rate} = I_a)$$

$$Cl + NO_2 + M \longrightarrow ClONO + M \tag{1a}$$

$$Cl + NO_2 + M \longrightarrow ClNO_2 + M \tag{1b}$$

$$ClONO + NO_2 \longrightarrow N_2O_4Cl \text{ (intermediate)} \tag{2}$$

$$ClONO \xrightarrow{\text{wall}} ClNO_2 \tag{3}$$

$$N_2O_4Cl \xrightarrow{\text{wall}} ClNO_2 + NO_2 \tag{4}$$

The low Arrhenius parameters for the dark decay of the chemiluminescence indicate that reaction (4) is heterogeneous. Since wall effects may influence the behavior of ClONO when it is prepared from Cl_2O and NOCl, reaction (3) may also be heterogeneous. In the chemiluminescent chamber N_2O_4Cl reacts with O_3 to produce the observed light (red) emission

$$N_2O_4Cl + O_3 \rightarrow \text{Products} + h\nu \text{ (red)} \tag{5}$$
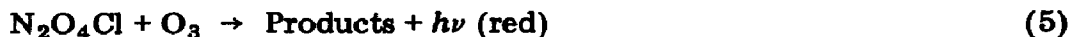
The reaction between chlorine atoms and NO_2 is well known. Clyne and White [6] have obtained a rate coefficient of 7.2×10^{-31} ($M \equiv N_2$ at 298 K) at low pressures using a discharge flow system. Glavas et al. [7] have found a value of 2.5×10^{-31} at about 1 atm of N_2 and a temperature of 294 K in a competitive steady state photolysis experiment. Niki et al. [2], using a photolysis study with Fourier transform IR spectroscopy detection, have shown that the principal reaction between chlorine atoms and NO_2 leads to the thermodynamically less favored ClONO isomer ($\geqslant 80\%$) rather than the more stable $ClNO_2$.

In order to account for our kinetic observations we must also assume that, for a significant part of the time, reaction (1a) is followed giving ClONO as product. We therefore propose reaction (2) for the formation of the intermediate responsible for the chemiluminescent reaction with O_3, because the relative emission quantum yield is $[NO_2]$ dependent at 273 K.

Since $\Phi_i\{I\}$ is $[NO_2]$ dependent, it is necessary to have the competing reaction (3) for ClONO removal; ClONO is known to isomerize readily via a heterogeneous process to $ClNO_2$ [2, 8]. The dark decay of the chemiluminescence with a very low pre-exponential factor and a low activation energy requires the introduction of reaction (4). The products of reaction (4) are very reasonable because of the proposed stoichiometry of reactions (1a) and (1b).

Since the chemiluminescence is proportional to the concentration of the intermediate, the proposed mechanism leads to the following steady state kinetic expression for the initial stages of photolysis when reaction (4) is negligible:

$$\Phi_i\{I\} = 2k_2(k_{1a}/k_1)[NO_2]/(k_3 + k_2[NO_2]) \tag{6}$$

Equation (6) predicts that a plot of $\Phi_i\{I\}^{-1}$ or $\Phi_i^{rel}\{I\}^{-1}$ versus $[NO_2]^{-1}$ should be linear with a slope/intercept of k_3/k_2. Absolute values of $\Phi_i\{I\}$ cannot be obtained, because the emission sensitivity for the reaction of N_2O_4Cl with O_3 is not known. The relative quantum yields were normalized to the maximum possible value for $2k_{1a}/k_1$ of 2.0, as predicted by eqn. (6). In Fig. 4 values of $\Phi_i^{rel}\{I\}^{-1}$ (normalized to $\frac{1}{2}$) are plotted versus $[NO_2]^{-1}$ for three different temperatures. The lines are drawn with an intercept $k_1/2k_{1a}$ of 0.50.

At 273 K and low $[NO_2]$ the plot deviates slightly from that predicted by eqn. (6). However, the deviation is not sufficiently large to invalidate eqn. (6) since the data at low $[NO_2]$ are the least accurate.
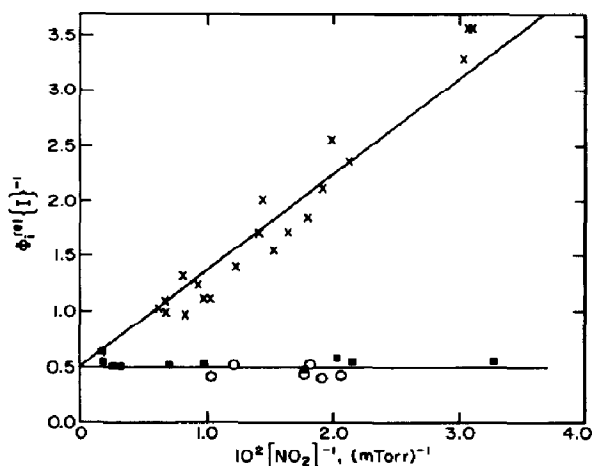
Fig. 4. Plots of $\Phi_i^{rel}\{I\}^{-1}$ vs. $[NO_2]^{-1}$ at various temperatures: $\bigcirc$, 219 K; $\blacksquare$, 238 K; $\times$, 273 K.

It is possible nevertheless that the proposed mechanism is not complete or that the ClONO is not completely in the steady state at low $[NO_2]$. At 239 and 219 K the plot has zero slope and an intercept of 0.5. This result is consistent with the mechanism if k_3 is much smaller than $k_2[NO_2]$ at 239 and 219 K; this is very reasonable and expected since ClONO isomerization to $ClNO_2$ has a significant activation energy [5, 8]. From the ratio of slope to intercept at 273 K, $k_3/k_2 = (6.2 \pm 0.9) \times 10^{15}$ cm^{-3} is obtained. Since reaction (3) must be slower than diffusion controlled to account for the lack of pressure dependence, k_3 is less than 0.6 s^{-1}. Thus k_2 is less than 1×10^{-16} cm^3 s^{-1}.

Acknowledgments

References

1 R. T. Watson, *J. Phys. Chem. Ref. Data, 6* (1977) 871.
2 H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenback, *Chem. Phys. Lett., 59* (1978) 78.
3 W. Wongdontri-Stuper, R. Simonaitis and J. Heicklen, *Geophys. Res. Lett., 5* (1978) 1005.
4 I. T. N. Jones and K. D. Bayes, *J. Chem. Phys., 59* (1973) 4836.
5 L. T. Molina and M. J. Molina, *Geophys. Res. Lett., 4* (1977) 83.
6 M. A. A. Clyne and I. F. White, as reported by Watson [1].
7 S. Glavas, R. Simonaitis and J. Heicklen, unpublished work, 1979.
8 B. Janowski, *Ph.D. Dissertation*, Keil University, F.R.G., 1975.