

Trichloroethene and tetrachloroethene: tropospheric probes for Cl- and Br-atom reactions during the polar sunrise

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ABSTRACT

We report the results of laboratory and modeling investigations of the atmospheric fate of chlorinated ethenes and their rôle as indicators of halogen reactions in the springtime Arctic troposphere. The kinetics and mechanism of the gas-phase reactions of Cl- and Br-atoms with tetrachloroethene were studied using a Fourier transform infrared spectrometer (FTIR) in 93.3 kPa air and $T = 296 \pm 2$ K. Along with our previous study on Cl and Br atom reactions of trichloroethene, using the known rate of the Cl+ethane reaction as reference, the values of $7.2 \pm 0.2 \times 10^{-11}$ and $3.8 \pm 0.2 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ were obtained for the Cl-atom reaction rate constants of tri- and tetrachloroethene, respectively. For the Br-atom reactions, using ethene and propane as the reference molecules, we report the absolute values of $1.1 \pm 0.1 \times 10^{-13}$ and $9.0 \pm 0.1 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ for the rates of Br attack on tri- and tetrachloroethene. The major products were XCl₂C-C(O)Cl (X=H in trichloroethene and X=Cl in tetrachloroethene) and XBrClC-C(O)Cl in Cl-atom and Br-atom initiated reactions, respectively. We also observed phosgene and formyl chloride in the reactions of trichloroethene and phosgene in the tetrachloroethene reactions and report the branching ratios for these channels. Our observations show that the addition of Cl-atoms to the less substituted carbon is the major reaction pathway and that a Cl-atom is subsequently released after either Cl- or Br-atoms add to trichloroethene or tetrachloroethene, leading to the recycling of active halogen. We carried out a box modeling exercise to apply the kinetic and mechanistic information obtained in this work to the interpretation of measurements of C₂HCl₃, C₂Cl₄ and other hydrocarbons in the Arctic troposphere. Our results demonstrate that the presence of both Cl- and Br-atoms is required to explain the decreases in the concentrations of these species during ozone depletion events in the Arctic, that the amount of Cl- and Br-atoms required to account for the observed decreases of chlorinated ethenes is also sufficient to completely destroy ozone. However, at the low concentrations of chlorinated species observed, the cycling of Br to Cl through the studied reactions is not a significant effect in the atmosphere.

1. Introduction

The phenomenon of boundary layer tropospheric ozone depletion has been observed at

several locations in the Arctic region (e.g., Barrie et al., 1988; Oltmans et al., 1989; Bottenheim et al., 1990; Barrie et al., 1994; Jobson et al., 1994; Ariya et al., 1997). During these ozone depletion events, the concentration of hydrocarbon species such as trichloroethene and tetrachloroethene, C₂-C₆ alkanes, alkyl nitrite, toluene and acetylene also showed clear decreases from their background levels (Jobson et al., 1994; Muthuramu et al., 1994; Yokouchi et al., 1994; Ariya et al., 1997). Analysis of the relative concentration changes of alkanes, benzene and toluene provided evidence for

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Cl-atom chemistry during the polar sunrise in the Arctic troposphere (Jobson et al., 1994; Ariya et al., 1997). The concentration changes in ethyne showed additional decreases beyond those attributed to Cl-atom reactions which were consistent with Br-atom chemistry. A strong positive correlation between ozone and tetrachloroethene and particularly trichloroethene was also observed after the polar sunrise, but the lack of information on Br-atom reactions of chlorinated ethenes prevented researchers from using these observations to provide further quantitative information on the importance of Br chemistry in the Arctic and in the destruction of ozone.

Chlorinated ethenes are formed through anthropogenic activities. These molecules are widely used as solvents, dry cleaning agents and degreasing agents (Wayne, 1991). These highly volatile molecules reach the atmosphere where they long-lived and may be transported to remote areas of globe, such as the Arctic region. During transport, the chlorinated ethenes are oxidized through various photochemical processes such as those initiated by HO radicals and in certain regions, as recently suggested, by Cl-atoms (Pszenny et al., 1993; Jobson et al., 1994; Ariya et al., 1997) and Br-atoms (Jobson et al., 1994; Ariya et al., 1997).

The previous studies of halogen reactions with chlorinated ethenes are confined to the Cl-atom reactions (Huybrechts and Meyers, 1966; Huybrechts et al., 1967; Bertrand et al., 1968; Mathias et al., 1974; Sanhueza et al., 1976; Atkinson and Aschmann, 1987; Kleindienst et al., 1989) and we are not aware of previous study of the Br-atom reactions of these species. The present work was undertaken to provide an internally consistent set of kinetic and mechanistic information on the Cl- and Br-atom reactions of tetrachloroethene along with our previous studies on trichloroethene (Catoire et al., 1996), required in the analysis of the field data obtained during the Polar Sunrise campaigns. This information allows measurements of the chlorinated ethenes to be used as indicators of the impact of halogen reactions in the troposphere and we used a box model to carry out this analysis for the Arctic springtime.

2. Experimental section

The details of experimental conditions and analysis procedures were explained elsewhere (Ariya,

1996). In short, experiments were performed in a Pyrex photochemical reactor/IR absorption cell with KBr windows, coupled to a Mattson FTIR spectrometer (Galaxy 4326C) with a KBr beam-splitter and a liquid N₂ cooled Hg/Cd/Te detector. A multipass cell (2 m long and typically 92 m pathlength) was used as the reaction vessel. This cell had 140 L volume and was surrounded by 26 fluorescent lamps (GTEF40/CW for $\lambda \geq 400$ nm or GEF40T12/BLB for $\lambda \geq 300$ nm). The IR spectra were collected over the frequency range 500–4000 cm⁻¹ at 1/8 cm⁻¹ resolution by co-adding 32 scans. Reactants and products were quantified by fitting IR reference spectra of the pure compounds to the observed product spectra using integrated absorption features. Reference spectra for most of the compounds encountered in this study were available from the extensive library of spectra compiled in the laboratory. In all cases, we estimate the potential systematic uncertainties associated with the calibrations of the reference spectra as well as subtractions to be about 5–10% each. This leads to an overall systematic uncertainty of 11% on average, calculated by the propagation of the mean error method (Cvetanovic et al., 1979).

Cl- and Br-atoms were produced by either UV ($\lambda \geq 300$ nm) or visible ($\lambda \geq 400$ nm) photolysis of Cl₂ and Br₂. Experiments were carried out to evaluate whether the photolysis of the reactants occur in the absence of the oxidants. Mixtures of both reactants and products were kept for extended periods in the dark to determine if any non-photolytic reactions might lead to the formation of products or the reformation of reactants. No positive evidence for such processes was observed in any of the systems studied. Typical reactant concentration varied from about 50 to 200 Pa. Irradiation time ranged typically from 5 s to 5 min. In the case of Br-atom reaction of tetrachloroethene, the irradiation time was increased to up to 25 minutes. Unless specified otherwise, all the uncertainties referring to least-squares analysis are two standard deviations (2 σ).

3. Results and discussion

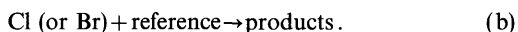
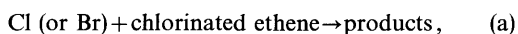
3.1. Kinetics

The relative rate technique was used to measure the Cl and Br-atom rate constants of trichloroe-

thene and tetrachloroethene. In this method, if two molecules, one of which used as reference, are solely removed by an oxidant such as Cl- or Br-atom, then the eq. (1) holds:

$$\ln([\text{molecule}]_{t_0}/[\text{molecule}]_t) = k_a/k_b \ln([\text{ref.}]_{t_0}/[\text{ref.}]_t), \quad (1)$$

where the subscripts t_0 and t indicate the concentration of trichloroethene and tetrachloroethene as well as that of the reference molecule initially and at a given time t and k 's are the rate constants for the two reactions;



The full description of these kinetic studies is explained elsewhere (Ariya, 1996; Catoire et al., 1996). In brief, ethane was used as the reference molecule in Cl reactions while ethene served as reference in the Br + C₂HCl₃ and propane in the Br + C₂Cl₄ systems. The slopes of plots suggested by eq. (1) represent the desired rate constant ratios which are obtained by a linear least-square analysis of the data. All plots had zero intercepts and correlation coefficients (r^2) were greater than 0.97. The results of these experiments are shown in Table 1, and, where possible, are compared to other values from the literature.

3.2. Mechanistic studies of Cl-atom + chlorinated ethenes

In the Cl-atom initiated oxidation of tetrachloroethene, we identified CCl₃C(O)Cl and CCl₂O with yields of 87 ± 11% and 27 ± 3%, respectively accounting for 101 ± 11% of the carbon in the system. In our previous mechanistic studies of Cl-atom initiated reaction of trichloroethene (Catoire et al., 1996), we identified CHCl₂C(O)Cl, CCl₂O and CHClO as products with the yields of 91 ± 11%, 9 ± 2% and 9 ± 2%, respectively. This accounts for 100 ± 11% of the trichloroethene loss. The yields of products were calculated using the linear regressions of plots of Δ (product) versus Δ (chloroethene). Fig. 1 shows an example of such plots. The quoted uncertainties on the product yields are overall which include the systematic errors.

As in the case of other unsaturated molecules such as ethene, the Cl-atom adds to the double bond of chlorinated ethenes leading to the formation of haloethyl radicals (Sanhueza et al., 1976; Yarwood, 1992) which will rapidly recombine with O₂. Like ethyl peroxy radicals (Niki et al., 1982), haloethyl peroxy radicals should, in the absence of NO_x, react with themselves or other peroxy radicals. The presence of chlorinated acetyl chlorides (XCl₂C—C(O)Cl; X = H in HClC=CCl₂ and X = Cl in Cl₂C=CCl₂ system) as the main products in the system is a clear indication that the predominant reaction pathway, includes the addi-

Table 1. Comparison of absolute rate constant for the Cl-atom reactions of trichloroethene and tetrachloroethene at $T = 296 \pm 2$ K

Reaction	Our ratios ^{a)}	This study (absolute)	Literature (absolute) ^{b)}
Cl + Trichloroethene ^{c)}	1.27 ± 0.04	7.2(±0.2) × 10 ^{-11d)}	7.7(±0.1) × 10 ^{-11e)}
Cl + Tetrachloroethene	0.66 ± 0.03	3.8(±0.2) × 10 ^{-11d)}	3.9(±0.2) × 10 ^{-11e)}
Br + Trichloroethene ^{c)}	0.88 ± 0.07	1.1(±0.1) ^{f)} × 10 ^{-13g)}	
Br + Tetrachloroethene ^{g)}	2.07 ± 0.04	9.0(±0.1) ^{f)} × 10 ⁻¹⁷	

^{a)} Quoted uncertainties are 2σ.

^{b)} Atkinson and Aschmann (1987). Units of absolute are constants (cm³ molecule⁻¹ s⁻¹).

^{c)} Our previous results (Catoire et al. 1996).

^{d)} Ethane as reference and the absolute value of 5.7 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ (DeMore et al. 1994) for its Cl-atom reactions was used.

^{e)} Ethene used as reference with an absolute value of 1.1 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (Atkinson and Aschmann, 1987) and 1.3 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ (Yarwood et al. 1992) for its Cl-atom and Br-atom reactions, respectively.

^{f)} Upper limit for uncertainties.

^{g)} Propane was used as the reference (Seakins et al. 1992).

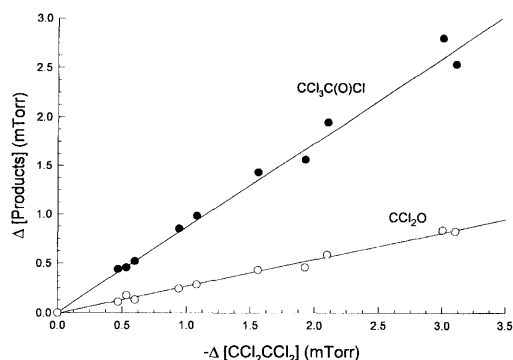
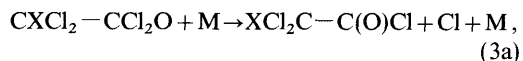
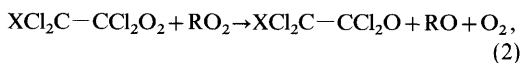
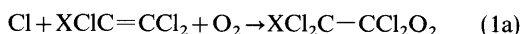
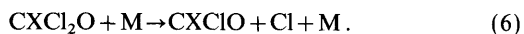
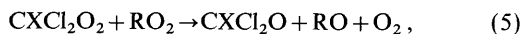
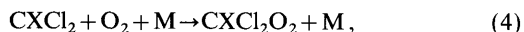


Fig. 1. Plot of observed yields of $\text{CCl}_3\text{C(O)Cl}$ (filled circles) and CCl_2O (open circles) versus the CCl_2CCl_2 loss after UV irradiation of $\text{Cl}_2\text{C}=\text{CCl}_2/\text{Cl}_2/\text{air}$.

tion of Cl atoms to the double bond in trichloroethene and tetrachloroethene proceeds via reaction (1a) followed by the reactions (2) and (3a):

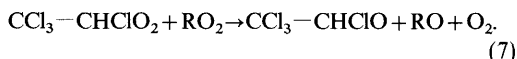


where RO_2 and RO represent any peroxy and alkoxy radicals present in the system, for example due to Cl-atom attack on the reference hydrocarbons. Thus, in reaction (3a), Cl-atoms are regenerated, leading to a chain reaction consuming the initial reactants. The breakage of the C—C bond is also a possibility (Atkinson and Carter, 1991) for the decomposition of ethoxy radicals produced in reaction (2), forming CCl_2O and CXCl_2 . The latter would rapidly associate with O_2 (Niki et al., 1980).

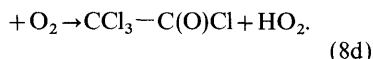
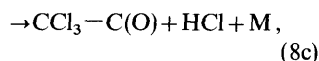
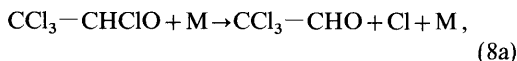


For trichloroethene, reaction (1b), i.e., addition

to the more substituted carbon, would lead to the formation of the $\text{CCl}_3-\text{CHClO}$ radical:



By analogy to the behaviour of other ethylperoxy radicals (Niki et al., 1982; Shi et al., 1993) this radical has four possible reactions:



No CCl_3CHO , HCl , or $\text{CCl}_3\text{C(O)Cl}$ were detected indicating that the collisional decompositions ((8a) and (8c)), and reaction with O_2 channels (8d) are negligible. It is to be noted that secondary reactions of Cl-atoms with CCl_3CHO and $\text{CCl}_3\text{C(O)Cl}$ are slow compared to the Cl-atom reaction of trichloroethene should thus be negligible in the range of conversion of trichloroethene used here. We observed CHClO in this system, but as explained in detail by Catoire et al. (1996) who studied the product distributions of channels (1a) and (1b) individually, the amount of formyl chloride from the reaction (1b) ought to be negligible. Therefore, reaction (1a) followed by reactions (3a) and (3b) account for the total degradation of trichloroethene. Hence, we report branching ratios of $91 \pm 11\%$ and $9 \pm 2\%$ for the channels (3a) and (3b) which correspond to the observed yields of $\text{HCl}_2\text{C}-\text{C(O)Cl}$, and CHClO and CCl_2O . In the case of tetrachloroethene, reactions (1a) and (1b) are equivalent and the branching ratios of $87 \pm 11\%$ and $13 \pm 2\%$ can be derived for channels (3a) and (3b).

We investigated the potential secondary reactions of the major products observed in the systems studied here. Neither $\text{CHCl}_2\text{C(O)Cl}$ nor $\text{CCl}_3\text{C(O)Cl}$ were photolysed by UV irradiations. In addition, we studied the kinetics of Cl-atom reactions of these molecules. In both cases, the reaction rates are relatively slow ($\leq 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ariya, 1996)), and their secondary

reactions are therefore not significant in these systems.

3.3. Br-atom mechanistic studies

In the course of experiments of Br-atom initiated reactions of C_2HCl_3 and C_2Cl_4 , we sometimes observed $Cl_2HCC(O)Cl$ and $Cl_3CC(O)Cl$. As discussed above these products can be formed as the result of Cl-atom initiated reactions. Therefore, these initial observations suggested that there is a source for Cl-atoms in Br-atom initiated reactions. To avoid potential complications due to Cl-atoms, we carried out 2 types of experiments in which Cl-atoms were scavenged. In one group of experiments excess Br_2 was added such that the ratio of $[Br_2]_0/[chlorinated\ ethene]_0$ was > 5 (Catoire et al., 1996). In this case, Br_2 acts as the scavenger for Cl-atoms through,



In a 2nd group of experiments, the scavengers were alkanes, specifically *n*-butane and ethane which react rapidly with Cl-atoms. Both kinetic and mechanistic results presented here are derived only from experiments in which no evidence for interfering Cl-atom reactions was observed, i.e., no $Cl_2HCC(O)Cl$ or $Cl_3CC(O)Cl$ was identified in the Br+trichloroethene and Br+tetrachloroethene experiments respectively.

We identified $BrClHCC(O)Cl$ ($93 \pm 11\%$), CCl_2O ($3 \pm 1\%$) and $CHClO$ ($2 \pm 1\%$) as the products of Br-atom initiated reaction of trichloroethene, accounting for $96 \pm 11\%$ of total carbons. $BrCl_2CC(O)Cl$ ($80 \pm 11\%$), CCl_2O ($22 \pm 4\%$) and CO_2 ($8 \pm 4\%$) were identified as the products of the reactions of Br+tetrachloroethene, accounting for $95 \pm 12\%$ of the carbon. Fig. 2 is an example of product yield plots for these reactions. The assignment of the IR spectra of $BrClHCC(O)Cl$ and $BrCl_2CC(O)Cl$ were based on similarities between the absorption of products and corresponding chlorinated acetyl chlorides, i.e., $HCl_2CC(O)Cl$ and $Cl_3CC(O)Cl$, respectively. Traces of CO was observed in both systems that were possibly due to the contamination of the cell, but no firm conclusion was drawn on the source

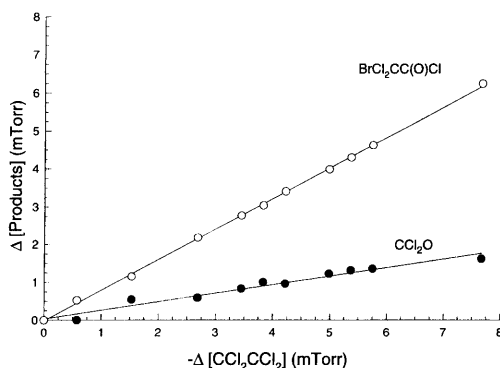
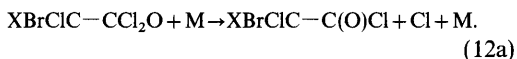
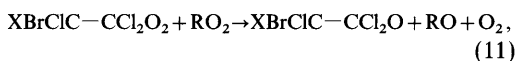
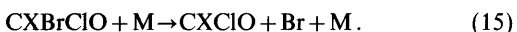
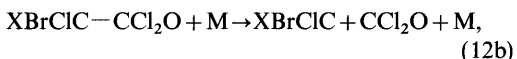


Fig. 2. Plot of observed yields of $BrCl_2CC(O)Cl$ (filled circles) and $COCl_2$ (open circles) versus the $Cl_2C=CCl_2$ loss after UV irradiation of $Cl_2C=CCl_2/Br_2/air$.

of CO. The observation of these products suggests the following mechanism:



The production of CCl_2O and $CHClO$ in Br+trichloroethene, and CCl_2O in Br+tetrachloroethene, can be explained by the following reactions:



Therefore, CCl_2O can be formed from C_2Cl_4 via reactions (12b) and (15). In the C_2HCl_3 system, reaction (15) leads to the formation of observed $CHClO$. Under our experimental conditions, $BrClHCC(O)Cl$ and $BrCl_2CC(O)Cl$ were stable in the cell and did not undergo photolysis under irradiation by the visible lights. Their reactions with Br-atoms are expected to be slower than the analogous reactions with Cl-atoms, which were found to be negligible (see Sub-

section 3.2). Therefore, no significant secondary reactions of the products is expected to occur in the system.

3.4. Generalized mechanism of for Cl and Br-atom additions

Fig. 3 shows the generalized mechanism of Cl/Br-initiated reaction of tri- and tetrachloroethenes. Our observed products suggest that the Cl- and Br-atoms predominantly add to the less chlorine-substituted carbon of the double bonds. This is consistent with the fact that steric effects may govern the halogen addition processes (Sanhueza et al., 1976) with addition of Cl- and Br-atoms to the less hindered carbon atom being the major reaction pathway. In addition, the likelihood of carbon-carbon cleavage increases, as a chlorinated ethene becomes more substituted by halogens.

4. Modeling of an ozone depletion event

We used the box model "MoccaIce" (Model Of Chemistry Considering Aerosols in Cold Environments) to investigate the chemistry of C_2HCl_3 and C_2Cl_4 during the Arctic tropospheric ozone depletion events. Previously used for the marine air at mid-latitudes (Sander and Crutzen, 1996; Vogt et al., 1996), MoccaIce has now been modified to model the polar sunrise in the Arctic, as described by (Sander et al., 1997). We summar-

ize the most important aspects of the model including the recent addition of hydrocarbon and halocarbon chemistry.

MoccaIce contains 145 reactions in the gas phase and 102 in aerosol particles. The number of chemical species is 82 in the gas phase and 68 in the aqueous phase. Since the Arctic air mass is very stagnant during ozone depletion periods, the boundary layer can be treated as a "smog chamber" reactor (Jobson et al., 1994; Ariya et al., 1996). Aside from the standard tropospheric chemistry of ozone, methane and nitrogen species, the reaction mechanism includes a large set of reactions of halogen compounds that are of potential importance for the ozone budget. Photolysis rates vary according to the solar declination during polar sunrise. The hydrocarbon chemistry includes C_1 – C_5 alkanes, ethene, ethyne, benzene, as well as the halocarbons CH_3Br , $CHBr_3$, C_2HCl_3 and C_2Cl_4 . Secondary reactions of the intermediates have been simplified in the model by combining different alkyl groups into a generic R (e.g., RO, RO_2). The reactions of C_2HCl_3 and C_2Cl_4 with HO, Cl and Br, are parameterized in the model considering only the initial attack and the generation of Cl-atoms.

The model runs start at Julian day (JD) 90 (JD 1 = January 1) with initial concentrations set to typical values for the Arctic spring (Jobson et al., 1994; Yokouchi et al., 1994). For C_2HCl_3 and C_2Cl_4 the initial mixing ratios are 4 pptv and 8 pptv, respectively. During the period of JD 94–97, fluxes of Cl_2 and Br_2 into the system were switched on. Their rates are adjusted in order to destroy ozone within 3 days and to match the observed decay of hydrocarbons. Choosing a different time interval for the ozone depletion period does not change the hydrocarbon decay provided that the integral of halogen atom concentration over time remains constant. The daytime concentrations of HO, Cl and Br are approximately 10^5 cm^{-3} , 10^4 cm^{-3} and 10^7 cm^{-3} , respectively. Once ozone is completely depleted, the concentration of Br atoms increases further to about 10^9 cm^{-3} , since the equilibrium between Br and BrO is now shifted to the former. The modeled mixing ratios of O_3 , C_2HCl_3 and C_2Cl_4 are shown in Fig. 4 (solid line). More results of this base run are shown in Sander et al. (1997). Here, we only focus on the chemistry of C_2HCl_3 and C_2Cl_4 .

Also shown in Fig. 4 are the results from a

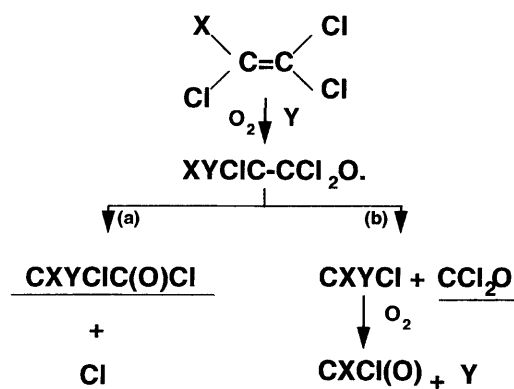


Fig. 3. The generalized proposed mechanisms for Cl- and Br-atom initiated reactions of tri- and tetrachloroethenes; X = H in trichloroethene and X = Cl in tetrachloroethene; and Y = Cl or Br in Cl-atom initiated and Br-atom initiated reactions, respectively.

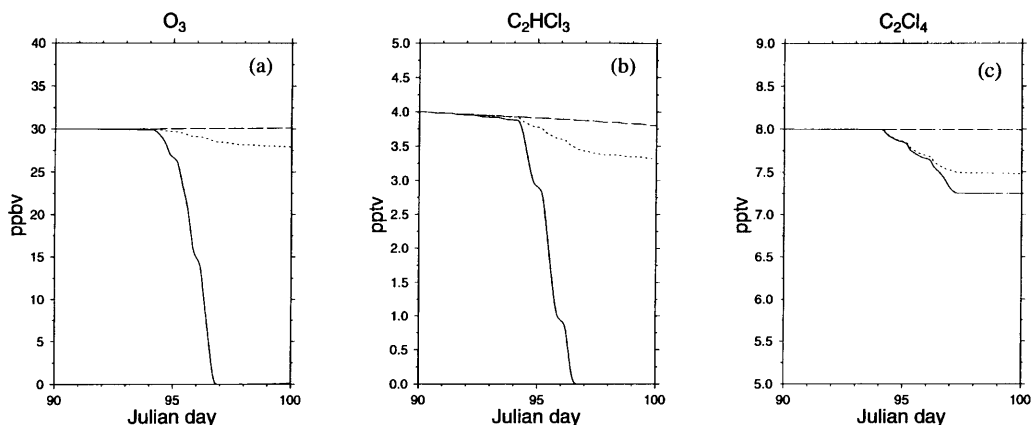


Fig. 4. Modeled gas-phase mixing ratios of (a) O_3 , (b) C_2HCl_3 and (c) C_2Cl_4 ; HO, Cl and Br chemistry are all switched on (solid line), HO and Cl are switched on (dotted), and HO only conditions (dashed).

sensitivity study in which only Cl_2 but no Br_2 is emitted into the air (dotted line). It can be seen that in the absence of bromine neither O_3 nor the chlorinated ethenes decay very significantly. Note that there is a difference for C_2Cl_4 between the runs with and without bromine although C_2Cl_4 reacts only slowly with Br. Two factors contribute to this effect. First, through synergetic reactions the presence of bromine increases the concentration of chlorine (Le Bras and Platt, 1995; Abbatt, 1994). Aqueous-phase HOBr reacts with chloride in the model producing BrCl. After volatilization, BrCl is photolyzed to Br and Cl in the gas phase. Thus without bromine, there is also less chlorine to attack C_2Cl_4 . Secondly, after complete depletion of ozone, which occurs only in the presence of bromine in the model, the concentration of Br rises high enough to influence C_2Cl_4 concentrations directly.

Another sensitivity study (dashed line in Fig. 4) did not include any emissions of either Cl_2 and Br_2 . The decreases in the concentrations of C_2HCl_3 and C_2Cl_4 in this run are small and are solely due to reactions with HO. This is consistent with the assumption that HO radicals do not play a significant rôle in the hydrocarbon chemistry during ozone depletion. Finally, we tested if the generation of Cl-atoms from the reactions of chlorinated ethenes with HO, Cl and Br plays a rôle in the chlorine budget. Since the concentrations of C_2HCl_3 and C_2Cl_4 are very small, we found no

difference in the model results if we assume that these reactions do not produce Cl-atoms.

5. Atmospheric implications

It is reasonable to expect that the major features of the generalized mechanism in Fig. 3 will also apply to the reaction of HO radicals with the chlorinated ethenes (Kleindienst et al., 1989), thus the major products of the atmospheric oxidation of these molecules will be variously substituted acetyl chlorides. In the course of this study, it became apparent that these molecules do not readily photolyse under UV and visible irradiations at comparable wavelengths to those available in the troposphere. Furthermore, the reactions of Cl- and Br-atom with substituted acetyl chlorides are too slow to be significant (Ariya, 1996) which leads to a reasonable assumption that HO radical reactions with trichloroethene and tetrachloroethene are also not fast enough to be significant in the removal of these species in the troposphere. On the other hand, by analogy to fluorinated acetyl chloride, the reaction of these acetyl chlorides with water is theoretically possible and this can lead to the formation of carboxylic acids (WMO, 1995). Therefore, as the result of photochemical reactions of chlorinated ethenes in the troposphere, acetyl chlorides will

be formed which may then react with water in the troposphere to produce carboxylic acids.

The results of our experiments and box modeling suggest that the decreases in the concentrations of trichloroethene and tetrachloroethene observed during the ozone depletion events in the Arctic are due to the action of Cl and Br chemistry. In particular, Br-atom chemistry can account the additional decreases in the concentrations of trichloroethene and ethyne, beyond that expected from Cl-atom chemistry. The Cl-atom and Br-atom concentrations required to account for the observed decreases in the concentrations of trichloroethene and tetrachloroethene, are also sufficient to effectively destroy ozone in the springtime Arctic troposphere. Although the source of the halogen atoms to the Arctic boundary layer is not known and may be specific to conditions in the polar regions, our model calculations, based on

observations in the Arctic, indicate that the concentrations of Br-atoms is several orders of magnitude higher than that of Cl-atoms. We suggest that more emphasis should be placed on the further research concerning the potential importance of Br-atoms elsewhere in the troposphere and in particular in the marine boundary layer at other latitudes.

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