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Atmospheric Chemistry of CH_3I: Reaction with Atomic Chlorine at 1−700 Torr Total Pressure and 295 K

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The title reaction was studied using long path length FTIR spectroscopy coupled to a smog chamber. In 1 Torr of N_2 diluent at 295 K a large kinetic isotope effect was observed, $k_H/k_D = 6$, suggesting that the reaction of Cl atoms with CH_3I proceeds via H atom abstraction to give CH_2I radicals and HCl with a rate constant of $(9.0 \pm 1.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. In 700 Torr total pressure of N_2, O_2, and air diluents the reactivity of Cl toward CH_3I was 50% greater than that at 1 Torr. The increase in reactivity is ascribed to the formation of the $CH_3I{-}Cl$ adduct. In 700 Torr of O_2 the majority (≈98%) of the adduct decomposes back to reactants, and a small fraction (≈2%) is lost via one or more processes that do not regenerate reactants. In 1 atm of air at 295 K the reaction of Cl atoms with CH_3I produces less than 20% yield of CH_3Cl. The potential role of the title reaction in atmospheric chemistry is discussed.

1. Introduction

The atmospheric chemistry of iodine is a topic of current interest. It has been suggested that iodine chemistry may influence tropospheric HO_2/OH and NO_2/NO concentration ratios and hence the oxidizing capacity of the atmosphere.[1,2] Unlike the corresponding chlorinated and brominated compounds, iodo compounds and reservoir species are easily photodissociated in the near-UV and visible. As a consequence, iodine in its various forms is rapidly converted to iodine atoms which can take part in ozone-depleting cycles in the troposphere and lower stratosphere.[3]

CH_3I is generally regarded as the main carrier of marine iodine to the atmosphere. It is emitted into the atmosphere from the oceans at a rate of 1−2 Tg/yr.[2,4] Concentrations of methyl iodide in the marine boundary layer are typically 1−4 pptv[5,6] but can be as high as 43 pptv.[7] The dominant atmospheric fate of CH_3I is photolysis which occurs at a rate of approximately 5×10^{-6} s^{-1}, corresponding to an atmospheric lifetime of a few days.[8,9]

The reaction of atomic chlorine with CH_3I has been the subject of three recent studies. Wine and co-workers[10,11] studied the kinetics of reaction 1 at 218−694 K in 5−500 Torr of N_2 and observed two reaction channels: H atom abstraction (channel 1a) and addition to form a weakly bound adduct (channel 1b).

$$Cl + CH_3I \rightarrow CH_2I + HCl \quad (1a)$$

$$Cl + CH_3I + M \rightleftharpoons CH_3I{-}Cl + M \quad (1b, -1b)$$

$$Cl + CH_3I \rightarrow CH_3Cl + I \quad (1c)$$

Under near ambient conditions (297 K, 500 Torr of N_2) reaction 1 proceeds predominately (≈95%) via adduct formation with an overall rate constant of $k_1 \approx 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[11] The rate constant reported for hydrogen abstraction was $k_{1a} = 5.4 \times 10^{-11} \exp(-1250/T)$ cm^3 molecule^{-1} s^{-1}.[11] Kambanis et al.[12] studied k_1 over the temperature range 273−363 K at a very low total pressure (2 mTorr of helium) where channel 1b should be of negligible importance. Kambanis et al. report $k_{1a} = 1.33 \times 10^{-11} \exp(-700/T)$ cm^3 molecule^{-1} s^{-1}.[12] Finally, Goliff and Rowland[13] conducted a product study of reaction 1 and report a 9% yield of CH_3Cl.

Combining $k_1 \approx 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [11] with an estimate of the chlorine atom concentration in the marine boundary layer of 10^4 cm^{-3} [14−16] gives a pseudo-first-order loss rate of CH_3I with respect to reaction 1 of 2×10^{-7} s^{-1} (approximately 25 times slower than loss of CH_3I via photolysis). The atmospheric fate of the $CH_3I{-}Cl$ adduct formed in channel 1b is uncertain. Conversion of the adduct into CH_3Cl would represent a small, but significant, oceanic flux of CH_3Cl. The global flux of CH_3Cl to the atmosphere is presently estimated to be of the order of 3−3.5 Tg yr^{-1}.[17,18] The FTIR smog chamber system at Ford Motor Company was employed to investigate the possible role of reaction 1 in atmospheric chemistry.

2. FTIR Smog Chamber System

The apparatus consists of a Mattson Sirus 100 FTIR spectrometer coupled to a 140 L Pyrex reactor described in detail elsewhere.[19] Radicals were generated by the UV irradiation (22 black lamps) of mixtures of CH_3I, CD_3I, Cl_2, CH_3OCHO, C_2H_5Cl, C_2H_5F, CH_4, and CH_3Cl in 1−700 Torr total pressure with N_2, O_2, or air diluent at 295 K. Reagents and concentrations used were as follows: CH_3I, 2.9−749 mTorr; CD_3I, 13−

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14 mTorr; Cl_2, 51−1950 mTorr; CH_3OCHO, 0−26.6 mTorr; C_2H_5Cl, 0−11.7 mTorr; C_2H_5F, 0−33.8 mTorr, CH_4, 0−60 mTorr; and CH_3Cl, 0−16 mTorr. Reactants loss and product formation were monitored by FTIR spectroscopy using the wavenumber range 700−2000 cm^{-1}, an analyzing path length of 28 m, and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added spectra. Reference spectra were acquired by expanding known volumes of reference materials into the reactor. A reference spectrum of HC(O)Cl was obtained from the reference library at Ford Motor Company. Oxygen, nitrogen, synthetic air, Cl_2, CH_4, C_2H_5Cl, C_2H_5F, CH_3OCHO, CH_3Cl, and CH_3I were obtained at the highest purities available from commercial sources and used as received. CH_3I, CD_3I, and CH_3OCHO are liquids at 295 K and were degassed by freeze−pump−thaw cycling before use. Control experiments were performed to test for loss of CH_3I via either photolysis or heterogeneous reactions in the chamber; no such effects were significant. Tschuikow-Roux et al.[20] have reported that reaction between CH_3I and Cl_2 in the dark occurs at a "surprisingly fast" rate. In a control experiment a mixture of 24.1 mTorr of CH_3I and 238 mTorr of Cl_2 in 700 Torr of air was left in the chamber in the dark for 3 h; there was no discernible (<1%) loss of CH_3I, showing that "dark" reactions are not a complication in the present work. The uncertainties reported in this paper are two standard deviations unless otherwise stated. Standard error propagation methods are used to calculate combined uncertainties.

3. Results

3.1. Relative Rate Study at 1 Torr Total Pressure. Relative rate experiments were performed to measure the kinetics of the reaction of Cl atoms with CH_3I at 1 Torr total pressure using techniques described elsewhere.[21] Reaction mixtures consisted of 7.7−44.7 mTorr of CH_3I, 4.8−16 mTorr of the reference compound (CH_3OCHO or CH_3Cl), and 188−302 mTorr of Cl_2 in 1 Torr total pressure of N_2 diluent. Photolysis of molecular chlorine was the source of chlorine atoms.

$$Cl_2 + h\nu \rightarrow 2Cl \tag{2}$$

The kinetics of reaction 1 were measured relative to reactions 3 and 4.

$$Cl + CH_3I \rightarrow \text{products} \tag{1}$$

$$Cl + CH_3OCHO \rightarrow \text{products} \tag{3}$$

$$Cl + CH_3Cl \rightarrow CH_2Cl + HCl \tag{4}$$

The loss of CH_3I versus those of CH_3OCHO and CH_3Cl in the presence of Cl atoms is shown in Figure 1 as open symbols. Variation of the initial concentration of CH_3I by a factor of 6 and the initial concentration ratio $[CH_3I]_{t_0}/[\text{ref}]_{t_0}$ by a factor of 4 had no discernible impact on the results. Linear least-squares analysis of the data in Figure 1 gives $k_1/k_3 = 0.62 \pm 0.04$ and $k_1/k_4 = 1.93 \pm 0.24$. Using $k_3 = 1.4 \times 10^{-12}$ [22] and $k_4 = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [23] gives k_1(1 Torr) = (8.7 ± 0.6) × 10^{-13} and (9.3 ± 1.2) × 10^{-13} cm^3 molecule^{-1} s^{-1}, respectively. We estimate that potential systematic errors associated with uncertainties in the reference rate constants could add an additional 10% to the uncertainty ranges for k_1(1 Torr). Propagating this additional uncertainty gives k_1(1 Torr) = (8.7 ± 1.1) × 10^{-13} and (9.3 ± 1.5) × 10^{-13} cm^3 molecule^{-1} s^{-1}. We choose to cite a final value which is an average of the two determinations with error limits that encompass the extremes of the individual determinations. Hence, k_1(1 Torr) = (9.0 ± 1.8) × 10^{-13} cm^3 molecule^{-1} s^{-1}.

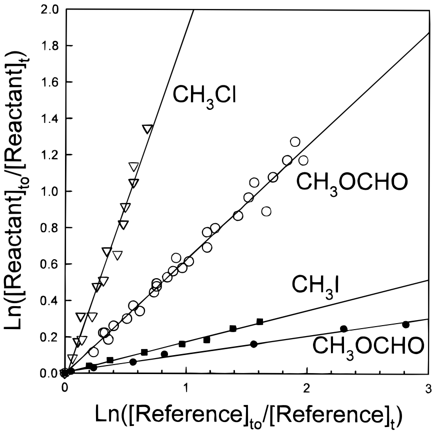

Figure 1. Loss of CH_3I (open symbols) and CD_3I (filled symbols) versus reference compounds: CH_3Cl (triangles), CH_3OCHO (circles), or CH_3I (squares), when mixtures containing these compounds were exposed to Cl atoms in 1 Torr of N_2 at 295 K.

For completeness, the rate of reaction of Cl atoms with CD_3I was studied at 1 Torr total pressure. Reaction mixtures consisted of 13−14 mTorr of CD_3I, 9−10 mTorr of reference compound (either CH_3OCHO or CH_3I), and 100−300 mTorr of Cl_2 in 1 Torr total pressure with N_2 diluent. The results are shown in Figure 1. Linear least-squares analysis gives $k(Cl+CD_3I)/k_3 = 0.099 \pm 0.007$ and $k(Cl+CD_3I)/k_1 = 0.17 \pm 0.02$. The rate constant ratio $k(Cl+CD_3I)/k_3 = 0.099 \pm 0.007$ can be combined with the measurement of $k_1/k_3 = 0.62 \pm 0.04$ (see above) to give an "indirect" measurement of $k(Cl+CD_3I)/k_1 = 0.16 \pm 0.02$, which is consistent with that measured directly. The fact that the reactivity of CD_3I toward Cl atoms is 6 times less than that of CH_3I suggests that at 1 Torr total pressure the reaction of Cl atoms with CH_3I proceeds mainly (perhaps solely) via H atom abstraction.

3.2. Products at 1 Torr Total Pressure. The aim of the experiments presented in this section was to investigate the relative importance of the possible reaction channels 1a−1c at 1 Torr total pressure. It should be noted that abstraction of iodine to give ICl and a CH_3 radical is endothermic by 26 kJ mol^{-1} [24] and is not considered further.

$$CH_3I + Cl \rightarrow CH_2I + HCl \tag{1a}$$

$$CH_3I + Cl + M \rightleftharpoons \text{adduct} + M \tag{1b, −1b}$$

$$Cl + CH_3I \rightarrow CH_3Cl + I \tag{1c}$$

Mixtures of 14.8−92.1 mTorr of CH_3I and 148−222 mTorr of Cl_2 in 1 Torr of N_2 diluent were irradiated, and the loss of CH_3I and the formation of products were monitored by FTIR spectroscopy. Figure 2 shows IR spectra acquired before (A) and after (B) a 5 min irradiation of a mixture of 15.4 mTorr of CH_3I and 142.1 mTorr of Cl_2 in 1 Torr of N_2 diluent. Comparison of panel B with reference spectra of CH_2Cl_2 and $CHCl_3$ given in panels C and D shows the formation of these species. In addition to CH_2Cl_2 and $CHCl_3$ trace amounts of CH_2ICl (≈1−2% yield) were observed; no other carbon-containing products were detected. The observed molar yield of $CHCl_3$ increased with the degree of consumption of CH_3I, indicating that $CHCl_3$ is a secondary product resulting from the chlorination of CH_2Cl_2.

$$Cl + CH_2Cl_2 \rightarrow CHCl_2 + HCl \quad (5)$$

$$CHCl_2 + Cl_2 \rightarrow CHCl_3 \quad (6)$$

The filled circles in Figure 3 show the observed formation of CH_2Cl_2 versus the loss of CH_3I. Corrections for the loss of CH_2Cl_2 via reaction 5 were computed using the Acuchem program[25] with $k_1 = 9 \times 10^{-13}$ and $k_5 = 3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1};[23] corrected data are indicted by open symbols in Figure 3. Variation of the initial concentration of CH_3I over the range 14.8−92.1 mTorr had no influence on the yield of CH_2Cl_2. Linear least-squares analysis of the corrected data gives a CH_2Cl_2 yield of 92 ± 8%. The absence of any observable CH_3Cl product (<4%) shows that pathway 1c is unimportant. The observation of trace amounts of CH_2ICl is a marker for hydrogen abstraction (pathway 1a) giving CH_2I radicals which then react with Cl_2 to give CH_2ICl. The reaction of Cl atoms with CH_2ICl is fast, $k = 8.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and proceeds via iodine abstraction to give CH_2Cl radicals which in the presence of Cl_2 are converted into CH_2Cl_2.[24] The formation of essentially 100% CH_2Cl_2 in the Cl-initiated oxidation of CH_3I in 1 Torr total pressure of N_2 shows that hydrogen abstraction is the only significant reaction pathway at 1 Torr total pressure.

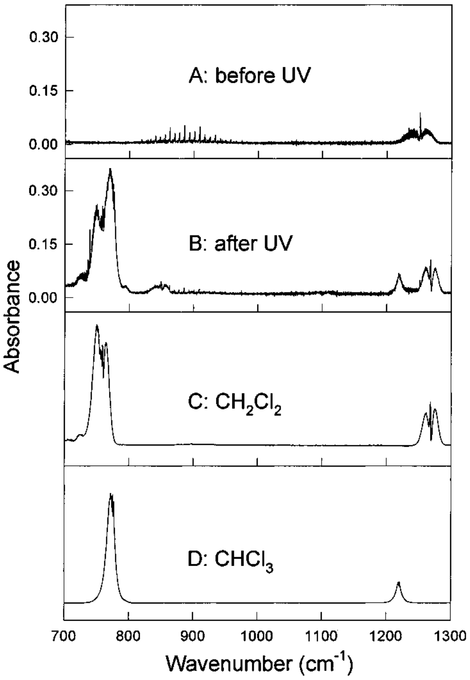

Figure 2. IR spectra acquired before (A) and after (B) a 5 min irradiation of a mixture of 15.4 mTorr of CH_3I and 142.1 mTorr of Cl_2 in 1 Torr of N_2 diluent. Reference spectra of CH_2Cl_2 and $CHCl_3$ are given in panels C and D.

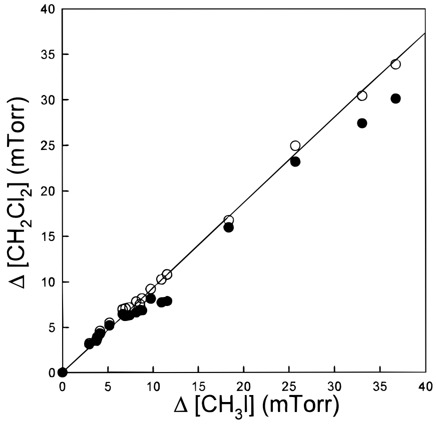

Figure 3. Formation of CH_2Cl_2 versus loss of CH_3I following UV irradiation of CH_3I/Cl_2 mixtures in 1 Torr of N_2. Filled symbols are observed data. Open symbols are corrected for secondary chemistry. See text for details.

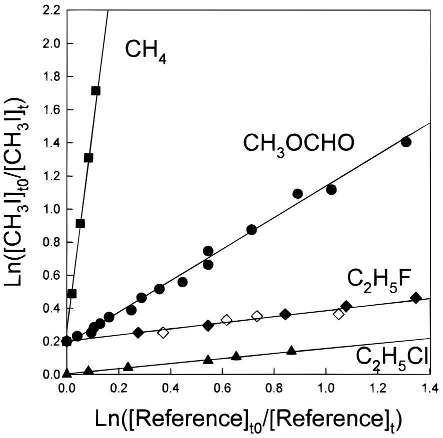

Figure 4. Decay of CH_3I versus CH_4 (squares), CH_3OCHO (circles), C_2H_5F (diamonds), and C_2H_5Cl (triangles) when mixtures containing these compounds were exposed to Cl atoms in 700 Torr of air or O_2 (filled symbols) or N_2 (open symbols). For clarity, data for CH_4 and CH_3OCHO have been shifted vertically by 0.2 units.

3.3. Relative Rate Studies at 700 Torr Total Pressure. The relative rate technique was also used to investigate the kinetics of the reaction of Cl atoms with CH_3I at 700 Torr total pressure. Reaction mixtures consisted of 2.9−100 mTorr of CH_3I, 3.4−60 mTorr of one of the reference compounds (CH_3OCHO, C_2H_5F, C_2H_5Cl, and CH_4), and 107−304 mTorr of Cl_2 in 700 Torr total pressure of N_2, air, or O_2 diluent. Photolysis of molecular chlorine was the source of chlorine atoms. The kinetics of reaction 1 were measured relative to reactions 3, 7, 8, and 9.

$$Cl + CH_3OCHO \rightarrow \text{products} \quad (3)$$

$$Cl + C_2H_5F \rightarrow C_2H_4F + HCl \quad (7)$$

$$Cl + C_2H_5Cl \rightarrow C_2H_4Cl + HCl \quad (8)$$

$$Cl + CH_4 \rightarrow CH_3 + HCl \quad (9)$$

Sensitivity toward five different parameters was investigated. First, the initial concentration of CH_3I was varied over the range 2.9−100 mTorr. Second, the concentration ratio $[CH_3I]_{t_0}/[\text{ref}]_{t_0}$ was varied by a factor of 5. Third, the concentration of Cl_2 was varied by a factor of 3. Fourth, experiments were performed in 700 Torr of either N_2, air, or O_2 diluent. Finally, four different reference compounds were employed. The values of k_1 derived in these experiments were independent of all the above parameters except for the initial CH_3I concentration. Experiments employing initial concentrations of CH_3I in the range 2.9−7.9 mTorr gave indistinguishable results. However, experiments using higher CH_3I concentrations (>10 mTorr) gave larger values of k_1. Figure 4 shows the observed loss of CH_3I versus CH_3OCHO, C_2H_5F, C_2H_5Cl, and CH_4 for experiments using CH_3I concentrations in the range 2.9−7.9 mTorr. Linear least-squares analysis gives $k_1/k_3 = 0.95 \pm 0.06$, $k_1/k_7 = 0.18 \pm 0.02$, $k_1/k_8 = 0.15 \pm 0.01$, and $k_1/k_9 = 14.7 \pm 1.6$. Using $k_3 = 1.4 \times 10^{-12}$,[22] $k_7 = 7.5 \times 10^{-12}$,[26] $k_8 = 8.0 \times 10^{-12}$,[27] and $k_9 = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [23] gives k_1(700 Torr) = $(1.33 \pm 0.08) \times 10^{-12}$, $(1.35 \pm 0.15) \times 10^{-12}$, $(1.20 \pm 0.08) \times 10^{-12}$, and $(1.47 \pm 0.16) \times 10^{-12}$, respectively. We estimate

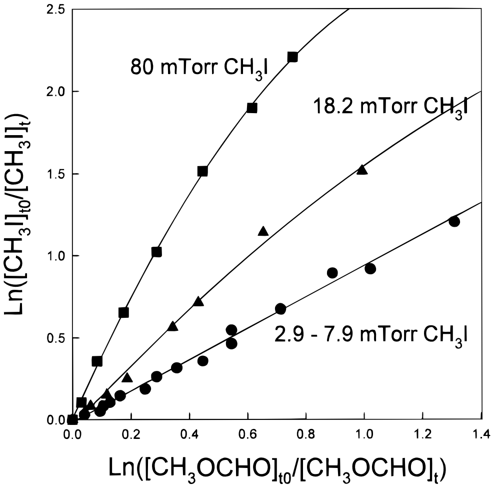

Figure 5. Decay of CH_3I versus CH_3OCHO for $[CH_3I]_0 = 2.9-7.9$ mTorr (squares), 18.2 mTorr (triangles), and 80 mTorr (diamonds) when mixtures containing these compounds were exposed to Cl atoms in 700 Torr of O_2.

that potential systematic errors in the reference constants could add an additional 10% to the uncertainty ranges for k_1(700 Torr). Propagating this additional uncertainty gives $(1.33 \pm 0.15) \times 10^{-12}$, $(1.35 \pm 0.20) \times 10^{-12}$, $(1.20 \pm 0.15) \times 10^{-12}$, and $(1.47 \pm 0.22) \times 10^{-12}$, respectively. We choose to cite the average of these values with error limits that encompass the extremes of the individual determinations; hence, $k_1(700\ \text{Torr}) = (1.3 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

It is interesting to compare the rate constant ratio $k_1/k_3 = 0.95 \pm 0.06$ measured at 700 Torr total pressure with that of $k_1/k_3 = 0.62 \pm 0.04$ measured in 1 Torr total pressure. There is a significant increase in reactivity of Cl atoms with CH_3I on moving from 1 to 700 Torr total pressure. This finding is consistent with the formation of an adduct via channel 1b, some fraction of which is removed via one or more processes that do not regenerate CH_3I. The "effective" rate constant for adduct formation, $k_{1b}k_{10}/(k_{-1b} + k_{10})$, is given by the increase in k_1/k_3 from 1 to 700 Torr, i.e., $(0.33 \pm 0.10) \times k_3 = (4.6 \pm 1.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Ayhens et al.[11] used resonance fluorescence to monitor the loss of Cl atoms in the presence of CH_3I on a millisecond time scale in 500 Torr of N_2 at 297 K and concluded that the rate constant for addition of Cl atoms to CH_3I was $k_{1b} = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. In the present study we monitor the loss of CH_3I in the presence of Cl atoms on a time scale of minutes. The fact that the "effective" rate constant for adduct formation in 700 Torr total pressure measured here is ≈43 times less than the value of k_{1b} reported by Ayhens et al. shows that in 700 Torr of air $(k_{-1b} + k_{10})/k_{10} \approx 43$. The dominant (≈98%) fate of the CH_3I-Cl adduct in 700 Torr of air at 295 K is decomposition to regenerate CH_3I and Cl atoms. Experiments performed in 700 Torr of O_2 and N_2 gave indistinguishable values of k_1, showing that there is no significant reaction of the adduct with O_2.

$$CH_3I + Cl + M \rightleftharpoons CH_3I{-}Cl + M \qquad (1b, -1b)$$

$$CH_3I{-}Cl \rightarrow \text{products} \qquad (10)$$

As mentioned above, in experiments using initial CH_3I concentrations greater than 8 mTorr, the observed loss of CH_3I was faster than in experiments employing lower CH_3I concentrations. Figure 5 shows the loss of CH_3I versus CH_3OCHO in 700 Torr of O_2 for experiments using mixtures of 15 mTorr of CH_3OCHO, 200 mTorr of Cl_2, and either 2.9, 7.3, 7.9, 18.2, or 80 mTorr of CH_3I. As seen from Figure 5, the kinetic data obtained from experiments using $[CH_3I]_0 = 2.9-7.9$ mTorr are indistinguishable; however, there is a noticeable increase in the rate of CH_3I loss in the experiments using $[CH_3I]_0 = 18.2$ and 80 mTorr. The same effect was observed in experiments using C_2H_5Cl as the reference. We conclude that under the present experimental conditions there are three fates of the CH_3I-Cl adduct: decomposition back to reactants, reaction with CH_3I, and loss via one or more other processes that do not regenerate CH_3I.

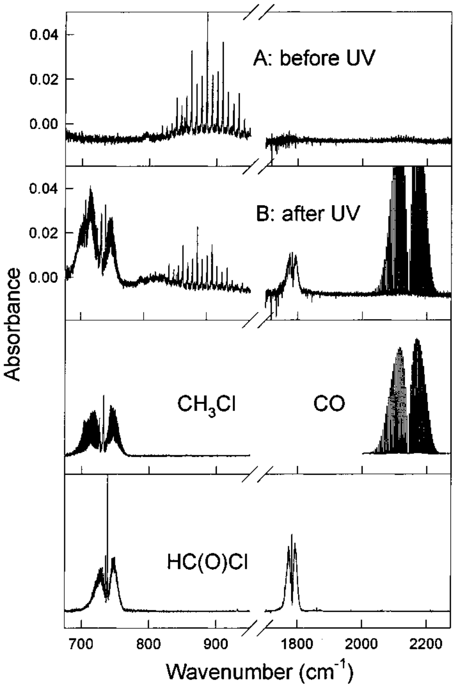

Figure 6. IR spectra acquired before (A) and after (B) a 1.5 min irradiation of a mixture of 15.2 mTorr of CH_3I and 326 mTorr of Cl_2 in 700 Torr of O_2 diluent. Reference spectra of CH_3Cl, CO, and HC(O)Cl are also displayed.

3.4. Product Studies at 700 Torr Total Pressure. The aim of the experiments presented in this section was to establish the yield of CH_3Cl from reaction 1. The absence of any observable CH_3Cl at 1 Torr total pressure shows that CH_3Cl is not formed via direct substitution. The remaining question is, "what fraction of the CH_3I-Cl adduct formed at 700 Torr total pressure undergoes decomposition to give CH_3Cl and I?" To address this question, mixtures of 4.3−749mTorr of CH_3I and 44−1075 mTorr of Cl_2 in 700 Torr total pressure of N_2 or O_2 diluent were irradiated in the FTIR smog chamber system. The loss of CH_3I and the formation of products were monitored by FTIR spectroscopy. Figure 6 shows typical IR spectra acquired before (A) and after (B) a 90 s irradiation of a mixture of 15.2 mTorr of CH_3I and 326 mTorr of Cl_2 in 700 Torr of O_2 diluent. Comparison of Figure 6B with reference spectra of CH_3Cl, CO, and HCOCl shows the formation of these species. In addition to these compounds, CH_2ClOOH was observed in trace quantities and an unknown product(s) with IR features at 707, 1060, 1309, and 1359 cm^{-1}. Figure 7 shows the formation of CH_3Cl, HC(O)Cl, and CO versus loss of CH_3I for mixtures of 15 mTorr of CH_3I and 44−1075 mTorr of Cl_2 in 700 Torr of O_2 diluent. The yield of HC(O)Cl increased with the fractional consumption of CH_3I, indicating that this species is formed in secondary reactions. Linear least-squares analysis of the data in Figure 7 gives product yields of 44 ± 3% for CH_3Cl and 43 ± 4% for CO; when HC(O)Cl and CH_2ClOOH are included, we can

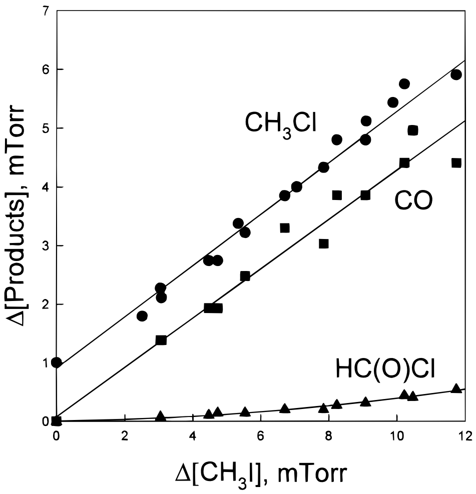

Figure 7. Formation of CH$_3$Cl (circles), CO (squares), and HC(O)Cl (triangles) versus loss of CH$_3$I in 700 Torr of O$_2$ diluent. For clarity, the data for CH$_3$Cl have been shifted vertically by one unit.

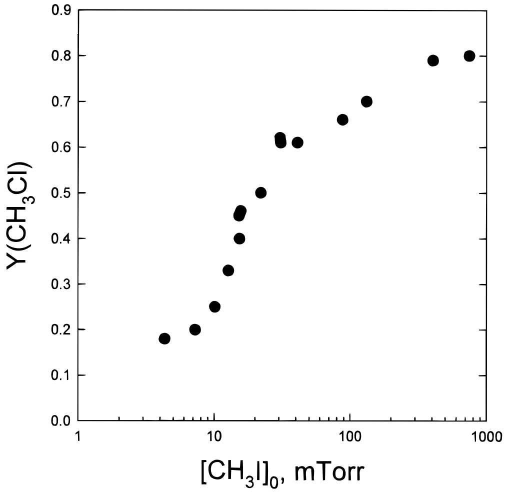

Figure 8. Yield of CH$_3$Cl versus the initial concentration of CH$_3$I when mixtures of CH$_3$I and Cl$_2$ in 700 Torr total pressure of O$_2$ were irradiated in the chamber.

account for 95 ± 11% of the loss of CH$_3$I. Variation of the concentration of Cl$_2$ by a factor of 24 had no discernible influence on the product yields. The magnitudes of the HC(O)Cl and CH$_2$ClOOH yields are consistent with those expected following secondary loss of CH$_3$Cl via reaction with Cl atoms.[28]

Variation of the initial CH$_3$I concentration over the range 4.3−749 mTorr with the Cl$_2$ concentration fixed at 200 mTorr caused a change in the relative importance of CH$_3$Cl and CO products. Figure 8 shows the yield of CH$_3$Cl versus the initial concentration of CH$_3$I. As the initial CH$_3$I concentration increased from 4.3 to 749 mTorr, the yield of CH$_3$Cl increased from 18 to 80%; conversely, the CO yield decreased from 80 to 14%. Finally, an experiment was performed using 17 mTorr of CH$_3$I and 213 mTorr of Cl$_2$ in 700 Torr of N$_2$ diluent. The CH$_3$Cl yield from this experiment was 38 ± 5%, which is indistinguishable from that observed with O$_2$ diluent; in addition, CH$_2$Cl$_2$ was observed in a yield of 45 ± 6%.

4. Discussion

The reaction of Cl atom with CH$_3$I was studied at 1 and 700 Torr total pressure at 295 K. In 1 Torr of N$_2$ the reaction proceeds via H atom abstraction to give CH$_2$I radicals and HCl with a rate constant of $(9.0 \pm 1.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The H atom abstraction could either proceed directly in a concerted bimolecular reaction or indirectly via the formation of the CH$_3$I−Cl adduct, which then decomposes via HCl elimination. Kambanis et al.[12] studied reaction 1 at 303 K in 2 mTorr of He diluent and reported a rate constant of $(1.37 \pm 0.05) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} with essentially 100% conversion of Cl atoms into HCl. Kambanis et al. conducted experiments with both CH$_3$I and CD$_3$I and did not observe any evidence for a kinetic isotope effect $k_H/k_D = 1.1 \pm 0.1$ and concluded that H atom abstraction occurs via a weakly bound CH$_3$I−Cl adduct.

In contrast to the findings of Kambanis, a large kinetic isotope effect, $k_H/k_D = 6 \pm 1$, was observed in the present work in experiments conducted in 1 Torr of N$_2$ and 295 K. The origin of the apparent discrepancy between our results and those of Kambanis et al. is unknown.

Ayhens et al.[11] have recently studied the kinetics of reaction 1 over a wide range of temperature and pressure. At temperatures >364 K Ayhens et al.[11] were able to study the kinetics of the direct H atom abstraction channel 1a in the absence of complications caused by formation of the adduct. Ayhens et al.[11] observed a significant kinetic isotope effect and reported $k_{1a} = 5.4 \times 10^{-11} \exp(-1250/T)$ cm^3 molecule^{-1} s^{-1}. Extrapolation to 295 K gives a value of $k_{1a} = 8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This result is indistinguishable from the rate constant for H atom abstraction of $(9.0 \pm 1.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 1 Torr measured herein. We conclude that in 1 Torr of N$_2$ at 295 K the reaction of Cl atoms with CH$_3$I proceeds predominately via the direct H atom abstraction channel 1a with a rate constant $k_{1a} = (9.0 \pm 1.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

On increasing the total pressure from 1 to 700 Torr, we observe a small, but significant, increase in the reactivity of Cl atoms toward CH$_3$I. Kinetic data from experiments conducted in 700 Torr of either N$_2$ or O$_2$ were indistinguishable. It seems reasonable to ascribe the increase in reactivity to the formation of an adduct via channel 1b, some fraction of which is lost via processes that do not regenerate reactants. In 700 Torr of air the "effective" rate constant for addition of Cl atoms to CH$_3$I, $k_{1b}(k_{10}/(k_{-1b} + k_{10}))$, is $(4.6 \pm 1.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Using $k_{1b} \approx 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[11] we conclude that the dominant fate of the CH$_3$I−Cl adduct is decomposition back to reactants. In experiments using >10 mTorr of CH$_3$I, anomalous kinetic behavior was observed with curved relative rate plots (see Figure 5). CH$_3$Cl and CO were the major products of reaction 1 in 700 Torr of O$_2$. The yield of CH$_3$Cl increased at the expense of CO in experiments employing higher CH$_3$I concentrations. For experiments using < 10 mTorr of CH$_3$I, it appears that the CH$_3$Cl yield is less sensitive to the initial CH$_3$I concentration and is about 20%. Product studies could not be performed for initial CH$_3$I concentrations < 4.9 mTorr. It is unclear from the present work whether the CH$_3$Cl yield "levels out" at 20% for initial CH$_3$I concentrations < 4.9 mTorr or whether the CH$_3$Cl yield continues to decrease. We choose to quote an upper limit of 20% for the CH$_3$Cl yield from reaction 1 at 295 K. This result is consistent with the observations by Goliff and Rowland of a 9% yield of CH$_3$Cl from reaction 1.

The exact mechanism by which CH$_3$I is lost in the high-pressure experiments is clearly complex and not entirely defined by the present experiments. The simplest chemical model that fits the experimental observations from this work and that of Ayhens et al.[11] is

$$CH_3I + Cl \rightarrow CH_2I + HCl \quad (1a)$$

$$CH_3I + Cl + M \rightleftharpoons CH_3I{-}Cl + M \quad (1b, -1b)$$

$$CH_3I{-}Cl + CH_3I \rightarrow CH_3Cl + \text{products} \quad (11)$$

$$CH_3I{-}Cl \rightarrow CH_3Cl + I \quad (12)$$

$$CH_3I{-}Cl \rightarrow CH_2I + HCl \quad (13)$$

At 700 Torr total pressure the reaction of Cl atoms with CH_3I proceeds via both H atom abstraction and via addition with the latter dominating. The H atom abstraction channel gives CH_2I radicals which react with O_2 to give CH_2IO_2 radicals which undergo self-reaction to give iodomethoxy radicals CH_2IO. By analogy to CH_2BrO, it is expected that CH_2IO radicals will eliminate an I atom to give HCHO. HCHO is 56 times more reactive than CH_3I toward Cl atoms[23] and will be oxidized to give the observed CO product. The overwhelming fate of the $CH_3I{-}Cl$ adduct is decomposition to re-form reactants; however, some of the adduct is lost via other processes (either HCl elimination or rearrangement to give CH_3Cl). The adduct appears to react with CH_3I to produce CH_3Cl with this process becoming very important in experiments using $[CH_3I] > 20$ mTorr.

The aim of the present work was to assess the potential role of reaction 1 in atmospheric chemistry, not to unravel the complexities of the behavior of the $CH_3I{-}Cl$ adduct in laboratory chambers. We show here that the effective bimolecular rate constant for reaction 1 in 700 Torr of air at 295 K is $(1.3 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and the CH_3Cl yield is $<20\%$. Combining these data with an estimate of the Cl atom concentration in the marine boundary layer, 10^4 cm^{-3}, and the CH_3I photolysis rate of 5×10^{-6} s^{-1}, it can be calculated that $<0.05\%$ of the CH_3I released into the atmosphere will be converted into CH_3Cl via reaction 1. Based upon our current understanding of the Cl atom concentration in the marine boundary layer, it appears that reaction 1 is of negligible atmospheric importance.

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