KINETIC STUDY OF THE REACTION OF OH RADICALS WITH NITROSYL CHLORIDE AS A POSSIBLE SOURCE OF CIOH

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The reaction of OH with NOCl has been studied using the discharge flow reaction-EPR technique. The absolute rate constant is $k_1 = (4.3 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. A mass spectrometric investigation of the products shows that this reaction occurs via two primary steps, OH + NOCl \rightarrow NO + ClOH (1a) and OH + NOCl \rightarrow HONO + Cl (1b) with $k_{1a} = k_{1b}$.

1. Introduction

The stratospheric behaviour of ClOH has been extensively discussed in recent publications [1-9]. UV spectroscopic studies of ClOH have been investigated by different groups to determine the role of this molecule as a possible stratospheric chlorine reservoir. But a discrepancy exists in the values of the absorption cross sections of ClOH, especially above 300 nm: theoretical calculations [5] and unpublished experimental data [6] indicate negligible absorption in the 300-350 nm wavelength region, whereas two groups have recently obtained a noticeable absorption in this region [7-9]. In these last investigations the cross sections which were derived from equilibrium mixtures of $H_2O + Cl_2O + ClOH$ were dependent on the value of the equilibrium constant $K_{eq} = [CIOH]^2/$ $[Cl_2O] [H_2O]$. Since this constant is not precisely known (at 298 K, $K_{eq} = 0.8$ [6], 0.25 [7], 0.082 [8]), it has been mentioned [10] that a study of the absorption cross sections of ClOH is still required in an anhydrous environment before the UV spectrum of ClOH can be considered to be established.

We report here a kinetic investigation of the reaction of OH with NOCl, which could be a new source of gaseous ClOH if this reaction occurs with a sufficient rate via

$$OH + NOC1 \rightarrow CIOH + NO.$$
 (1a)

Other sources of ClOH, such as the reactions of ClO radicals with hydrogenated molecules, are not suitable since these reactions are very slow at room temperature, even when they are exothermic. For example, the reaction ClO + $H_2CO \rightarrow ClOH + HCO$, which is 11 kcal/mole exothermic, has been found too slow to provide an alternate source of ClOH [11]. Concerning reaction (1a), no kinetic data exist. Some elementary reactions of NOCl with H, Cl, Br and O atoms have been studied. Since the reactions of H [12], Cl [13], Br [13] are quite fast ($k = 1.6 \times 10^{-11}$, 3.0×10^{-11} and 1.0×10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K respectively), NOCl is used as a titration reactant for these atoms in discharge flow experiments. However, for the reaction of O atoms with NOCl, which has been shown to occur via the primary step O + NOCl \rightarrow NO + ClO [14], a lower reactivity has been observed (at 298 K, $k = 3.3 \times 10^{-14}$ [14] or 4.7×10^{-14} [15]).

2. Experimental

Two discharge flow systems have been used. The kinetic study has been performed in a fast flow reactor with EPR detection of OH radicals. The analysis of the products has been made in another reactor using mass spectrometric detection.

The EPR spectrometer (Varian E112) and the modulated-beam mass spectrometer (V.G. Micromass Q.50) have been described in previous publications [16,17]. The kinetics of reaction (1a) was investigated in a teflon reactor (50 cm in length and 2.2 cm in internal diameter) at room temperature. The pressure was measured with a MKS pressure transducer and the pressure range was 0.47-1.10 Torr. OH radicals were produced from the fast reaction $H + NO_2$ \rightarrow OH + NO with an excess of NO₂ over H atoms. A double concentric injector was used, NO_2 was introduced into the reactor through the external tube of this injector, and NOCl was introduced downstream, through the internal tube. The reaction between H and NO₂ was complete before introducing NOC1. The relative position of the two tubes was kept constant during the experiments, these tubes being movable along the axis of the reactor. H atoms were produced from a microwave discharge in H_2 highly diluted in helium. In the kinetic experiments, the gases were pumped by a 180 m^3/h rotary pump giving high flow velocities up to 50 m s⁻¹ at 0.5 Torr in order to enhance time resolution in the EPR cavity. The kinetics were followed by monitoring the decay of OH radicals in the presence of an excess of NOC1. OH concentrations ranged from 8.0×10^{10} cm⁻³ to 2.7×10^{11} cm⁻³. These absolute concentrations were obtained using the NO spectrum as a reference and the reported transition probabilities [18]. The EPR signal as well as the flow rate parameters were processed on-line by a 32k microcomputer.

In the mass spectrometric experiments, a similar reactor was used, and the stable reactants and products were analyzed for a constant reaction time.

The following gases were used without further purification: H₂ (Air Liquide, 99.95%); He (Air Liquide, 99.995%); NO₂ (Matheson, \geq 99.5%); NOCl (Matheson, \geq 97%); Cl₂ (Matheson, \geq 99.9%). Dimerization of NO₂ was taken into account in the calculation of NO₂ concentration from its pressure drop in a 10 ℓ bulb. NOCl being sensitive to ambient light, its photodecomposition leads to the formation of small amounts of Cl₂ which was mass spectrometrically detected. Therefore, sampling of NOCl in a blackened bulb was done just before each experiment. Helium was passed through a liquid-nitrogen trap before being introduced into the reactor in order to remove impurities which produce H and O atoms in the microwave discharge.

3. Results and discussion

3.1. Rate measurements of the reaction $OH + NOCl \rightarrow products$

The kinetic analysis of the reaction

$$OH + NOCI \rightarrow products$$
 (1)

has been made using pseudo-first-order conditions. 32 kinetic runs have been performed at 298 K, with NOCl concentration in high excess over OH concentrations (between 57 and 800 fold), in order to keep negligible secondary reactions. The pseudo-first-order rate constant k_1^1 was directly calculated for each experiment: $k_1^1 = -\overline{v} d \ln[OH]/dx$ (in s⁻¹), where \overline{v} is the mean flow velocity and [OH] the radical concentration at the distance x between the NOCl injector and the position of the EPR cavity. A systematic correction to k_1^1 was done for axial diffusion of OH radicals. This correction never exceeded 3%. Logarithmic decay of OH concentration was observed for all the NOCl concentrations used which ranged from 7.88 $\times 10^{13}$ to 6.88×10^{14} molecules cm⁻³. The experimental results are shown in fig. 1 where the variations of $-d \ln [OH]/dt$ are plotted versus the initial concentrations of NOCl. Then, the absolute rate constant could be obtained $(k_1 = k_1^1 / [\text{NOCl}]_0)$, and a leastsquares treatment of all the experimental data yielded the following value for k_1 at 298 K,

 $k_1 = (4.3 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$

The error represents two standard deviations. A posi-



Fig. 1. Pseudo-first-order rate constant of reaction (1) at 298 K as a function of $[NOC1]_0$.

tive intercept of $33 \pm 9 \text{ s}^{-1}$ is observed, which represents the heterogeneous loss of OH radicals on the teflon wall. Independent measurements of the first-order rate constant of OH wall loss have been done, in the absence of NOCl, leading to the value 21 s^{-1} . Since these two values are of the same order, it can be concluded than a heterogeneous reaction between OH and NOCl is negligible on the teflon surface under the experimental conditions used.

The rate constant obtained for reaction (1) in the present work is the first kinetic determination for this reaction. This rate constant is lower than those obtained in earlier studies for the reactions of H, Cl and Br with NOC1 [12,13] but it is higher than that of the reaction of $O(^{3}P)$ with NOC1 [14,15]. All these elementary reactions are exothermic, but no correlation appears to exist between reactivity and heat of reaction.

3.2. Product analysis of reaction (1)

The following channels may be considered a priori with their enthalpy changes calculated from ref. [19]:

$OH + NOC1 \rightarrow NO + CIOH$,	$\Delta H \approx -22.2 \text{ kcal/mole}$,
	(1a)

 \rightarrow HONO + Cl, $\Delta H \approx -11.2$ kcal/mole, (1b)

 \rightarrow HNO + ClO, $\Delta H \approx$ +26.2 kcal/mole, (1c)

 $\rightarrow NO_2 + HCl, \quad \Delta H \approx -35.9 \text{ kcal/mole.}$ (1d)

First, reaction (1c) which is highly endothermic can be ruled out. Among the three exothermic channels (1a), (1b) and (1d), reaction (1d) which proceeds via a four-center complex is unlikely. Channels (1a) and (1b), which are respectively abstraction and exchange reactions, remain to be considered.

The analysis of the products was done using the quadrupole mass spectrometer coupled with a flow reactor quite similar to that used for the kinetic study. Before introducing NOCl, H atoms were detected at m/e = 1 and it was verified that these atoms were entirely consumed by NO₂ which was flowed in excess over H. In the first runs, using initial concentrations of NOCl and OH ranging from 10^{14} to 10^{15} cm⁻³ and from 10^{12} to 10^{13} cm⁻³ respectively, the mass spectra of the products were observed for a reaction time for which reaction (1) was complete. Under these

conditions, ClOH and HONO were detected simultaneously at their parent peak m/e = 52 and m/e = 47respectively. This observation suggested that the two elementary processes (1a) and (1b) occurred. The absolute and direct calibration for these two species was not easy to achieve, due to the unability to obtain pure samples of these two unstable species. Then, the branching ratio of the two primary steps (1a) and (1b) was determined by measuring the concentration of Cl atoms formed in reaction (1b). This concentration was indirectly obtained from the measurement of Cl₂ concentration. Effectively, Cl atoms were rapidly converted to Cl₂ by the fast reaction with NOC1 used in excess:

$$Cl + NOCl \rightarrow NO + Cl_2$$
. (2)

Molecular chlorine was detected at m/e = 70. The completion of reaction (2) could be verified since no Cl atoms were observed either in the mass spectra or in the EPR spectra. Consequently, calibration of Cl₂ was used as a measurement of the branching ratio of reactions (1a) and (1b).

The moveable double injector was kept at a fixed position. For this constant reaction time, the Cl₂ produced was directly related to the NOCl consumption (Δ [NOC1]). This consumption was measured at m/e = 49 corresponding to the NCl⁺ ion, since NOCl has no significant molecular ion. The calibration of the mass spectrometer for Cl₂ was made using a standard mixture of chlorine highly diluted in argon. In all experiments, the observed contribution of Cl₂ issued from NOCl was taken into account. This contribution, which results from a small but unavoidable photodecomposition of NOCl, was always found to be lower than 0.2% of the NOCl concentration. If α and β are the respective branching ratios of reactions (1a) and (1b), β is experimentally deduced from the observed value of Δ [NOC1] and the calibrated [Cl₂] resulting from reaction (2):

$$OH + NOCl \rightarrow \alpha ClOH + \alpha NO, \qquad (1a)$$

$$\rightarrow \beta \text{ HONO} + \beta \text{ Cl}, \tag{1b}$$

$$\alpha + \beta = 1.$$

Thus, it is easy to obtain $\beta = [Cl_2]/(\Delta[NOCl] - [Cl_2])$. From 8 experiments carried out at 298 K and at pressures ranging from 0.50 to 0.77 Torr, β has been calculated from the values of $\Delta[NOCl]$ and $[Cl_2]$ range ing from 1.85×10^{12} to 1.23×10^{13} cm⁻³ and from 6.0×10^{11} to 3.81×10^{12} cm⁻³ respectively. Finally, it is concluded that the value of the branching ratio for reaction (1b) is $\beta = 0.50 \pm 0.04$, where the error is one standard deviation.

In order to be sure that no systematic error has been made, some experiments have also been performed using absolute titration of OH radicals. The reaction $OH + C_3H_6 \rightarrow products$ was first considered as a titration reaction because it is fast ($k \approx 1.7 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ [20]). But the high value of the stoichiometry [OH]_{reacted}/[C₃H₆]_{reacted}, previously measured [20] and confirmed in the present work, led us to use a more suitable titration reaction: OH + HBr \rightarrow H₂O + Br. The rate constant of this reaction seems to be well established [21,22] and high enough for titration, $k \approx 1.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K, and the stoichiometry is unity. The introduction of HBr at the place of NOCl through the central tube allowed us to measure the absolute initial concentration $[OH]_0$ in the part of the reactor where the reaction of OH with NOCl starts. Thus, under the conditions p = 0.50 Torr, $[OH]_0 = 1.8 \times 10^{12} - 2.7 \times 10^{13}$ cm⁻³ and $[NOCI]_0 = (4.3 - 7.4) \times 10^{13}$ cm⁻³, $[Cl_2]$ was experimentally measured and ranged from 1.4×10^{12} to 3.2×10^{12} cm⁻³. These experimental values of Cl_2 concentration ($[Cl_2]_{exp}$) were compared to the calculated values ([Cl₂]_{calc.}) obtained from the simulation of the complete reaction system using the appropriate rate constants (see table 1). Assuming that reactions (1a) and (1b) had the same importance $(\alpha = \beta = 0.50)$, it was found that $[Cl_2]_{calc.} = [Cl_2]_{exp.}$ within experimental error (≤10%). These experiments

and calculations confirm that the reaction OH + NOCl \rightarrow products proceeds following two equivalent primary steps:

$$OH + NOCl \rightarrow ClOH + NO$$
, (1a)

$$OH + NOCl \rightarrow HONO + Cl.$$
 (1b)

Hence, the rate constant k_1 , which has been measured in the present work, corresponds to the overall reaction rate and $k_{1a} = k_{1b} = (2.15 \pm 0.20) \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹. One of the two channels, step (1b), is an exchange reaction. Such a mechanism does not appear to exist for the other elementary reactions of NOCl previously studied. For the reaction of Cl with NOCl an exchange would give a "do nothing" reaction. The similar reaction with Br, Br + NOCl \rightarrow NOBr + Cl, is negligible at room temperature because it is 8 kcal mole⁻¹ endothermic. The following reaction pathways of NOCl with H and O would be thermochemically possible:

$H + NOCI \rightarrow HNO + CI,$	$\Delta H \approx -11.8$ kcal/mole,
$0 + \text{NOCl} \rightarrow \text{NO}_2 + \text{Cl},$	$\Delta H \approx -35.2$ kcal/mole.

However these channels were not believed to occur in the previous studies [12,15] which considered that the only possible step was chlorine atom abstraction.

4. Conclusion: application to the study of the UV absorption spectrum of ClOH

Since the present kinetic results show that reaction

Table 1

Input kinetic parameters used for the simulation of the reaction system producing ClOH

Reaction	Rate constant at 298 K $(cm^3 molecule^{-1} s^{-1})$	Ref.
$H + NO_2 \rightarrow OH + NO$ $OH + OH \rightarrow H_2O + O$ $O + OH \rightarrow O_2 + H$	$1.2 \times 10^{-10} \\ 1.0 \times 10^{-11} \\ 4.0 \times 10^{-11}$	[23] [23] [23]
$\begin{array}{c} \text{OH} \xrightarrow{\text{wall}} \text{products} \\ \text{OH} + \text{NOCl} \rightarrow \text{CIOH} + \text{NO} (1a) \\ \text{OH} + \text{NOCl} \rightarrow \text{HONO} + \text{Cl} (1b) \\ \text{Cl} + \text{NOCl} \rightarrow \text{NO} + \text{Cl}_2 (2) \\ \text{H} + \text{NOCl} \rightarrow \text{NO} + \text{HCl} \\ \text{Cl} + \text{CIOH} \rightarrow \text{CIO} + \text{HCl} \end{array}$	$30 s^{-1}$ 2.15×10^{-13} 2.15×10^{-13} 3.0×10^{-11} 1.6×10^{-11} 1.9×10^{-12}	this work this work [13] [12] [24]



Fig. 2. Absorption cross sections of species participating in the reaction system used as a source of ClOH (values taken from ref. [23] and from ref. [25] for HONO).

(1) is rather slow and occurs via two channels, it seems a priori that a spectroscopic study would be difficult to perform using this new source of ClOH. The experimental conditions of such a study have been determined for a flow reactor coupled to an optical cell in a similar manner to that used in a UV spectroscopic study of ClO [26]. A computer simulation of the chemical system summarized in table 1 has been done and analysed from the UV absorption spectra of all the species to be considered (fig. 2). Since NOCl is an absorbing species over the whole spectral range, it is suggested that addition of an excess of H atoms, after a reaction time for which reaction (1) is completed, would convert all the remaining NOCl into NO and HCl. But, from fig. 2, it is apparent that Cl₂ also absorbs beyond 270 nm. As reaction (1b) followed by the reaction $Cl + NOCl \rightarrow NO + Cl_2$ yields as much Cl_2 as reaction (1a) yields ClOH, absorption measurements of CIOH cannot easily be done above 300 nm, which is the atmospheric wavelength region of interest. Nevertheless at 250 nm, for example, the absolute value of the cross section of ClOH could be measured using the computed initial concentrations of H $(1 \times 10^{15} \text{ cm}^{-3})$, NO₂ $(1 \times 10^{15} \text{ cm}^{-3})$, NOCl $(2 \times 10^{15} \text{ cm}^{-3})$ and additional H $(2 \times 10^{15} \text{ cm}^{-3})$ after 2 ms), yielding the same and rather low concentra-tion of ClOH and Cl₂ $[(5-6) \times 10^{13} \text{ cm}^{-3}]$. Under these conditions, as only ClOH absorbs at 250 nm, 1% absorption would be measurable using a multipass cell with 10 m optical path.

In conclusion, the present complex chemical system using the OH + NOCl reaction to produce ClOH does not seem to be a clean source for determining the important question as to whether ClOH absorbs significantly above 300 nm.

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