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Absolute reaction rate of chlorine atoms with iodomethane

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Abstract

The reaction of atomic chlorine with iodomethane was studied in the gas phase with the very low pressure reactor technique over the temperature range 273-363 K. The absolute rate constant was given by the expression $k = (1.33 \pm 0.49) \times 10^{-11} \exp[-(5.73 \pm 1.00 \text{ kJ mol}^{-1})/RT] \text{ cm}^3$ molecule⁻¹ s⁻¹. The reaction proceeds through an intermediate weakly bound adduct CH₃I-Cl and results in the formation of HCl and iodomethyl radical CH₂I. The kinetic isotope effect k_H/k_D of the reaction was independent of temperature and found to be 1.09 ± 0.4 .

1. Introduction

Iodomethane is considered as the most important iodine containing species in the atmosphere, and it has been detected in the atmosphere of several geographical regions, especially close to coastal areas [1-5]. The oceans provide the major source of CH₃I emissions, and its biogenic emission rate is estimated to be ca. 4×10^6 kg per year [6,7]. Iodomethane is suggested as a possible substitute of CH₃Br, which is under replacement according to the Montreal Protocol [8]. Photolysis constitutes the main removal process of CH₃I from the troposphere; however, a small fraction of its tropospheric loss could be carried over by its reactions with OH radicals and Cl atoms. The kinetics of the reaction of Cl atoms with CH₃I have not been studied in the past, although they may be important in marine environments, where the concentrations of both species are much higher. Chlorine atoms are important atmospheric species that are mainly produced by photolytic decomposition of man-made chlorinated compounds or heterogeneous oxidation processes on sea-salt [9], and have been monitored at considerable concentrations in coastal atmospheres [10].

In this work we elucidate the mechanism and measure the absolute rate constant of the reaction of Cl with CH₃I at four different temperatures and at low pressures (ca. 2 mTorr), using the very low pressure reactor (VLPR) technique [11]. This technique is a reliable tool for the kinetic study of fast bimolecular reactions, without interference from secondary radical reactions. It also permits the simultaneous monitoring of both reactants and products, often including free radical species [12]. Finally, the reaction of Cl atoms with deuterated iodomethane CD₃I was studied in a series of relative rate experiments with CH₃I, in order to determine the kinetic isotope effect $k_{\rm H}/k_{\rm D}$ for the hydrogen atom abstraction.

2. Experimental

The reaction was studied using the very low pressure reactor (VLPR) which is briefly described

below. It consists of a cylindrical Knudsen cell with two capillary inlets at the upper side and an exit at the lower side, which is attached to a variable aperture system on the first stage of a differentially pumped system. Reactants and products are continuously flowing out of the reactor forming an effusive molecular beam that is modulated by a tuning fork chopper operating at 200 Hz, before it reaches the ionization region of a quadrupole mass spectrometer (Balzers QMG511). The mass spectrometric signal is amplified by a lock-in amplifier (NF 570), and is further stored on a microcomputer (DEC PDP-11/23) for the subsequent data analysis.

Chlorine atoms were produced by flowing mixtures of 5% Cl₂ in helium through a quartz tube (coated with a dried slush of phosphoric and boric acid mixture to inhibit Cl atom recombination), enclosed in a 2.45 GHz microwave cavity operating at 35 W. The Cl₂ dissociation was complete, and there was no parent peak at m/e 70. Iodomethane gas was of 99% purity (Aldrich) and deuterated iodomethane was of 99.5% isotopic purity (Aldrich). Equimolar gaseous mixtures of CH₃I/CD₃I were used to determine the isotope effect. The flow rates of all the gases were measured by following the pressure drop in a known volume as the gases were flowing through a 1 mm \times 20 cm capillary.

The chlorine atom steady-state concentration was determined by its mass spectral peak at m/e 35. The electron ionization energy was kept low at 19 eV to suppress the fragmentation of HCl to Cl^+ (m/e 35) at negligible levels (0.3%). At this electron energy, the mass spectrum of iodomethane shows the following peaks (m/e, intensity): 15 (100.00), 127 (1.62), 128 (0.04), 140 (0.15), 141 (0.75) and 142 (21.42). The parent peak at m/e 142 was employed to determine the steady-state concentration of CH₃I. In our system, the mass spectrometric signal intensity $I_{\rm M}$ of a species M is given by the expression: $I_{\rm M} = \alpha_{\rm M} F_{\rm M} = \alpha_{\rm M} k_{\rm esc,M} V[{\rm M}]$, where $\alpha_{\rm M}$ is a mass spectrometric calibration factor, $F_{\rm M}$ is the flow rate (in molecule s^{-1}), V is the reactor volume, and $k_{\rm esc,M}$ is the escape constant (in s⁻¹). The $\alpha_{\rm M}$ factor for iodomethane was determined from calibration runs, by plotting I_{142} versus F_{CH_3I} . The initial concentration of Cl atoms was ca. 9×10^{11} molecule cm⁻³, and the initial concentration of iodomethane was in the range $(1-50) \times 10^{12}$ molecule cm⁻³. The uncertainty of the mass spectral intensities measurement was 3%, and thus the ratio $[Cl]_o/[Cl] = I_{Cl,o}/I_{Cl}$ was determined with an accuracy of ca. 5%.

The reactor ($V = 168 \text{ cm}^3$) was coated with a thin film of teflon in order to inhibit wall reactions, and its temperature was controlled by circulating a thermostatted liquid through the outer jacket. The escape constants of various species were determined by monitoring the first order decay of their mass spectrometric signal after a fast halt of the flow. The escape aperture diameter was 5 mm and the escape constants of various species were given by the expression $k_{\text{esc,M}} = 1.86(T/M)^{1/2}$ where T is the reactor temperature, and M is the molecular weight (in amu).

3. Results

The reaction of atomic chlorine with CH_3I molecules may proceed via the following primary reaction pathways:

$$HC1 + CH_2 \Delta H_r = +3.3$$
 (1a)

$$Cl + CH_3 I \longrightarrow ICl + CH_3 \qquad \Delta H_r = +26.4 \qquad (1b)$$

$$\downarrow \downarrow \downarrow + CH_3 Cl \qquad \Delta H_r \simeq -110.1 \qquad (1c)$$

$$Cl + CH_2 I \rightarrow CH_2 Cl + I \quad \Delta H_r = -125.9,$$
 (2)

$$CH_{2}I + CH_{2}I \longrightarrow ICH_{2}CH_{2}I' \longrightarrow CH_{2}\neg CH_{2} + l_{2} \qquad \Delta H_{r} = -345.7$$

$$CH_{2}\neg CH_{2}\neg CH_{2} + H_{I} \qquad \Delta H_{r} = -305.0$$
(3)

The reaction enthalpies (in kJ mol⁻¹) were estimated by adopting the published heats of formation of all species [13,14].

The mass spectrometric analysis of the reaction products showed the appearance of a peak at m/e36 (HCl⁺) and an increase in the peak at m/e 127 (I⁺). The peak at m/e 36 is due to the primary product HCl, while the peak at m/e 127 is probably due to the iodomethyl radical CH₂I since the intensity I_{127} increases proportionally with the reaction yield. Traces of ICl were detected at its parent peak (m/e 162) suggesting that the yield of reaction (1b) is small in our conditions. Furthermore, there was no mass spectroscopic evidence of CH₃Cl product at its



Fig. 1. Plot of $(R - 1)k_{esc,Cl}$ versus [CH₃I] at 303 K. Error bar reflects the propagated errors (2σ) .

parent peak at m/e 50 suggesting the absence of reaction (1c), which is improbable considering that it involves a very tight transition state. Furthermore, there was no indication of the secondary products ICH₂CH₂I, CH₂=CH₂ and CH₂=CHI (absence of

their parent or distinctive fragment peaks), implying the insignificance of secondary reactions (2) and (3).

Furthermore, there was no increase in mass spectral intensities of Cl and CH₃I upon the addition of HCl ([HCl] ca. 7×10^{12} molecules cm⁻³) through a



Fig. 2. Arrhenius plot of $\ln k_1$ versus 1/T. Error bars reflect the total propagated errors (2σ) .

third inlet to the reactor, suggesting that the reverse reaction of (1a) does not occur in our experimental conditions.

The yield of HCl product was equal to the loss of Cl reactant, considering that the ratio of the mass spectrometric sensitivities of HCl and Cl, $\alpha_{\rm HCl}/\alpha_{\rm Cl}$ is 1.1 ± 0.1 [11]. In addition, the experiments of CD₃I with Cl showed that the yield of DCl (monitored at m/e 37) was found to be equal to the Cl loss, correcting for the mass spectral contribution of ³⁷Cl atoms to the intensity of D ³⁵Cl. This constitutes an additional piece of evidence that the title reaction occurs exclusively via a hydrogen atom transfer (pathway 1a), and the other competing pathways do not occur in our system.

Application of the steady-state approximation for chlorine atoms results in the expression:

$$\Delta[\mathrm{Cl}]k_{\mathrm{esc,Cl}} = k_1[\mathrm{Cl}][\mathrm{CH}_3\mathrm{I}], \qquad (\mathrm{I})$$

Table i

Typical experimental data (steady state concentrations of CH₃I and Cl and the ratio $R = I_{Cl,o} / I_{Cl}$) for each of the temperatures studied (concentration units: molecule cm⁻³)

[CH ₃ I] _o	[CH ₃ I]	[C1] ₀	[CI]	R	
10 ¹²	1012	10 ¹²	1012		
T = 273 K					
8.26	7.14	0.95	0.39	2.46	
9.96	8.79	0.93	0.32	2.88	
21.29	19.80	0.93	0.18	5.24	
29.03	27.58	0.89	0.13	6.95	
37.37	35.79	0.88	0.10	8.47	
<i>T</i> = 303 K					
6.22	5.21	0.91	0.40	2.26	
15.59	14.20	0.89	0.19	4.64	
23.49	21.93	0.91	0.14	6.38	
32.82	31.37	0.86	0.09	9.29	
41.35	39.82	0.85	0.08	10.91	
<i>T</i> = 333 K					
5.64	4.65	0.88	0.36	2.42	
12.37	11.03	0.89	0.21	4.32	
21.60	20.22	0.85	0.11	7.43	
31.42	30.04	0.81	0.08	10.67	
38.26	36.91	0.78	0.06	12.95	
T = 363 K					
6.09	5.12	0.81	0.30	2.72	
14.43	13.17	0.80	0.15	5.50	
20.73	19.31	0.84	0.12	7.28	
28.23	26.73	0.83	0.09	9.74	
36.58	35.18	0.78	0.06	13.01	

Table 2 Rate constants of the reaction $CH_3I + CI$ at four different temperatures

Т (К)	k (10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	Number of points	
273	1.05 ± 0.08	28	
303	1.37 ± 0.05	82	
333	1.71 ± 0.07	48	
363	1.97 ± 0.08	71	

where $\Delta[Cl] = [Cl]_o - [Cl]_r$, and $k_{esc,Cl}$ is the escape rate of Cl atoms. Furthermore, expression (I) becomes:

 $(R-1)k_{\rm esc,Cl} = k_1[CH_3I],$

where $R = [Cl]_{o}/[Cl]_{r} = I_{35,o}/I_{35,r}$ (subscripts o and r denote the absence or presence of CH₃I respectively). A typical plot of the above equation at T = 303 K is presented in Fig. 1. The linear least-squares fits to the data yield the rate constant k_{1} with an accuracy ca. 5% (2 σ).

Experiments were performed at four different temperatures (273, 303, 333 and 363 K). Typical experimental data are presented in Table 1 and the rate constants obtained are listed in Table 2. The Arrhenius plot is presented in Fig. 2; linear least-squares analysis of the temperature dependence data yield the activation energies and the pre-exponential A factors for the reaction. The rate constant k_1 is given by the expression:

$$k_1 = (1.33 \pm 0.49) \times 10^{-11}$$

 $\times \exp[-(5.73 \pm 1.00 \text{ kJ mol}^{-1})]$
 $/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$

The isotope effect $k_{\rm H}/k_{\rm D}$ of the reaction was studied by performing a series of relative rate experiments using an equimolar mixture of CH₃I/CD₃I. In these experiments, the intensity of the parent peaks of both iodomethanes (at m/e 142 and 145 respectively) was monitored as the flow of chlorine atoms to the reactor was interrupted. By employing the steady-state approximation the following expression is derived:

$$\Delta [CH_3I] k_{esc,CH_3I} / \Delta [CD_3I] k_{esc,CD_3I}$$
$$= k_{H} [CH_3I] / k_{D} [CD_3I],$$

which after minor transformation becomes:

$$k_{\rm H}/k_{\rm D} = (R_{\rm CH_3I} - 1)k_{\rm esc, CH_3I}/(R_{\rm CD_3I} - 1)k_{\rm esc, CD_3I}$$

where $R_{\rm CH_3I}$ is the ratio $I_{142,o}/I_{142,r}$ and $R_{\rm CD_3I}$ is the ratio $I_{145,o}/I_{145,r}$ (subscripts o and r denote the absence or presence of Cl respectively). Experiments were performed at four temperatures (273, 303, 333 and 363 K). The data show no temperature dependence within experimental error and the average value of $k_{\rm H}/k_{\rm D}$ is 1.09 ± 0.04 .

4. Discussion

To our knowledge, there have been no previous kinetic studies on the reaction of atomic chlorine with CH₃I. However, there are kinetic data available for the reactions of atomic chlorine with methane and halomethanes, and the relevant information is listed in Table 3. The room temperature rate constant k_1 is higher than those of CH₃Cl and CH₃Br molecules [15,16]. This implies a high reaction cross-section, which is in accordance with the formation of an intermediate complex between Cl and I atoms. Early molecular beam studies by Hoffmann et al. [17,18] proposed the existence of long-lived collision complexes in the reactions of Cl atoms with a variety of iodoalkanes, including CH₃I. Recently, our group has considered the formation of a CH₃OCH₂I-Cl adduct to explain the negative activation energy of -6.23 kJ mol⁻¹ observed in the reaction of CH₃OCH₃I with Cl [19], and Piety et al. have suggested similar intermediate adducts in the reactions of Cl atoms with several iodoalkanes [20]. Further experimental evidence of adduct formation

in similar reactions was provided by the gas-phase detection of CF₂HBr-F and CH₃Br-F adducts using their UV absorbance ($\lambda_{max} = 290$ nm) in the reactions of F atoms with CF₂HBr and CH₃Br [21,22]. In order to explore the possibility of an adduct formation between Cl and CH₃I molecules we have performed ab initio calculations at the MP2/ UHF/3-21 + + G(2d, 2p) level of theory. The results show that a weak adduct is formed with a potential well of 57.75 kJ mol⁻¹ and an I-Cl bond strength D_{298}^0 of 52.41 kJ mol⁻¹. The predicted C-I and Cl-I bond lengths are 2.20 and 2.75 Å respectively and the C-I-Cl angle is 82.11° [23]. Moreover, the large size of the iodine atom, the shape of the potential energy surface and the range of attractive interactions (ca. 3.5 Å) leads to adduct formation even if Cl approaches from the methyl side. At low pressure conditions the adduct can not be stabilized by collisions and decomposes unimolecularly to the CH₂I radical and HCl. This indirect hydrogen transfer mechanism is consistent with the low isotope effect of 1.09 observed, since a low frequency breathing motion of the adduct becomes the reaction coordinate with a small dependence on the H/D isotopic variation.

The temperature dependence of a reaction involving an intermediate adduct is mainly determined from the height of the forward potential barrier and if this is sufficiently high, the reaction exhibits a positive activation energy. The barriers for HCl elimination in the reactions of CH_3OCH_2I and CH_3I with Cl should follow the trend of the C–H bond dissociation energies (estimated to be ca. 380.7 [19] and 434.3 kJ mol⁻¹ [14] respectively). Thus, the activation energies observed in both cases are consis-

Table 3

The room temperature rate constants, activation energies and pre-exponential factors for the reactions of atomic chlorine with methane and halomethanes and the strengths of the corresponding C-H bonds

Reactant	$k_{298} (10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$A(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	E_{α} (kJ mol ⁻¹)	D_{298}^0 (C-H) ^a (kJ mol ⁻¹)	Ref.
CH₄	1.00	0.96	11.21	439.74	[25]
CH	3.72	3.33	11.17	418.40	[26]
CH ₃ Cl	5.02	2.93	10.08	422.17	[15]
CH ₃ Br	5.36	1.55	8.91	426.77	[16]
CH ₃ I	13.7	1.33	5.73	430.95	this work
-	8.1	5.5	10.49		[20]

^a The bond dissociation energies were taken from Refs. [13,14].

tent with the magnitudes of the corresponding C-H bond dissociation energies. However, the C-H bond dissociation energy in CH₃I obtained by the iodination technique [14] seems unusually high and we have attempted to derive it using ab initio molecular calculations. The calculations were performed with the GAMESS program package [24] at the MP2/3-21 + + G(2d, 2p) level of theory. Unrestricted Hartree-Fock (UHF) wavefunctions were used for the open-shell species CH₂I and H and restricted Hartree-Fock (RHF) for the CH₃I molecule. Møller-Plesset second order perturbation theory (MP2) was employed in the geometry optimization and the thermochemical calculations of CH₃I, as well as for the potential energy calculations of all the species. The iodomethyl radical CH₂I, optimized at the UHF/3-21 + + G(2d, 2p) level, is planar with C-I and C-H bond lengths of 2.0966 and 1.0700 Å respectively and the I-C-H angles are 118.550°. Iodomethane, CH₂I, optimized at the MP2/RHF/3-21 + + G(2d, 2p) level, has C-I and C-H bond lengths of 2.1986 and 1.0826 Å respectively and the I-C-H angles are 107.294°. The C-H bond dissociation energy was calculated at two temperatures (0 and 298 K) to be 418.258 and 425.270 kJ mol⁻¹ respectively. The theoretical value at 298 K is ca. 9 kJ mol⁻¹ lower than the currently accepted experimental value; however, it should be noted that the accuracy of these ab initio theoretical calculations is about 10 kJ mol⁻¹.

Recently, Piety et al. [20] have studied the reaction of Cl with CH₃I by the flash photolysis-resonance fluorescence technique at temperatures 364-694 K and pressures in the range 3-600 Torr. They report a rate constant $k_{298} = 8.1 \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹ and an activation energy $E_2 = 10.49$ kJ mol⁻¹ which are in fair agreement with our results. The differences may be due to pressure effects pertaining to bimolecular atom-molecule reactions involving intermediate adducts. At high pressures (several Torr), the adduct CH₃I–Cl is possibly stabilized and the forward unimolecular reaction pathway has a barrier to cross, while at low pressures the exothermicity of adduct formation (ca. 50 kJ mol⁻¹) is available to surmount the barrier and the apparent activation energy is lowered.

Our study and that of Piety have concluded that the primary products of the reaction are HCl and CH₂I radical. However, molecular beam studies by Hoffmann et al. [17,18] found that the reaction of CH₃I with Cl leads to ICl product without being able to determine the relative contribution of this pathway to the overall reaction yield. The disagreement must be due to the much higher translational energy available by the molecular beam technique (the energy threshold measured for reaction (1b), E_{th} , was 18.5 kJ mol⁻¹) which results in a higher yield of the more endothermic but entropically favoured iodine metathesis reaction (1b).

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