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Halogens and the Chemistry of the Free Troposphere

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Abstract. The role of halogens in both the marine boundary layer and the stratosphere has long been recognized, while their role in the free troposphere is often not considered in global chemical models. However, a careful examination of free-tropospheric chemistry constrained by observations using a full chemical data assimilation system shows that halogens do play a significant role in the free troposphere. In particular, the chlorine initiation of methane oxidation in the free troposphere can contribute more than 10%, and in some regions up to 50%, of the total rate of initiation. The initiation of methane oxidation by chlorine is particularly important below the polar vortex and in northern mid-latitudes. Likewise, the hydrolysis of $BrONO_2$ alone can contribute more than 35% of the HNO_3 production rate in the free-troposphere.

1 Introduction

Halogens play a variety of roles in atmospheric chemistry. Most notable is their involvement in catalytic ozone loss and the formation of the stratospheric ozone hole (Johnston and Podolske, 1978; Cicerone et al., 1983; Farman et al., 1985). Like OH, they are also involved in the initiation and catalysis of hydrocarbon oxidation and consequently also play a role in the partitioning of OH and HO_2. Similarly they are involved with the partitioning of NO and NO_2. Some of the same reactions involved in ozone hole chemistry also lead to the production of nitric acid, namely the hydrolysis of $BrONO_2$ and $ClONO_2$ on sulphate aerosols. These roles are well known and accepted when stratospheric chemistry is being discussed (DeMore et al., 2000). The role of halogens is also important in the marine boundary layer (Vogt et al., 1996; Sander and Crutzen, 1996; Richter et al., 1998; Dickerson et al., 1999; Sander et al., 2003; von Glasow and Crutzen, 2004). However, when the chemistry of the free troposphere is considered the role of halogens is not normally considered important.

A chemical data assimilation analysis using a full Kalman filter (Fisher and Lary, 1995; Lary et al., 2003a, 1995; Lary, 1996; Lary et al., 2003b; Lary, 2003) (`http://pdfcentral.shriver.umbc.edu/AutoChem/`) starting in October 1991 reveals that halogens are also playing a significant role in the chemistry of the free troposphere. Comprehensive results from the analysis are available online at `http://pdfcentral.shriver.umbc.edu/CDACentral/`. In this study sulphate aerosol observations from SAGE II (Ackerman et al., 1989; Oberbeck et al., 1989; Russell and McCormick, 1989; Thomason, 1991, 1992; Bauman et al., 2003) and HALOE (Hervig et al., 1993, 1996; Hervig and Deshler, 1998; Massie et al., 2003) were used, ozone observations from UARS (Reber et al., 1993) MLS v6 (Froidevaux et al., 1996; Waters, 1998), HALOE v19 (Russell et al., 1993), POAM, ozone sondes and LIDAR, nitric acid observations from UARS MLS v6 (Santee et al., 1997, 1999), CLAES, ATMOS, CRISTA (Offermann and Conway, 1999) and ILAS (Wood et al., 2002), hydrochloric acid observations from UARS HALOE and ATMOS, water observations from UARS HALOE v19, ATMOS and MOZAIC (Marenco et al., 1998), methane observations from UARS HALOE v19, ATMOS and CRISTA were used. All though the bulk of these observations were in the stratosphere a significant number of satellite observations were available for the free troposphere down to 5 km, and from sondes and aircraft data is also available below 5 km (e.g. Figure 1).

The analyses grid used in this study is cast in equivalent PV latitude, potential temperature coordinates. With 32 latitudes between 80°S and 80°N, and 24 logarithmically spaced isentropic surfaces between the earth's surface and 2400 K. As the potential temperature at the surface changes with time we use a fixed number of isentropic levels be-

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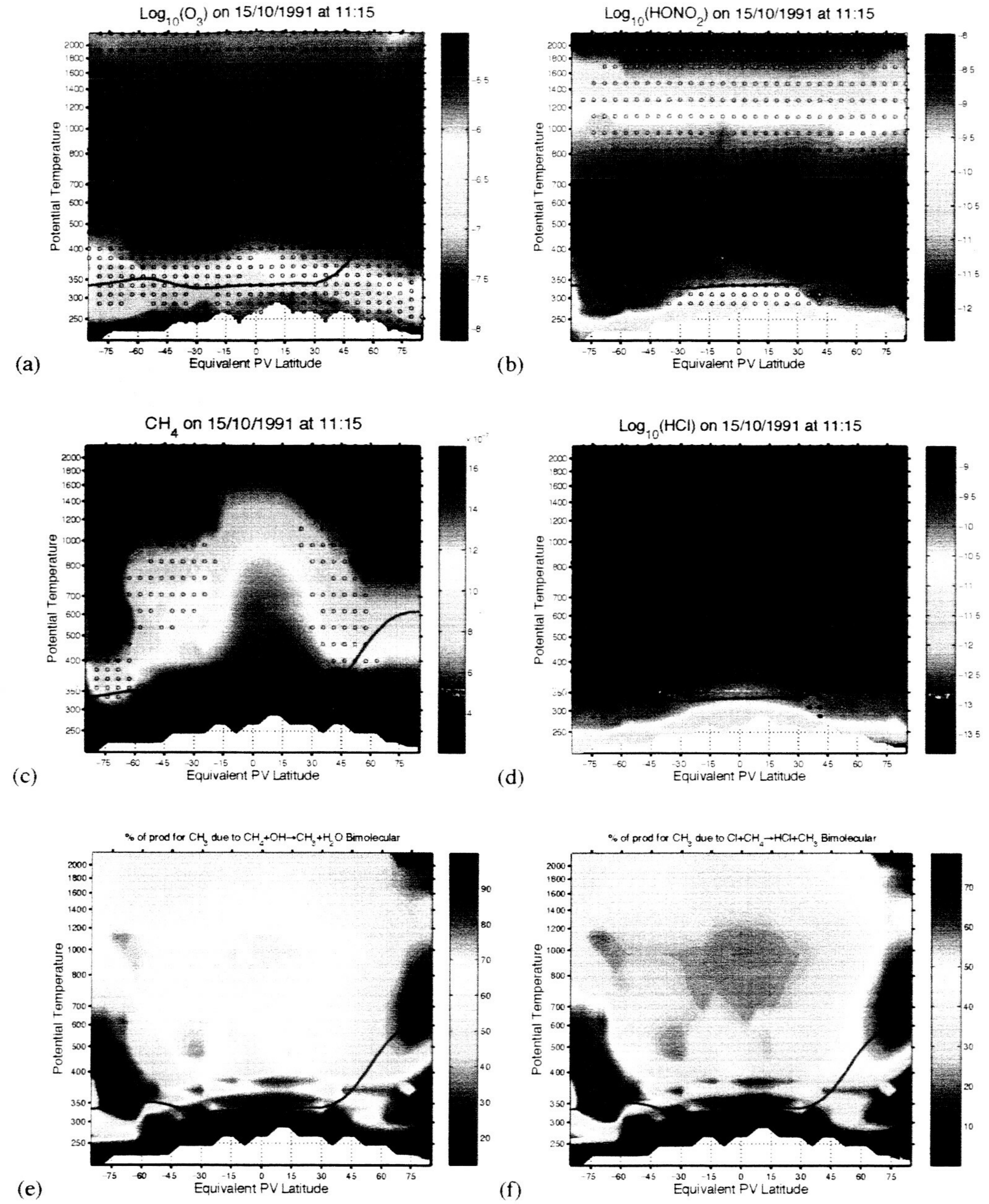
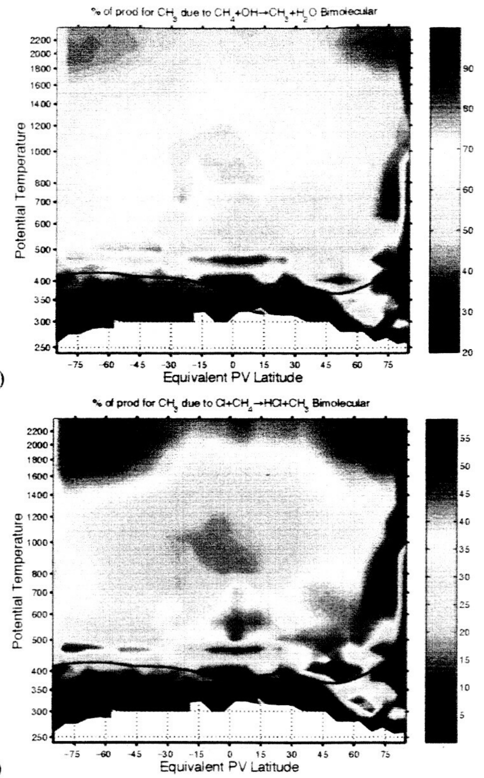


Fig. 1. Panels (a) to (d) show the global ozone, nitric acid, methane and hydrochloric acid analyses from the surface up to the lower mesosphere produced by chemical data assimilation for mid-October 1991. The analyses are presented as equivalent PV latitude - potential temperature cross sections. The background colors show the $\log_{10}$ of the volume mixing ratio and the overlaid color filled circles show the observations used. The thick red line overlaid on the plots is the thermal tropopause diagnosed from the UKMO analyses. The white space at the bottom of the plots is because the analysis is terrain following and the surface potential temperature changes with time and location. It can be seen that although the bulk of the observations are in the stratosphere many observations are also available below the tropopause. Based on the analyses produced by chemical data assimilation system panel (e) shows the percentage of the initiation of methane oxidation due to OH. At first glance it confirms the conventional position that in the free-troposphere the initiation by OH is all that needs to be considered. However, on closer examination it can be seen that there are extensive regions within the troposphere where the initiation of methane oxidation due to Cl (Panel (f)) contributes more than 10% and some regions where it contributes up to 50%. The regions of significant initiation by Cl are, as would be expected, in the region below the polar vortex, and more surprisingly in northern mid latitudes. The northern mid-latitude feature persists. For example, it can be seen that the mid-latitude role of chlorine initiation is greater in February 1993 (Figure 2 panel (b)).



(a)

(b)

Fig. 2. This is the analogue to Figure 1 panels (e) and (f) for mid-February 1993. It can be seen that the northern mid-latitude role of chlorine initiation is slightly greater than for December 1991.

tween the surface potential temperature for a given day and equivalent latitude band and 500 K, above 500 K the levels remain fixed with time. The isentropic levels correspond approximately to the UARS surfaces spaced at 6 per decade in pressure (c.f. the UARS reference atmosphere levels `http://code916.gsfc.nasa.gov/Public/Analysis/UARS/urap/home.html`).

The following sections examine some of the roles halogens play in tropospheric chemistry.

2 Initiation of Hydrocarbon Oxidation

Methane and hydrocarbon oxidation are some of the most significant atmospheric chemical processes. The hydroxyl radical (OH) is an important cleansing agent of the lower atmosphere, in particular, it provides the dominant sink for CH_4 and HFCs as well as the pollutants NO_x, CO and VOCs. Once formed, tropospheric OH reacts with CH_4 or CO within a second. It is generally accepted that the local abundance of OH is controlled by the local abundances of NO_x, CO, VOCs, CH_4, O_3, and H_2O as well as the intensity of solar UV; and thus it varies greatly with time of day, season, and geographic location (Houghton and Ding, 2001).

Methane oxidation is usually initiated by hydrogen abstraction reactions such as

$$OH + CH_4 \longrightarrow CH_3 + H_2O \quad (1)$$

$$O(^1D) + CH_4 \longrightarrow CH_3 + OH \quad (2)$$

$$Cl + CH_4 \longrightarrow CH_3 + HCl \quad (3)$$

$$Br + CH_4 \longrightarrow CH_3 + HBr \quad (4)$$

The rate at which hydrogen is abstracted from CH_4 by OH and Cl is a strong function of temperature, altitude, and the total reactive chlorine loading ($ClO_y = 2Cl_2 + Cl + ClO + 2Cl_2O_2 + HCl + HOCl + ClONO_2$).

Initiation of methane oxidation by Cl is a strong function of ClO_y. Burnett and Burnett (1995) have inferred from their OH column measurements that chlorine is likely to be involved in the initiation and oxidation of methane. In agreement with this, Figures 1 and 2 show that significant initiation of methane oxidation is due to Cl.

However, the halogen initiation and catalysis of hydrocarbons is not usually considered in global chemistry models. This is not due to a lack of kinetic knowledge but rather an assumption that halogens play a minor role outside of the boundary layer (Vogt et al., 1996; Sander and Crutzen, 1996; Richter et al., 1998; Dickerson et al., 1999; Sander et al., 2003; von Glasow and Crutzen, 2004) and stratosphere (Johnston and Podolske, 1978; Cicerone et al., 1983; Farman et al., 1985). Figures 1 and 2 show that in the lower stratosphere and even in the free troposphere, halogen-catalyzed, and halogen-initiated, methane oxidation can be important. Halogen-catalyzed methane oxidation can play a significant role in the production of HO_x (= H + OH + HO_2) radicals in just the region where it is usually accepted that nitrogen-catalyzed methane oxidation is one of the main sources of ozone (Houghton and Ding, 2001). Aspects of methane oxidation by halogens has been previously mentioned by Crutzen et al. (1992); Burnett and Burnett (1995) and the mechanism specifically described by Lary and Toumi (1997).

Figure 1 panels (a) to (d) show the global ozone, nitric acid, methane and hydrochloric acid analyses from the surface up to the lower mesosphere produced by chemical data assimilation for mid-October 1991. The analyses are presented as equivalent PV latitude - potential temperature cross sections. The background colors show the $\log_{10}$ of the volume mixing ratio and the overlaid color filled circles show the observations used. The thick red line overlaid on the plots is the thermal tropopause diagnosed from the UKMO analyses. The white space at the bottom of the plots is because the analysis is terrain following and the surface potential temperature changes with time and location. It can be seen that although the bulk of the observations are in the stratosphere many observations are also available below the tropopause. Based on the analyses produced by chemical data assimilation system Figure 1 panel (e) shows the percentage of the initiation of methane oxidation due to OH. At first glance it confirms the conventional position that in the

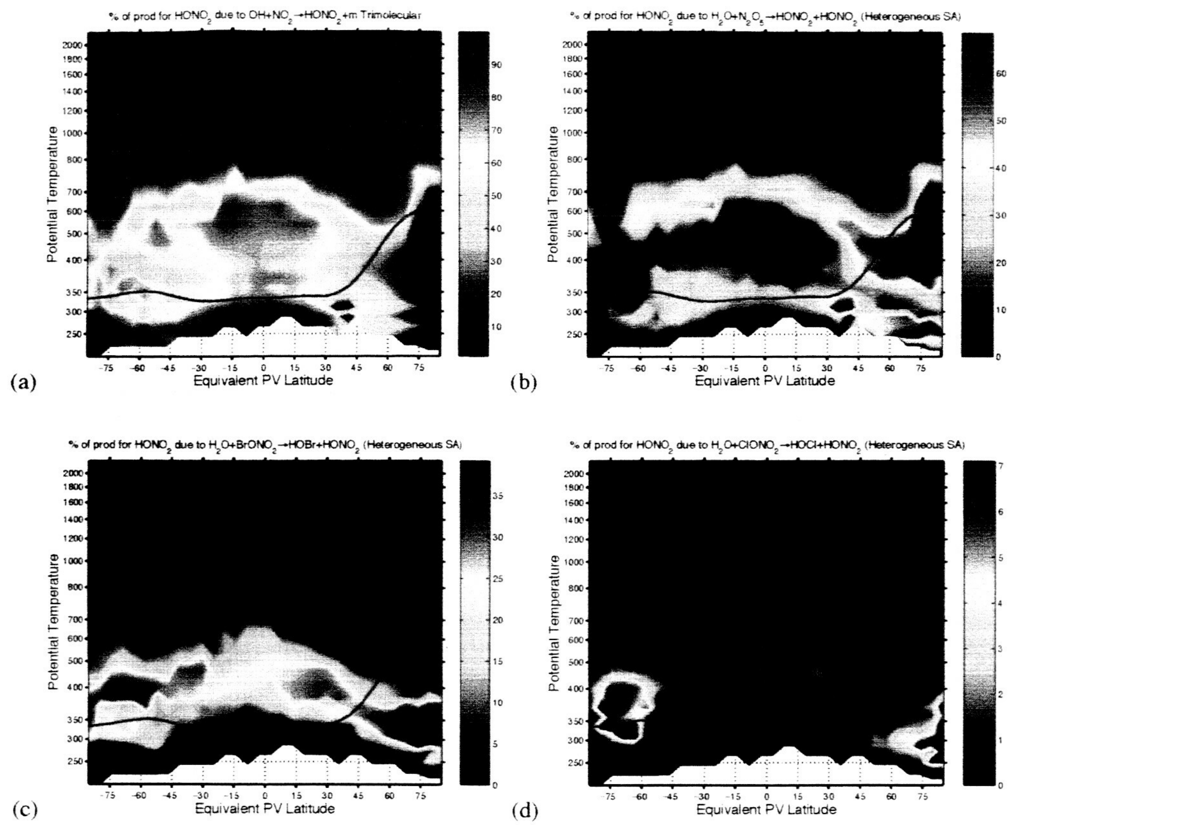


Fig. 3. The contribution of four of the main HNO_3 production channels. It is well known that two of the key nitric acid production channels in the troposphere are the bimolecular reaction of OH with NO_2 (panel (a)) and the heterogeneous hydrolysis of N_2O_5 on sulphate aerosols (panel (b)). In the stratosphere the heterogeneous hydrolysis of $ClONO_2$ (panel (c)) and $BrONO_2$ (panel (d)) is also routinely considered. It can be seen that they are also significant sources of HNO_3 in the free troposphere.

free-troposphere the initiation by OH is all that needs to be considered. However, on closer examination it can be seen that there are extensive regions within the troposphere where the initiation of methane oxidation due to Cl (Figure 1 panel (f)) contributes more than 10% and some regions where it contributes up to 50%. The regions of significant initiation by Cl are, as would be expected, in the region below the polar vortex, and more surprisingly in northern mid latitudes. The northern mid-latitude feature persists. For example, it can be seen that the mid-latitude role of chlorine initiation is greater in February 1993 (Figure 2 panel (b)).

3 Production of Nitric Acid

It is well known (DeMore et al., 2000) that two of the key nitric acid production channels are the bimolecular reaction of OH with NO_2 and the heterogeneous hydrolysis of N_2O_5 on sulphate aerosols (please see Figure 3 (a) and (b)). In the stratosphere the heterogeneous hydrolysis of $ClONO_2$ and $BrONO_2$ are also routinely considered (DeMore et al., 2000). However, as halogens are often normally not considered in models of the free troposphere these channels are not normally considered in the troposphere. Figure 3 (c) shows that the hydrolysis of $BrONO_2$ alone can contribute more than 35% to the HNO_3 production rate. Therefore excluding halogen chemistry from global chemical models can lead to a significant error in these regions, yet another reason for considering halogen chemistry in the free troposphere.

4 Partitioning of OH and HO_2

HOBr is readily photolyzed in the visible and yields OH. Figure 4 (a) shows that HOBr photolysis can contribute close to 10% of the total OH production rate at high latitudes in the free-troposphere. Likewise Figure 4 (b) shows that the production of HOBr by the bimolecular reaction of BrO with HO_2 contributes more than 5% to the total HO_2 loss rate at high latitudes in the free-troposphere.

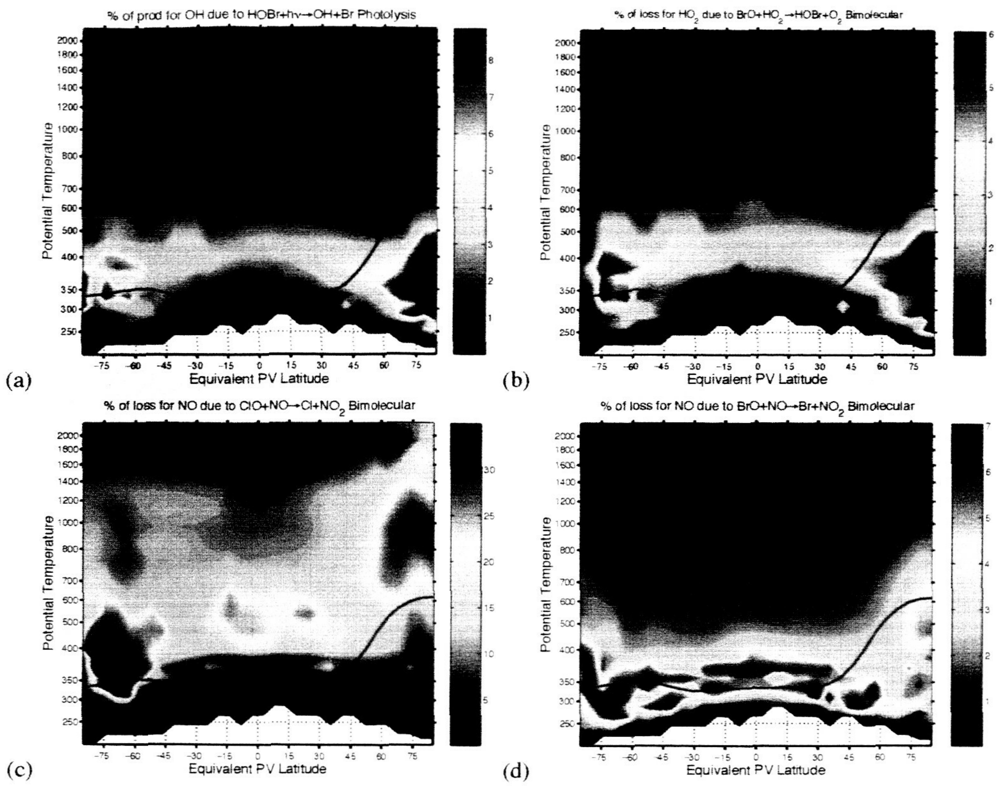


Fig. 4. HOBr is readily photolyzed in the visible and yields OH. Panel (a) shows that HOBr photolysis can contribute close to 10% of the total OH production rate at high latitudes in the free-troposphere. Likewise panel (b) shows that the production of HOBr by the bimolecular reaction of BrO with HO_2 contributes more than 5% to the total HO_2 loss rate at high latitudes in the free-troposphere. The tropospheric partitioning of NO and NO_2 is affected by halogen interactions. Panel (c) shows that there are large regions in northern mid-latitudes and below the southern polar vortex where more than 10% of the loss of NO is due to reaction with ClO. Panel (d) shows that for much of the free-troposphere the reaction of NO with BrO contributes more than 5% to the loss of NO.

5 Partitioning of NO and NO_2

The tropospheric partitioning of NO and NO_2 is affected by halogen interactions. Figure 4 panel (c) shows that there are large regions in northern mid-latitudes and below the southern polar vortex where more than 10% of the loss of NO is due to reaction with ClO. Figure 4 Panel (d) shows that for much of the free-troposphere the reaction of NO with BrO contributes more than 5% to the loss of NO.

6 Conclusions

A careful constraint of a photochemical modelling system using chemical data assimilation and a variety of atmospheric observations has been conducted. A detailed analysis of the results shows that halogens are playing a role in the chemistry of the free troposphere. In particular, methane oxidation is initiated by Cl as well as OH in the troposphere. The Cl initiation of methane oxidation can contribute more than 10% to the total rate of initiation below the polar vortex and in mid-latitudes. In addition, the hydrolysis of $BrONO_2$ alone can contribute more than 35% of the HNO_3 production rate in the free troposphere. The partitioning of NO and NO_2 in the free troposphere is also significantly affected by halogen reactions.

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