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Temperature Dependent Rate Constants for the Reactions of Chlorine Atom with Methanol and Br_2

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Abstract

Kinetics of the reaction of Cl atoms with methanol has been investigated at 2 Torr total pressure of helium and over a wide temperature range 225 – 950 K, using a discharge flow reactor combined with an electron impact ionization quadrupole mass spectrometer. The rate constant of the reaction Cl + CH_3OH $\rightarrow$ products (1) was determined using both absolute measurements under pseudo-first order conditions, monitoring the kinetics of Cl-atom consumption in excess of methanol and relative rate method, k_1 = (5.1±0.8)$\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, and was found to be temperature independent over the range T = 225-950K. The rate constant of the reaction Cl + Br_2 $\rightarrow$ BrCl + Br (3) was measured in an absolute way monitoring Cl-atom decays in excess of Br_2: k_3 = 1.64$\times10^{-10}$ exp(34/T) cm^3 $molecule^{-1}$ s^{-1} at T = 225 -960 K (with conservative 15% uncertainty). The experimental data for k_3 can also be adequately represented by the temperature independent value of k_3 = (1.8±0.3) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. The kinetic data from the present study are compared with previous measurements.

Keywords: Cl, CH_3OH, Br_2, kinetics, rate coefficient.

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Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

1 INTRODUCTION

Methanol (CH_3OH) is a smallest representative of alcohols, chemical species belonging to a large family of Oxygenated Volatile Organic Compounds playing an important role in the tropospheric chemistry.[1] CH_3OH is one of the most abundant volatile organic species in the atmosphere due to important biogenic emissions and in situ production in atmospheric oxidation of methane and other organic compounds.[2] Atmospheric degradation of methanol is triggered mainly by its reaction with OH radicals,[1] however contribution of the reaction with Cl atoms can be significant in certain locations with elevated concentration of Cl.[3-5] Cl-atom reaction with CH_3OH is a well-known and very often used in laboratory source of CH_2OH and, in the presence of O_2, of HO_2 radicals:

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \quad (1a)$$

$$Cl + CH_3OH \rightarrow CH_3O + HCl \quad (1b)$$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O \quad (2)$$

Hence, the information on kinetics and products of Cl reaction with methanol in an extended temperature range is of interest also for laboratory studies of other reactions important in atmospheric and combustion chemistry.

Kinetics of the reaction

$$Cl + CH_3OH \rightarrow \text{products} \quad (1)$$

has been extensively studied using both absolute and relative rate methods.[6-18] Room temperature data for the reaction rate constant from different studies are consistent with each other;[7-15] however the temperature dependence of the rate constant is not well established.[6,16-18] As noted in a most recent temperature dependent study of reaction (1), "additional experiments that cover temperatures both below and above room temperature are needed for further assessment."[18] In this regard, the objective of the present work was to measure the rate constant of reaction (1) in a wide temperature range in order to harmonize existing experimental data on temperature dependence of k_1.

In addition, the rate constant of the reaction of Cl atoms with Br_2 was measured as a part of this study. In the present work, this reaction was used for indirect detection of Cl by mass spectrometry via conversion of Cl-atom to BrCl and as a reference reaction in the relative measurements of k_1:

$$Cl + Br_2 \rightarrow BrCl + Br \quad (3)$$

Previously, the reaction rate constant was measured only at relatively low temperatures (T < 400K): the available data for k_3 are spread within a factor of 1.4.[19-23] In the present work, we report the measurements of the rate constant in an extended temperature range, T = 225 – 960 K.

2 EXPERIMENTAL

Experiments have been conducted at total pressure of 2 Torr of Helium using a conventional fast-flow reactor combined with a molecular beam sampling electron-impact ionization mass spectrometer.[22,24-26] Depending on the temperature range two different flow reactors were used. Low temperature reactor, used at T = 225 – 320 K, consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) surrounded by a jacket through which a thermostated ethanol was circulated (Figure S1, Supporting Information (SI)). To reduce the heterogeneous loss of Cl, the inner surface of the reactor as well as of the movable injector of Cl atoms was coated with halocarbon wax. High temperature reactor, used at T = 335 – 960 K, consisted of a Quartz tube (45 cm length and 2.5 cm i.d.) with an electrical heater and water-cooled attachments (Figure S2, SI).[26]

Chlorine atoms were generated by dissociation of Cl_2, diluted in He, in a microwave discharge and introduced into the main reactor through the movable injector as shown in Figures S1 and S2 (SI). Three methods were used for the detection of chlorine atoms. Firstly, Cl atoms were detected at their parent peaks at m/z = 35/37 (Cl^+). In this case, the contribution at these peaks of Cl_2 (precursor of Cl atoms) and chlorinated products of reactions (1) and (3) due to their fragmentation in the ion source of the mass spectrometer (always operating at ca. 25 eV) should be taken into account. In another method, Cl atoms were monitored at m/z = 114/116/118 ($BrCl^+$) after being scavenged with an excess of Br_2 ($[Br_2] \approx 3\times10^{13}$ molecule cm^{-3}, added in the end of the reactor 5 cm upstream of the sampling cone, as shown in Figure S2 (SI)) in reaction 3:

$$Cl + Br_2 \rightarrow BrCl + Br \qquad (3)$$

$k_3 = 1.64\times10^{-10} \exp(34/T)$ cm^3 $molecule^{-1}$ s^{-1} (T = 225 – 960 K, this work).

This method of Cl-atom detection is free of the possible complications which may arise from the fragmentation of the chlorinated species in the ion source. It can also be noted that the concentration of BrCl is not affected by side reactions, for example, with organic radicals

formed in reaction (1), since they are rapidly removed by Br_2, which is present in the reaction system in high concentrations. Finally, Cl atoms were detected also at m/z = 162/164 (ICl^+) upon their titration with an excess of I_2 ($[I_2]$ = (1.0-1.5)×10^{13} molecule cm^{-3}, added in the end of the reactor (Figures S1 and S2, SI):[27]

$$Cl + I_2 \rightarrow ICl + I \quad (4)$$

k_4 = (2.1 ± 0.3)×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (T = 296 – 365 K).

The absolute concentrations of Cl atoms were determined using their chemical conversion to BrCl in reaction (3) with an excess of Br_2: [Cl] = [BrCl] = $\Delta[Br_2]$. The absolute calibrations of MS signals of the stable species (CH_3OH, Br_2, Cl_2 and O_2) were derived from measured flows of known mixtures of the species with helium.

The purities of the gases used were as follows: He (99.9999%, Alphagaz), passed through liquid nitrogen trap; O_2 (99.999%, Alphagaz); Br_2 (>99.99%, Aldrich); Cl_2 (>99%, Ucar); I_2 (99.999%, Aldrich); methanol (> 99.9%, Aldrich).

3 RESULTS AND DISCUSSION

3.1 Rate constant of reaction (1): absolute measurements

Experiments were carried out under pseudo-first order conditions monitoring kinetics of Cl consumption ($[Cl]_0$ = (1 – 2)×10^{11} molecule cm^{-3}) in an excess of methanol (see Table 1 for the concentrations of CH_3OH used). It was observed that generally the consumption of CH_3OH was insignificant due to its sufficiently high excess over Cl atoms. Under such conditions, $[Cl] = [Cl]_0 \times \exp(-k_1' \times t)$, with pseudo-first-order rate constant $k_1' = k_1 \times [CH_3OH] + k_w$, where k_w represents the loss of Cl-atom in the absence of methanol in the reactor. Figure 1 displays examples of the exponential decays of Cl-atoms in the presence of different concentrations of CH_3OH in the reactor. Examples of second-order plots observed at different temperatures are shown in Figure 2. All the pseudo-first order rate constants, k_1', were corrected for axial and radial diffusion of Cl atoms[28] with diffusion coefficient of Cl in He calculated as $D_0 = 504 \times (T/298)^{1.85}$ Torr cm^{-2} s^{-1}.[29] The corrections were typically within a few percent, being somewhat higher in a few kinetic runs (up to 15%). The results of the absolute measurements of k_1 are shown in Table 1. The measurements of k_1 at T ≥ 360 K have been conducted in an uncoated quartz reactor and those between 225 and 320 K in a Pyrex reactor coated with halocarbon wax. The combined uncertainty on k_1 was estimated

to be about 15% by adding in quadrature statistical error (≤ 5%) and those on the measurements of the absolute concentration of methanol (~10%), flows (3%), pressure (2%), temperature (1%).

The possible impact of secondary chemistry on the measurements of k_1 can be discussed. Firstly, it should be noted that thermal decomposition of methanol is negligible in the temperature range of the present work. Lu et al.[30] in their shock tube study reported the rate constant of 3.2×10^{-9} exp(-29470/T) $cm^3molecule^{-1}s^{-1}$ for the thermal decomposition of CH_3OH at T = 1660-2050 K. Extrapolation of this expression to 950 K, the highest temperature of the present study, provides the rate constant of $\sim10^{-22}$ $cm^3molecule^{-1}s^{-1}$, which is too low to affect the measurements of k_1. Secondary reactions involving CH_2OH radical formed in reaction (1a) can lead both to production and consumption of Cl atoms in reactions of CH_2OH with Cl_2 (precursor of Cl) and Cl, respectively:

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \quad (1a)$$

$$CH_2OH + Cl_2 \rightarrow CH_2ClOH + Cl \quad (5)$$

$$CH_2OH + Cl \rightarrow CH_2O + HCl \quad (6)$$

The possible reproduction of Cl atoms in reaction (5) (k_5 = $(2.9\pm0.6)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at T = 295 K)[12] is insignificant under experimental conditions of the study due to relatively low concentrations of Cl_2 in the reactor, $[Cl]_2$ = (2-4) $\times10^{11}$ molecule cm^{-3}. In order to experimentally confirm this fact, we have carried out the measurements of k_1 in the presence of O_2 ($\approx2\times10^{14}$ molecule cm^{-3}) in the reactor. In the presence of O_2, CH_2OH radicals are rapidly scavenged via reaction (2) (k_2 = $(9.1\pm2.7)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at T = 298 K):[31]

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \quad (2)$$

Figure S3 (SI) demonstrates the second-order plot measured for reaction (1) at T = 440 K. As one can see, the results of the measurements of k_1' in the presence and in the absence of O_2 in the reactor are indistinguishable within the experimental error, which indicates a negligible role of reaction (5) under the experimental conditions of the measurements of k_1. Among the data presented in Table 1, those at T = 360 and 770 K were obtained in the presence of O_2 in the reactor.

To our knowledge the rate constant of reaction (6) was reported in two studies at room temperature: k_6 = 1.4×10^{-10} [32] and 6.64×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.[33] The last, rather high, value of k_6 was extracted from the simulation of the experimental profiles of CH_2OH observed

upon the pulse radiolysis of $SF_6/HCl/CH_3OH$ mixtures.[33] With k_6 as high as 6.6×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, in the present experiments, the contribution of the secondary reaction of Cl with CH_2OH to the measured Cl decays would be significant, especially at low concentrations of methanol. This would lead to increase of the intercepts in the second-order plots shown in Figure 2. In fact, this was not the case: the intercepts of the second-order plots were always in good agreement with the values of k_w measured in the absence of CH_3OH in the reactor, as shown in Figure 2. Experiments with addition of O_2 into reactive system (see above) also seem to indicate that impact of reaction (6) is insignificant. In the presence of O_2, CH_2OH is transformed via reaction (2) into CH_2O and HO_2, which are less reactive toward Cl-atom compared with CH_2OH ($k_7 = 4.3\times10^{-11}$ and $k_8 = 8.1\times10^{-11}$ exp(-30/T) cm^3 $molecule^{-1}$ s^{-1} at T = 230-420 and 200-500 K, respectively):[31]

$$Cl + HO_2 \rightarrow \text{products} \quad (7)$$

$$Cl + CH_2O \rightarrow HCO + HCl \quad (8)$$

For complete confidence in the minor role of the secondary chemistry in the absolute measurements of k_1, we have carried out relative rate measurements under conditions where secondary reactions (5) and (6) are obviously not important.

3.2 Rate constant of reaction (1): relative measurements

In the relative measurements of k_1, reaction of Cl atoms with Br_2 was used as a reference. The experiments consisted in a fast consumption of Cl in reaction with a mixture of Br_2 and CH_3OH and the measurements of BrCl yield as a function of the $[CH_3OH]/[Br_2]$ ratio:

$$Cl + CH_3OH \rightarrow \text{products} \quad (1)$$

$$Cl + Br_2 \rightarrow BrCl + Br \quad (3)$$

The fraction of the initial concentration of Cl atoms, $[Cl]_0$, transformed to BrCl in reaction 3, is:

$$[\mathrm{BrCl}] = \frac{k_3[\mathrm{Br_2}]}{k_3[\mathrm{Br_2}]+k_1[\mathrm{CH_3OH}]+k_w} \times [\mathrm{Cl}]_0$$

After rearrangement of this expression one has:

$$\frac{[\mathrm{Cl}]_0}{[\mathrm{BrCl}]} - 1 = \frac{k_1[\mathrm{CH_3OH}]}{k_3[\mathrm{Br_2}]} + \frac{k_w}{k_3[\mathrm{Br_2}]} \quad (\mathrm{I})$$

At a constant concentration of Br_2, the second term in equation (I) is constant and k_1/k_3 can be determined as a slope of the linear dependence of ($[Cl]_0/[BrCl]$ - 1) on the $[CH_3OH]/[Br_2]$ ratio. In the experiments, BrCl was monitored in both CH_3OH -free system, corresponding to

$[Cl]_0$, and in the Br_2 and CH_3OH -containing system, corresponding to the fraction of $[Cl]_0$ reacted with Br_2. Reaction time was (0.012 – 0.017) s, $[Cl]_0$ = (2-5)×10^{11} molecule cm^{-3}, concentrations of CH_3OH and Br_2 are shown in Table 2. The relative measurements of k_1 were carried out in an uncoated quartz reactor, except T = 227, 243 and 295 K, where the reactor coated with halocarbon wax was used. Typical examples of the experimental data are shown in Figure 3. Final values of k_1 (Table 2) were calculated with k_3 = 1.64×10^{-10} exp(34/T) cm^3 $molecule^{-1}$ s^{-1} determined in this study with conservative 15% uncertainty at all temperatures (T = 225 -960K).

One can note that the results of the relative measurements are in excellent agreement with the absolute measurements of k_1. It should be emphasized that secondary reactions (5) and (6) are not operative under the experimental conditions of the relative measurements. Firstly, in the presence of high concentrations of Br_2 and CH_3OH, Cl atoms are rapidly titrated in primary reactions (1) and (3). Secondly, CH_2OH radical is expected to be rapidly scavenged by Br_2 ($[Br_2]$>>$[Cl_2]$):

$$CH_2OH + Br_2 \rightarrow CH_2BrOH + Br \quad (9)$$

Although the rate constant of reaction (9) is unknown, it is expected to be higher than k_5 by analogy with reactions of Br_2 and Cl_2 with other organic radicals.

It can also be noted that reaction of CH_3OH with Br atoms formed in reactions (1) and (9):[34]

$$Br + CH_3OH \rightarrow CH_2OH + HBr \quad (10)$$

k_{10} = 5.66×10^{-15} $(T)^{1.5}$ exp(-3600/T) cm^3 $molecule^{-1}$ s^{-1} (T = 439 – 713 K)

is relatively slow, and, in any case, has a negligible impact on the concentrations of CH_3OH, considering that $[CH_3OH]$ >> [Br] ~$[Cl]_0$.

3.3 Rate constant of reaction (3)

The rate constant of reaction (3) was determined from Cl decays ($[Cl]_0$ = (0.5 – 1.5)×10^{11} molecule cm^{-3}) monitored in excess of Br_2 (Table 3). Examples of the kinetics of Cl consumption observed at different concentrations of Br_2 are shown in Figure S4 (SI). The consumption of Br_2 was generally within a few percent: only in a few measurements (at lowest concentrations of Br_2) it was significantly higher (up to 25 %). The reaction rate constant was always calculated using the mean concentration of Br_2 along the reaction zone.

Typical plots of the pseudo-first-order rate constant, $k_3' = k_3 \times [Br_2] + k_w$, versus concentration of Br_2 are shown in Figure 4. Diffusion corrections on k_3' were usually less than 10% and up to 16% in a few kinetic runs. The Y-intercepts of all the second-order plots, k_w, were in the range (0 - 22) s^{-1}, in good agreement with the rate of Cl decay measured in the absence of Br_2 in the reactor. All the results of the absolute measurements of k_3 (with estimated total uncertainty on k_3 of ≈15%) are shown in Table 3. At T ≤ 320 and ≥ 340 K, the measurements were carried out in a Pyrex reactor coated with halocarbon wax and in an uncoated quartz reactor, respectively.

3.4 Comparison with previous studies

Figure 5 summarizes the results of the measurements of the rate constant of reaction (3). In earlier room temperature discharge-flow studies using Cl detection by atomic resonance fluorescence, the values of $k_3 = (1.20 \pm 0.15)\times10^{-10}$ [19] and $(1.9 \pm 0.2)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} [20] were reported at T = 298 K. The difference between two values measured with the same method and in the same group was explained[20] by Br_2 loss in the flowmeter when passing a dilute mixture of Br_2 with inert gas, leading to an underestimation of k_3 in the study of Clyne and Cruse.[19] Nicovich and Wine[21] employed a laser flash photolysis-resonance fluorescence technique to measure the rate constant of reaction (3) as a function of temperature at T = 298-401 K. $k_3 = (1.58 \pm 0.22)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} was found to be virtually independent of temperature, although a slight positive temperature dependence was observed (E/R = 144 K).[21] The k_3 data of Nicovich and Wine[21] shown in Figure 5 have been adjusted upward by 11%, as proposed by Khamaganov and Crowley,[23] considering currently recommended[31] absorption cross section for Br_2 at 415.8 nm of 6.5×10^{-19} cm^2 $molecule^{-1}$ instead of 5.87×10^{-19} cm^2 $molecule^{-1}$ used by Nicovich and Wine[21] in optical measurements of the Br_2 concentrations. In previous study from our group,[22] essentially similar (to those of the present work) experimental equipment and experimental approach were used except that Cl atoms were titrated at the end of the reactor with C_2H_3Br to be monitored at m/z = 62/64 ($C_2H_3Cl^+$):

$$Cl + C_2H_3Br \rightarrow Br + C_2H_3Cl \qquad (11)$$

As one can see in Figure 5, the values of k_3 from the earlier study[22] are by up to 30% lower than those measured in the present work. The reason for this disagreement is most likely due to a systematic error in previous measurements, which is difficult to identify at present.

Khamaganov and Crowley[23] measured the rate coefficient of the Cl +Br_2 reaction, k_3 = (1.94 ± 0.12)×10^{-10} $cm^3 molecule^{-1} s^{-1}$ at T = 298 K, using laser-pulsed photolysis of Cl_2 in the presence of Br_2 with detection of the reaction product, Br atoms, using resonance fluorescence. A limited data set obtained by the authors at 228 K provided k_3 = (2.1 ± 0.3)×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at this temperature. Khamaganov and Crowley[23] combined their data with those of Nicovich and Wine[21] (corrected for absorption cross section) and recommended a value of k_3 =(1.81±0.10) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, independent of temperature from 200 to 400 K. This value is in excellent agreement with the mean of all the measurements of k_3 carried out in the present study, k_3(±1σ) = (1.8±0.1) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} at T = 225-960K (dotted line in Figure 5), although we observe a slight decrease of the rate constant with increasing temperature. Least-squares fit to k_3 data from the present work (solid line in Figure 5) provides the following Arrhenius expression:

k_3 = 1.64×10^{-10} exp(34/T) cm^3 $molecule^{-1}$ s^{-1} at T = 225 -960K.

The dashed lines in Figure 5 correspond to ± 15% deviation from this expression, showing that practically all temperature dependent data for k_3 (except earlier measurements from this group)[22] fall into this range. Based on this, we would recommend the above expression for k_3 for use in the temperature range 225–960 K with conservative 15% uncertainty. The observed small negative temperature dependence of k_3 may be considered as an indication of a complex reaction mechanism that includes formation of an intermediate energized complex followed either by its dissociation back to reactants or to reaction products.

The results of room temperature measurements of k_1[7-15] (summarized, for instance, in ref. 18), employing various experimental techniques and both absolute and relative rate methods, are consistent with each other and fall in the range (4.57-6.14))×10^{-11} cm^3 $molecule^{-1}$ s^{-1} with an average value of k_1 (±2σ) = (5.35±0.90)×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at T = 298 K. The available temperature dependent k_1 data[6,16-18] are shown in Figure 6 along with the results of the present work. The first determination of the rate constant of reaction (1) was realized by Michael et al.[6] using the flash photolysis-resonance fluorescence technique. The reaction rate constant was found to be k_1 (±1σ) = (6.33±0.70)×10^{-11} cm^3 $molecule^{-1}$ s^{-1} independent of temperature over the range 200-500 K. In contrast, Garzón et al.[16] in their laser photolysis-resonance fluorescence study of reaction (1) reported significant temperature dependence for k_1 at T = 266-380 K: k_1 = (3.55±0.22)×10^{-10} exp(-559±40)/T) cm^3

molecule^{-1} s^{-1}. Kaiser and Wallington[17] employed relative rate technique with C_2H_6 as the reference compound and reported a weaker temperature dependence over the temperature range 291−475 K: k_1 = (8.6±1.3)×10^{-11} exp(-167±60)/T) cm^3 molecule^{-1} s^{-1}. Finally in a most recent study of Hui et al.,[18] the rate constant of reaction (1) was determined from the kinetics of HO_2 formation upon pulsed laser photolysis of Cl_2 in presence of CH_3OH and O_2: k_1 = (5.02±1.5)×10^{-11} exp(20±88)/T) cm^3 molecule^{-1} s^{-1} over the range T = 230-297 K. Within experimental uncertainty, the rate constant was temperature independent with the average value of k_1 = (5.45±0.37)×10^{-11} cm^3 molecule^{-1} s^{-1} over this temperature range.

As one can see in Figure 6, on the absolute basis the k_1 data from the present work are in agreement within stated experimental uncertainties with all the previous temperature dependent measurements, except a few points from Garzón et al.[16] The present data obtained in a wide temperature range seem to definitely confirm the temperature independence of k_1 reported in previous studies of Michael et al.[6] and Hui et al.[18] and question quite a strong temperature dependence of k_1 measured by Garzón et al.[16] The observed independence of k_1 of temperature is in line with empirical correlations between the R-H bond energy and corresponding temperature dependence of the H-atom abstraction by Cl[6,7,18] and with theoretical calculations of k_1 in the range T = 300-1000 K shown in Figure 6 by dotted line.[35] Solid line in Figure 6 corresponds to the mean value of k_1 from the present measurements at all temperatures which is recommended from this study with conservative 15% uncertainty (dashed lines):

k_1 = (5.1±0.8)×10^{-11} cm^{3}molecule^{-1}s^{-1} over the temperature range 225 – 950 K.

There is an experimental[7,36] and theoretical[35] evidence that reaction of Cl-atom with methanol proceeds predominantly through hydrogen atom abstraction from the methyl group (reaction 1a):

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \quad (1a)$$

$$Cl + CH_3OH \rightarrow CH_3O + HCl \quad (1b)$$

Dóbé et al.[36] have reported the yield of CH_3O radical in reaction (1) of 0.01±0.01 and 0.04±0.02 at T = 298 and 482 K, respectively. Theoretical calculations predict nearly 1% for the branching ratio of the CH_3O forming channel (1b) at T = 1000 K.[35] In the present work, we have tried to estimate the branching ratio for channel (1b) at two temperatures, T = 300 and 900 K. The experiment consisted in successive titration of the same initial concentration of Cl atoms with CH_3OH and CD_3OH with detection of HCl formed. In the case of Cl titration

with CH_3OH, the concentration of HCl formed corresponds to the initial concentration of Cl atoms: $[HCl]_{CH_3OH} = [Cl]_0$. HCl, if formed upon titration of Cl with CD_3OH, should come from the H-atom abstraction from OH group, and the branching ratio for channel (1b) could be determined as the ratio $[HCl]_{CD_3OH}/[HCl]_{CH_3OH}$, in a relative way without measurements of the absolute concentrations. Unfortunately, the designed experiments were unsuccessful. At both temperatures (300 and 900K), the HCl signal monitored in Cl+CD_3OH system was found to be relatively high and to increase with reaction time, most likely, due to isotopic exchange reactions in the gas phase and on the wall of the reactor. Additional experimental work including a thorough analysis of this phenomenon is necessary in order to measure the branching ratio of the CH_3O forming channel of reaction (1) which is expected to be very small.

4 CONCLUSION

In this work, we investigated the kinetics of the reaction of Cl atoms with methanol using a discharge flow reactor combined with an electron impact ionization mass spectrometer. The total rate constant of the reaction, $k_1 = (5.1\pm0.8)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, was determined using both absolute and relative rate method for temperatures in the range 225 -950 K. Temperature dependence of k_1, measured over a wide temperature range, seems to harmonize existing experimental data for k_1 and confirms independence of the rate constant of temperature up to 1000 K in agreement with theoretical predictions. The temperature dependence of the rate constant of the Cl + Br_2 reaction, measured as a part of this study, $k_3 = 1.64\times10^{-10}$ exp(34/T) $cm^3 molecule^{-1} s^{-1}$ at T = 225 -960 K, and found to be in good agreement with most of the previous low temperature data, was extended to higher temperatures (T = 960K).

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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TABLES LEGENDS

TABLE 1 Reaction Cl + CH_3OH: summary of the absolute measurements of the rate constant

TABLE 2 Reaction Cl + CH_3OH: summary of the relative measurements of the rate constant

TABLE 3 Reaction Cl + Br_2: summary of the measurements of the rate constant

TABLES

TABLE 1 Reaction Cl + CH_3OH: summary of the absolute measurements of the rate constant

T (K)	Number of kinetic runs	[CH_3OH] (10^{12} molecule cm^{-3})	k_1[a] (10^{-11} cm^3 $molecule^{-1}$ s^{-1})
225 [b]	11	0.41-10.8	5.17
245 [b]	7	0.78-12.6	4.96
266 [b]	9	0.59-16.0	5.14
298 [b]	10	1.16-17.3	5.11
320 [b]	10	1.79-17.6	5.06
360 [c,d]	7	1.82-13.0	5.10
440 [c]	12	0.76-12.2	5.20
495 [b]	9	0.42-15.5	4.92
500 [b]	11	0.55-15.2	5.01
560 [c]	13	0.81-11.8	5.16
650 [b]	13	0.83-15.4	5.16
770 [c,d]	9	1.00-13.0	5.02
950 [b]	12	0.90-12.7	5.14

[a] Statistical uncertainty on k_1 is ≤ 5%, total estimated uncertainty is nearly 15%;
[b] Cl atoms monitored at m/z = 116 ($BrCl^+$) (see text);
[c] Cl atoms monitored at m/z = 162 (ICl^+) (see text);
[d] In presence of O_2 in the reactor (see text).

TABLE 2 Reaction Cl + CH_3OH: summary of the relative measurements of the rate constant

T (K)	No./exp.[a]	[CH_3OH] [b]	[Br_2] [b]	k_1/k_3[c]	k_1[d]
227	9	0.67-8.68	1.34	0.264	5.03
243	12	0.56-9.67	1.10	0.278	5.24
295	11	0.65-13.6	1.22	0.273	5.02
335	10	0.45-10.5	1.36	0.279	5.06
355	13	0.38-8.91	1.09	0.285	5.14
385	9	0.38-11.2	1.44	0.292	5.23
456	11	0.40-6.77	0.62	0.282	4.98
600	13	0.23-5.96	1.09	0.305	5.29

[a] Number of data points;
[b] Units of 10^{13} molecule cm^{-3};
[c] Statistical uncertainty on k_1/k_3 is ≤ 4%, total estimated uncertainty is nearly 15%;
[d] Units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, estimated uncertainty on k_1 is nearly 20% and includes that on reference reaction.

TABLE 3 Reaction Cl + Br_2: summary of the measurements of the rate constant

T (K)	Number of kinetic runs	$[Br_2]$ (10^{12} molecule cm^{-3})	k_3 [a] (10^{-10} cm^3 $molecule^{-1}$ s^{-1})
225 [b]	10	0.71-3.84	1,97
237 [b]	9	0.35-3.53	1,94
257 [b]	10	0.59-4.43	1,80
280 [b]	9	0.69-4.41	1,74
298 [b]	9	0.33-5.02	1,85
320 [b]	9	0.48-4.40	1,87
340 [b]	9	0.54-4.44	1,85
370 [c]	7	0.46-3.78	1,71
400 [b]	7	0.28-3.57	1,87
440 [b]	6	0.29-3.31	1,75
500 [b]	11	0.40-3.62	1,75
567 [c]	11	0.21-3.66	1,74
650 [b]	7	0.20-2.14	1,70
785 [b]	8	0.26-2.17	1,75
960 [c]	13	0.21-3.57	1,70

[a] Statistical uncertainty on k_3 is ≤ 5%, total estimated uncertainty is nearly 15%.
[b] Cl atoms monitored at m/z = 35 (Cl^+) (see text);
[c] Cl atoms monitored at m/z = 164 (ICl^+) (see text).

FIGURE LEGENDS

FIGURE 1 Reaction Cl + CH_3OH: examples of Cl decay profiles in presence of different amounts of methanol at T = 560 K.

FIGURE 2 Reaction Cl + CH_3OH: plot of pseudo-first-order rate constant (k_1') versus concentration of CH_3OH at different temperatures. Error bars represent typical uncertainties (≤ 5%) on the determination of k_1'. For clarity, the data for T = 560 and 950 K are *Y*-shifted by 100 and 200 s^{-1}, respectively.

FIGURE 3 Yield of BrCl from Cl-atom titration with Br_2 + CH_3OH mixtures at different temperatures. Partially shown error bars represent typical uncertainties of the measurements (≤ 10%). For clarity, the data for T = 385 and 600 K are *Y*-shifted by 0.5 and 1.0, respectively.

FIGURE 4 Reaction Cl + Br_2: plot of pseudo-first-order rate constant (k_3') versus concentration of Br_2 at different temperatures. Partially shown error bars represent typical uncertainties (≤ 5%) on the determination of k_3'.

FIGURE 5 Reaction Cl + Br_2: summary of the measurements of the temperature dependence of the reaction rate constant. Partially shown for the present data error bars correspond to estimated 15 % uncertainty on the measurements of k_3. Solid line: Arrhenius fit to the present data; dashed lines: present fit ±15%.

FIGURE 6 Reaction Cl + CH_3OH: summary of the temperature dependent measurements of the reaction rate constant. AM: absolute measurement, RM: relative rate method. The error bars partially shown for the present data correspond to estimated 15 and 20 % uncertainty on the measurements of k_1 in the present work by absolute and relative rate method, respectively; uncertainties on previous measurements are given as reported in respective studies.