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Kinetics of the reaction of the CH₂Cl radical with oxygen atoms

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Abstract

The kinetics of the reaction of CH_2Cl with $O({}^{3}P)$ has been investigated in a heatable tubular reactor coupled to a photoionization mass spectrometer. The decay of CH_2Cl was monitored as a function of O atom concentration $([O]_0/[CH_2Cl]_0 > 30)$ to determine the rate constant of the reaction as a function of temperature and pressure. The rate constant measured is independent of density and was fitted to an Arrhenius expression: $k = (1.49 \pm 0.35) \times 10^{-10} \exp[(1.46 \pm 0.38) \text{ kJ mol}^{-1}/RT] \text{ cm}^3$ molecule⁻¹ s⁻¹ over the temperature range 297–823 K. Both CHClO and CH₂O were detected as products of the CH₂Cl + O({}^{3}P) reaction. The production of CHClO is the major reaction channel. © 1997 Elsevier Science B.V.

1. Introduction

The reactions of chlorinated methyl radicals with oxygen atoms are important in order to understand the oxidation processes of chlorinated wastes which contain chlorine-bearing polymeric materials. At typical combustion conditions it is most likely that only a small number of polyatomic free radicals live long enough to undergo chemical reactions to any significant extent with the other reactants such as O atoms. Thermal stability of these polyatomic free radicals will be greatly improved if they contain Cl atoms coupled directly to the radical center. Surprisingly, little kinetic information on the reactions of chlorinated free radicals with O atoms as a function of temperature is available in the literature. The only previous time-resolved experimental investigation is the reaction of $CCl_3 + O(^3P)$ [1].

In this Letter the results of an investigation of the reaction of CH_2Cl with $O({}^3P)$ as a function of pressure and temperature are presented.

$$CH_2Cl + O \rightarrow products.$$
 (1)

The reaction between the CH_2Cl radical and ground state oxygen atoms was studied in a heatable tubular reactor coupled to a photoionization mass spectrometer. The kinetics of Reaction (1) were determined by monitoring the decay of CH_2Cl radical under pseudo first-order conditions where the concentration of oxygen atoms were varied (in a set of experiments) in order to determine the second-order rate constant, k_1 . In similar conditions the exponential growth of both CHClO and CH_2O were also investigated to confirm that they were the products of the reaction.

2. Experimental

The experimental apparatus used for this study has been described previously [2,3]. Briefly, pulsed,

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unfocused 193 nm radiation from a Lambda Physik EMG 201 MSC exciplex laser operated at 5 Hz was collimated and then directed along the axis of a heatable, 10.5 mm in diameter quartz reactor. It was coated with boric oxide to reduce heterogeneous radical reactions on the wall of the reactor. Gas flowing through the tube at 5 m s⁻¹ was completely replaced between laser pulses. The flowing gas contained SO₂ (the O atom source, typically below 0.04%), CH_2Cl_2 (the CH_2Cl source, between 0.002-0.005%) and the carrier gas, He, which was always in large excess. A homogeneus mixture of gases was sampled through a 0.44 mm in diameter hole located at the end of a nozzle in the wall of the reactor and was formed into a beam by a conical skimmer before it entered the vacuum chamber containing the quadrupole mass filter. As the gas beam traversed the ion source, a portion was photoionized by atomic resonance lamp radiation and then mass selected. The following lamps were used in the current study to ionize molecules and radicals: a neon lamp (16.7, 16.9 eV) for ionizing O and SO₂; an argon lamp (11.6, 11.8 eV) for CHClO, CH_2O , CH_2 and CH_2Cl_2 ; a hydrogen lamp (10.2 eV) for SO; and a chlorine lamp (8.9–9.1 eV) for CH_2Cl . Temporal ion signal profiles were recorded shortly before and after the laser pulse by a multichannel scalar. Data from 1000 to 33000 repetitions of the experiments were accumulated before the data were analyzed.

2.1. Generation of radicals

Both CH_2Cl radicals and O atoms were generated by the simultaneous, in situ 193 nm laser photolysis of CH_2Cl_2 and SO_2 [4].

$$SO_2 \rightarrow SO + O(^3P)$$
 (2)

$$CH_2Cl_2 \to CH_2Cl + Cl. \tag{3}$$

The experimental conditions (see below) were such that the formation of Cl atoms did not interfere with the determination of k_1 .

2.2. Measurement of the $CH_2Cl + O$ rate constants

The experimental conditions were chosen such that the initial concentration of O atoms was always

in great excess over the concentration of CH_2Cl radicals, i.e. pseudo first-order conditions. Both the initial concentrations of O atoms and CH_2Cl radicals (in known SO₂ or CH_2Cl_2 concentrations) were determined from the measured extents of depletion of SO₂ and CH_2Cl_2 . The initial CH_2Cl concentration was kept low (below 4×10^{10} cm⁻³) to ensure that radical-radical reactions or a heterogeneous wall reaction of the radical had negligible rates compared to the rate of Reaction (1). Low CH_2Cl concentrations were primary achieved by lowering the CH_2Cl_2 concentration in the reactor.

The following three radical reactions were taken into account in the mechanism of Reaction (1):

$$CH_2Cl + O \rightarrow products, (1)$$

- $CH_2Cl \rightarrow$ heterogeneous loss on the wall, (4)
- $O \rightarrow$ heterogeneous loss on the wall. (5)

The first-order rate constants for the determination of k_1 were obtained using the following function:

$$[CH_2Cl]_t = [CH_2Cl]_0 \exp(-k_4t)$$
$$\times \exp\{k'' [\exp(-k_5t) - 1]/k_5\},\$$

which has been derived by assuming that the primary loss for O atoms is due to heterogeneous wall loss (5). In the above expression $k'' = k_1[O]_0$. Separately measured heterogeneous rate constants, k_4 and k_5 , for each different experimental condition, were used in the above rate function to determine the rate constant of the $CH_2Cl + O$ reaction. The temporal ion signal profiles of CH_2Cl^+ and O^+ , were always exponential in shape and were fitted to a function $R = R_0 \exp(k't)$ by using a nonlinear least-squares analysis program. Both experimentally measured rate constants, k_4 and k_5 , were incorporated into the rate function before it was used to reproduce the CH₂Cl ion signal profile under the conditions when both reactants were present (see the lower insert in Fig. 1). The bimolecular rate constant of Reaction (1) was calculated from a set of such experiments where the only changed parameter was the initial O atom concentration. It was varied either by changing the $[SO_2]$ or by attenuating the laser fluence by quartz plates (see the results at 298 K in Fig. 1).

At the beginning of the experiments, tests were conducted to verify that the reaction with $O(^{3}P)$ was the only homogeneous reaction with a non-negligible



Fig. 1. Plot of $[CH_2Cl]_t$ first-order decay constant vs. [O] for series of experiments conducted at 298 K. Third-body number density, [He], was 5.81×10^{16} molecule cm⁻³. The solid circle represents the conditions ([O] = 1.50×10^{12} atom cm⁻³) where the both inserts were recorded. The lower insert is an ion-signal profile of CH₂Cl⁺. The decay fitted by an exponential function gives a value of $393.8 \pm 6.0 \text{ s}^{-1}$. The insert in the upper left corner is the other product, CHClO, of the reaction. The rise-constant of the product formation is equal to $342 \pm 44 \text{ s}^{-1}$.

rate removing the CH₂Cl radicals from the gas mixture. For this, the significance of the reaction between SO₂ and CH₂Cl was determined using 248 nm laser radiation under conditions similar to those used in the experiments to measure k_1 . SO₂ can only be photolyzed to a small extent by this emission radiation from the KrF laser. CH₂Cl₂ is not photodecomposed at this wavelength, therefore CH₂Cl was photogenerated from CH₂ClBr. The reaction between SO₂ and CH₂Cl was followed by monitoring the decay of the CH₂Cl radical with and without SO₂ in the reactor. The decays from these studies were equal, thus it was concluded that the reaction between these two species is negligible. It was also confirmed that the side reaction between O atoms and CH_2Cl_2 had no effect on the determination of k_1 [5]. Although its rate has a strong positive temperature dependence, it was too slow to have any influence on the magnitude of k_1 even at the highest temperature, 823 K, used in this investigation.

SO is the second photoproduct from SO_2 . It is significantly less reactive with CH_2Cl than the ground state O atom. This was confirmed with similar conditions to Reaction (1) by comparing the measured first-order decays of the SO signals in conditions where the ratio of $[CH_2Cl]/[SO]$ was over 20 to conditions where only SO_2 was in the reactor. The decays of SO from these different experiments were equal with respect to their statistical error limits i.e. SO does not react with CH_2Cl radicals to a measurable extent at the conditions used in the current study.

At a given temperature the magnitude of k_1 was



Fig. 2. Arrhenius plot of the CH_2Cl+O rate constants (k_1) . The open symbols represent the rate constant of the CH_2OH+O and CCl_3+O reactions [13,1].

T [K] ^a	10^{-16} [He] (cm ⁻³)	$10^{-12}[O]_0 (cm^{-3})$	[O] ₀ /[CH ₂ Cl] ₀	$k_5 (s^{-1})$	$k_4 (s^{-1})$	$10^{10}k_1^{b} (\text{cm}^3 \text{ s}^{-1})$
297	5.82	1.37-4.70	47-177	7-14	11-21	2.67 ± 0.23
297	11.8	1.30-3.68	46-137	6-8	7-8	2.61 ± 0.16
377	5.84	1.21-4.35	38-161	6-12	11-18	2.60 ± 0.19
377	11.9	1.22-4.98	47-191	2-9	9-10	2.28 ± 0.30
517	5.85	0.95-4.16	31-151	8-13	7–1 9	2.31 ± 0.28
517	11.9	1.98-4.51	79-175	1-4	3-4	1.87 ± 0.20
517	3.86	1.40-4.22	50-161	5-6	2-5	2.11 ± 0.14
823	5.90	1.39-5.42	50-201	7–9	2-3	1.91 ± 0.28
823	9.93	1.94-5.50	72-201	4-5	7	1.53 ± 0.28
$k_1 b = (1.4)$	$49 \pm 0.35 \times 10^{-10} \exp[10^{-10} \exp[10^{-10}$	(1.46 ± 0.38) kJ mol ⁻¹ /	RT] cm ³ molecule ⁻¹	s ⁻¹		

Experimental conditions and results to determine the rate constants for the $CH_2Cl + O(^{3}P)$ reaction

^a Temperature uncertainty: ± 2 K (297–377 K), ± 5 K (517 K), ± 10 K (823 K).

^b Error limits are 1σ + Student's t.

found to be invarient with respect to changes in laser fluence, extent of SO₂ photolysis and initial concentration of CH₂Cl. Furthermore, k_1 was independent of a change of a factor of 3 in carrier gas density. The experimental conditions used and the results of all k_1 determinations are presented in Table 1.

The values of k_1 as a function of temperature and pressure are shown as an Arrhenius plot in Fig. 2. The bimolecular rate constant, k_1 , was determined several times at all four temperatures. At each temperature it was obtained as a calculated arithmetic mean value, which was weighted by the statistical uncertainties associated with the measured values of k' and by the total variation of oxygen atom concentration during an experiment. The Arrhenius expression of the CH₂Cl + O reaction was determined to be (the stated error limits are 1σ + Student's t):

$$k_1 = (1.49 \pm 0.35) \times 10^{-10} \exp[(1.46 \pm 0.38)]$$

kJ mol⁻¹/RT] cm³ molecule⁻¹ s⁻¹.

2.3. Reaction products

Both CHClO and CH_2O were detected as the products of Reaction (1). The production of CHClO is the major reaction channel of these two compounds. This was concluded after comparing the signals of the products monitored at the same conditions qualitatively. The other product of this reaction, the Cl atom, could not be detected for kinetic purposes. However, it can be detected by neon resonance lamp radiation, but then the lamp has to be

used with a collimated hole structure. This filter actually has no transmission threshold to cut background radiation generated in a resonance lamp entering into a vacuum chamber. Such a high energy background radiation can easily fragment CH_2Cl_2 to atoms making the signal/noise ratio poor for the detection of Cl atoms.

The other reaction products of Reaction (1) were detected by low-energy resonance lamps: A typical ion signal profile of CHClO is shown in Fig. 1. As can be seen in Fig. 1 the rise-constant of the CHClO product formation is in close agreement with the decay-constant of the CH₂Cl radical (with respect to their error limits), monitored at the same conditions, supporting strongly that CHClO is a primary product of Reaction (1). However, CHClO signal always showed a slow decay after formation at all conditions where it was monitored. It is difficult to come to a conclusive reason for this phenomenon. The reaction between CHClO and Cl atoms should be slow $(< 1 \text{ s}^{-1})$ [6] at the concentrations of Cl atoms present during the experiments. Also the heterogeneous reaction of CHClO on the wall of the reactor should not happen during the time-scale used to investigate Reaction (1) since formyl chloride is a closed-shell molecule and should not behave as a free radical. The other CHClO-molecule reactions should also be too slow to occur in the reactor during the reaction time. Only a secondary reaction between O atoms and CHClO molecules may be fast enough to occur at the highest O atom concentration used in the current study. In this case the rate constant of the

Table 1

O + CHClO reaction should be about a factor of 100 higher than the rate constant of the OH + CHClO reaction [7]. This is doubtful because the rate constants of the O and OH radicals in their reaction with formaldehyde are almost equal [8,9].

The other product of Reaction (1) was formaldehyde. Its yield was always minor compared to the yield of CHCIO. The profile of CH_2O signal was always pure exponential in shape, showing no sign of decay.

3. Discussion

3.1. Rate constant of the $CH_2Cl + O$ reaction

The Arrhenius expression of the reaction of the CH_2Cl radical with $O(^{3}P)$ has not been previously determined. The rate constants of this reaction are



Fig. 3. Semilog plot of time-resolved R + O rate constants at 300 K for carbon centered polyatomic σ free radicals. The rate constants shown are for CH₃ [4], C₂H₅ [14], CH₂OH [13], CCl₃ [1] and CH₂Cl (the current study). Ionization potentials are taken from Ref. [15].

presented in Fig. 2 with two other substituted methyl radical reactions with ground state oxygen atom. As can be seen in Fig. 2 the CH_2Cl radical reacts faster than the CCl_3 radical with the oxygen atom. It is most likely that the number of Cl atoms directly coupled to the radical centre influences the reactivity of the radical.

A classical way of explaining radical reactivities is to plot their rate constants (with the same reactant) at a constant temperature against their ionization potential, IP_R , value. Such a method does not apply here. This is clearly demonstrated by five different σ radicals in Fig. 3. Fig. 3 does not show any correlation. All of the rate constants shown in Fig. 3 are from time-resolved experiments.

3.2. Mechanism of the $CH_2Cl + O$ reaction

The reaction between two open-shell species, $O({}^{3}P)$ and $CH_{2}Cl$, most likely takes place as the reactants are approaching one another to interact on an attractive potential surface. This addition reaction will proceed to the formation of (as a rate limiting step) a thermodynamically stable energy-rich adduct, $OCH_{2}Cl^{*}$. Its internal energy is high, 367 kJ mol⁻¹ [10–12], thus it subsequently decomposes either by C–H or C–Cl bond cleavage. Both of these decomposition processes are highly exothermic and thus can occur easily:

CH₂Cl + O → OCH₂Cl^{*} → CHClO + H,

$$\Delta H_{r,298}^{\circ} = -313 \text{ kJ mol}^{-1},$$
CH₂Cl + O → OCH₂Cl^{*} → CH₂O + Cl,

$$\Delta H_{r,298}^{\circ} = -354 \text{ kJ mol}^{-1}.$$

Other reaction channels which include the formation of HCO + HCl or COCl + H_2 or CO + Cl + H_2 or OH + CHCl are energetically feasible but involve a complex bond rupture-formation. However the formation of OCl + CH₂ seems to be excluded because of its endothermicity. The observed production of formylchloride and formaldehyde suggest that the significance of other reaction routes is minor.

The rate constant of the $CH_2Cl + O$ reaction has no pressure dependence in the pressure range used in the current study. This fact and also the observed products, CHClO and CH₂O, of the reaction suggest that the reaction proceeds forward irreversibly, once the initial adduct is formed.

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