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The dimethyl sulfide reaction with atomic chlorine and its implications for the budget of methyl chloride

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Abstract. DMS is produced in large quantities by natural oceanic processes. Its chemistry and emissions have been postulated to play a role in the radiative balance of the atmosphere. While its reactions with OH and NO₃ radicals are well known, the reaction with chlorine atoms in the marine boundary layer has also been suggested recently. If this produces CH₃Cl, it would contribute to the global budget of this naturally occurring halocarbon. Experiments were carried out to measure the yield of CH₃Cl in the Cl+DMS reaction. CH₃Cl was indeed formed in this reaction in laboratory experiments at 1 atm. and 298 K, with a small yield of $(1.34 \pm 0.07) \times 10^{-3}$. This yield is sufficiently small that the contribution to the global CH₃Cl budget is estimated to be $\leq 2\%$ and it is unlikely to be responsible for the anomalously high CH₃Cl concentrations measured recently over the Labrador Sea.

Introduction

Dimethyl sulfide (DMS) is produced by natural processes in surface seawater in large quantities. DMS emissions from the ocean have been estimated to range from 12 to 35×10^{12} g S/yr [see estimates by Bates et al., 1987; Erickson et al., 1990; Andreae, 1990; Spiro et al., 1992; Pham et al., 1995]. Atmospheric degradation of DMS initiated by OH and NO₃ leads to products which can contribute to acidic precipitation and influence global climate [Charlson et al., 1987]. There has also been recent interest in possible oxidation by Cl atoms [Keene et al., 1996].

The production of atomic chlorine at the ocean surface is currently an area of active research. There are a variety of potential reactions producing photochemically labile chlorine atom precursors, [Finlayson-Pitts, 1993; Graedel and Keene, 1995]. Keene, Pszenny and coworkers [Keene et al., 1993; Pszenny et al., 1993] have used a mist chamber technique to identify chlorine-containing compounds other than HCl, possibly Cl₂ or HOCl, in the marine boundary layer. They calculate that chlorine atom concentrations as high as $10^4 - 10^5$ cm⁻³ could be generated upon photolysis of these precursors. More recently, Spicer and coworkers (personal communication, 1996) identified Cl₂ over the North Atlantic Ocean using atmospheric pressure ionization mass spectrometry. Several other recent studies are

also consistent with the production of Cl atoms at these levels [Jobson et al., 1994; Singh et al., 1996; Wingenter et al., 1996]. Keene and coworkers [Keene et al., 1996] also suggest that contribution of chlorine atoms to the net loss of DMS in the marine boundary layer may contribute to the observed diurnal variation of DMS.

In a kinetic study of the DMS-Cl reaction, Wine and coworkers [Stickel et al., 1992] proposed a two-channel reaction mechanism:

At one atmosphere pressure and room temperature, channel (1) accounted for 40-50% of the overall reaction. The final products of the chlorine addition path (2) are not known, but Stickel et al. (1992) proposed methyl chloride as one possibility:

Methyl chloride, the most abundant halocarbon in the troposphere, has a major source in seawater [Singh et al., 1983]. It is also produced by microbial fermentation and biomass burning, and is of interest as a natural source of stratospheric chlorine. The total budget of CH₃Cl is estimated to be 3.5×10^{12} g/yr [Koppmann et al., 1993].

Measurements of methyl chloride in water and air samples were made during a cruise of CSS Hudson in the Labrador Sea in late May to early June 1994, and analyzed by oxygen-doped GC-ECD. While an average mixing ratio of methyl chloride in the troposphere of the northern hemisphere is around 530 pptv [Koppmann et al., 1993], it was found that occasionally much higher concentrations were measured in the atmosphere over the Labrador Sea, up to a maximum of 870 pptv. In contrast, surface waters were consistently undersaturated, the average saturation level being 83%. The local sea surface was therefore not the source of the anomalously high atmospheric signals. One possible source is the reaction (3c) of Cl atoms with DMS.

We report here the results of an investigation of the DMS-Cl reaction as a potential source of CH₃Cl and discuss the implications for chemistry in the marine boundary layer.

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Experimental

Gas chromatography was used to identify and quantify CH_3Cl produced in the reaction between DMS and atomic chlorine. In the first set of experiments, phosgene was used as the source of Cl atoms:

DMS and COCl_2 at initial concentrations of $[\text{DMS}]_0 \cong [\text{COCl}_2]_0 \cong (2.5 - 5) \times 10^{16} \text{ molecule cm}^{-3}$ (1000 - 2000 ppm) were introduced into a 200-ml quartz cell and the total pressure made up to 760 Torr using air. In the second set of experiments, photolysis of thionyl chloride was used as a source of Cl atoms:

DMS and SOCl_2 were vaporized into a stream of ultrahigh-purity air which filled a 50 L Teflon collapsible reaction chamber. Initial concentrations were $[\text{DMS}]_0 \cong [\text{SOCl}_2]_0 \cong (2.5 - 5) \times 10^{15} \text{ molecule cm}^{-3}$ (100 - 200 ppm). No dark reaction between DMS and phosgene or thionyl chloride was observed over time scales of the photolysis experiments. DMS is known to react with Cl_2 in the dark [Nielsen et al., 1990]. Using the value of $k_{(\text{DMS}+\text{Cl}_2)} \leq 2.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured in this laboratory and the lack of a dark reaction, the concentration of Cl_2 in phosgene was estimated to be insignificant.

To generate chlorine atoms, the reaction mixtures were irradiated by light at $\lambda = 254 \text{ nm}$ using low-pressure mercury lamps (Blak-Ray Lamp, Model XX-15S, Ultra-Violet Products, Upland, CA). Experiments carried out under similar conditions but without the chlorine atom sources confirmed that DMS did not photolyze under these conditions. At various reaction times, the mixture was sampled into a Carle gas sampling valve and analyzed by GC-FID (Hewlett Packard Model 5890) using a 80/120 Carbowax B/3% SP-1500, 10 ft x 1/8 in packed column (Supelco). The column was chosen to provide the best separation of DMS and CH_3Cl . With this column and our chromatographic conditions, no other products were observed in significant concentrations. In some experiments, the production of CH_3Cl was confirmed using GC-MS (Hewlett Packard Model 5890 Series II, mass selective detector 5971A) with a RTX2330, 30 m x 0.20 mm, ID 0.25 μm capillary column (Restek Corp.). The GC was calibrated independently for both DMS and CH_3Cl . Most experiments were carried out at 298 K and 1 atm. in air. Several experiments were also performed in 1 atm. of helium in order to observe products formed in the DMS-Cl reaction in the absence of molecular oxygen.

The reactants were from commercial sources: dimethyl sulfide 99+% (Aldrich), dimethyl disulfide 98% (Aldrich), ethyl methyl sulfide 99% (Aldrich), thionyl chloride 99+% (Aldrich), phosgene (J.T. Baker Chemical Co.), methyl chloride (Matheson Gas Products), air (Liquid Carbonic, Ultra-Zero air), helium 99.999% (Liquid Carbonic). All chemicals were used as received.

GC-MS analysis of the reactant DMS revealed small quantities of dimethyl disulfide (DMDS, ~0.4%) and ethyl methyl sulfide (EMS, ~5%), the latter being present at higher concentration than expected from the manufacturer's stated purity. As a result, some studies of the reactions of EMS and DMDS with chlorine atoms produced by the photolysis of thionyl chloride were also carried out to confirm that the CH_3Cl observed in the DMS reaction was not due to the reaction of EMS or DMDS impurities.

Figure 1. Concentrations of CH_3Cl formed, $\Delta[\text{CH}_3\text{Cl}]$, as a function of DMS reacted, $\Delta[\text{DMS}]$. Open triangles represent runs using COCl_2 as a chlorine atom source, and initial reactant concentrations of 1000-2000 ppm; filled triangles represent runs using SOCl_2 as the chlorine atom source and with initial concentrations of 100-200 ppm. These runs were carried out at one atm. in air and 298 K. The open circle represents a run carried out in He at 298 K.

Results and Discussion

Laboratory studies of the DMS-Cl reaction

Figure 1 shows the measured concentrations of methyl chloride produced in the DMS-Cl reaction, $\Delta[\text{CH}_3\text{Cl}]$, as a function of the concentration of DMS reacted, $\Delta[\text{DMS}]$. The slope of the linear least-square fit to all of the data is $(1.34 \pm 0.07) \times 10^{-3}$, which gives the yield of methyl chloride. The data in Figure 1 also represent varying extents of reaction from 10.1% loss to 76.1% loss of DMS. The yields of CH_3Cl using different chlorine atom sources are seen to be in agreement over a range of initial reactant concentrations of about a factor of 20, and over a large range of extents of reaction. The result of an experiment performed with helium as a bath gas (open circle in Figure 1) is in excellent agreement with the experiments using air. The cited error includes the statistical errors from the slope of Figure 1, as well as the statistical errors associated with the calibrations for DMS and methyl chloride.

Since EMS and DMDS were observed as impurities in the DMS, some experiments were also carried out to determine whether the Cl-EMS and Cl-DMDS reactions produced CH_3Cl . No methyl chloride was formed in the Cl-EMS reaction. A small amount of CH_3Cl (yield $\cong 0.2\%$) was observed in the Cl-DMDS reaction. With the small amount of DMDS present in dimethyl sulfide (0.4%), the contribution to the CH_3Cl observed in the DMS-Cl reaction is negligible.

Computer simulations

The independence of the CH_3Cl yield with the initial reactant concentrations and with the extent of reaction suggests that it is not formed in secondary reactions. However, to calculate the amount of CH_3Cl which could be formed via the radical recombination reaction (6),

computer simulations of the system were carried out using the ACUCHEM [Braun et al., 1988] modeling program. A 36-step reaction scheme which included reactions (1) - (6) as well as secondary reactions of the intermediates formed in these reactions was set up and run for initial conditions chosen to model selected experiments: $[DMS]_0 \approx [SOCl_2]_0 \approx 2.5 \times 10^{15} \text{ molecule cm}^{-3}$ (100 ppm) at 298 K and 1 atm. of air or of helium and using the rate constant for $DMS + Cl$ reaction of $(3.3 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ given by Stickel et al. (1992). The photolysis rate was chosen to match our observed DMS loss and was in agreement with that calculated using the measurements we performed of absorption cross sections of the Cl atom sources. To simulate the most extreme case and force the maximum production of CH_3Cl by reaction (6), it was assumed that the excited adduct only decomposes to $CH_3SCl + CH_3$, reaction (3b). The model then calculated time-concentration profiles for DMS and CH_3Cl with methyl chloride formed exclusively in the recombination reaction (6).

The peak concentration of CH_3Cl predicted by the model in the presence of O_2 is $9 \times 10^4 \text{ molecules cm}^{-3}$, approximately 7 orders of magnitude less than the experimentally observed concentration, which in this run was $1 \times 10^{12} \text{ molecule cm}^{-3}$. Using the value of $k_{(CH_3Cl+Cl)} = (4.4 \pm 0.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Beichert et al., 1995] and the maximum Cl atom concentration predicted in this system ($2.4 \times 10^6 \text{ cm}^{-3}$), we calculated that loss of CH_3Cl due to the reaction with Cl would be less than 1% during the approximately 20 minutes of photolysis.

Calculations performed for the system in the absence of oxygen predict that CH_3Cl formed by the recombination reaction (6) could reach concentrations as high as $4 \times 10^{10} \text{ molecule cm}^{-3}$, much higher than in the presence of O_2 . This is consistent with the fact that in the absence of molecular oxygen, CH_3 radicals are not scavenged by O_2 . Although these predicted CH_3Cl concentrations are much larger in the absence of O_2 , they are still lower than the experimentally measured values by two orders of magnitude. It should be noted that our measurement performed in helium is indistinguishable from the measurement done in air, demonstrating that the contribution of $CH_3 + Cl$ to CH_3Cl formation is negligible. This result is also in good agreement with the suggested low yield of CH_3 from the $DMS + Cl$ reaction (<2%) [Zhao et al., 1996]. In short, the most likely source is the decomposition of the excited Cl-DMS adduct to give CH_3Cl directly, reaction (3c).

Contribution to the global CH_3Cl budget

The contribution of reaction (3c) to the global budget of CH_3Cl can be calculated knowing the source strength of DMS, the fraction of DMS which reacts with Cl, and the yield of CH_3Cl from this study. Using the assumption that DMS is lost from the atmosphere only by gas phase reactions with Cl atoms, OH, and NO_3 radicals, the fraction F of DMS reacting with Cl atoms to its total loss can be calculated as $F = x_{Cl} / (x_{Cl} + x_{OH} + x_{NO_3})$, where $x_{Cl} = k_{(DMS+Cl)} [Cl]$, $x_{OH} = k_{(DMS+OH)} [OH]$, and $x_{NO_3} = k_{(DMS+NO_3)} [NO_3]$, and k is the appropriate rate constant. For the purposes of this simple calculation, the values taken for the rate constants and concentrations were as follows: $k_{(DMS+Cl)} = 3.3 \times 10^{-10}$ [Stickel et al., 1992], $k_{(DMS+OH)} = 4.4 \times 10^{-12}$, $k_{(DMS+NO_3)} = 1.1 \times 10^{-12}$ [Atkinson et al., 1992], $[Cl] = 10^4 - 10^6 \text{ cm}^{-3}$ [Jobson et al., 1994; Singh et al., 1996; Wingenter et al., 1996; Keene et al., 1996], $[OH] = 10^6 \text{ cm}^{-3}$, and $[NO_3] = 10^7 \text{ cm}^{-3}$ [Finlayson-Pitts and Pitts, 1986], with all rate constants in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Using the highest reported estimate for the DMS flux of $35 \times 10^{12} \text{ g S/yr}$ [Andreae, 1990], the total estimated global emissions of

Figure 2. Contribution of CH_3Cl formed in the DMS-Cl reaction (in %) to its total budget as a function of the assumed Cl atom concentration (in units of $1 \times 10^4 \text{ cm}^{-3}$) in the marine boundary layer. Concentrations of OH and NO_3 were assumed to be 1×10^6 and $1 \times 10^7 \text{ radicals cm}^{-3}$, respectively.

CH_3Cl , $3.5 \times 10^{12} \text{ g/yr}$ [Koppmann et al., 1993] and the calculated values of F , the amount of CH_3Cl formed in the reaction of DMS with chlorine atoms is then calculated to be: $\text{Flux}(CH_3Cl) = \text{Flux}(DMS) \times F \times (\text{yield in our DMS-Cl reaction result})$. The result of this calculation for a range of $[Cl]$ is shown in Figure 2. The contribution of CH_3Cl formed in the DMS-Cl reaction is between 0.37% and 2% of its total budget even with the extreme assumption of a constant chlorine atom concentration.

Conclusions

The yield of CH_3Cl from the $Cl + DMS$ reaction at 1 atm. pressure and 298 K was determined to be $(1.34 \pm 0.07) \times 10^{-3}$. This yield is sufficiently small that the DMS-Cl reaction cannot be a significant global source of CH_3Cl . In addition, the anomaly in the CH_3Cl measurements over the Labrador Sea remains unexplained at the present time.

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