Halogen Atom Concentrations in the Arctic Troposphere Derived from Hydrocarbon Measurements: Impact on the Budget of Formaldehyde

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Abstract. As part of the Polar Sunrise Experiment in 1998 measurements of hydrocarbons were made at the Canadian Arctic station Alert. Halogen atom concentrations play a key role in determining formaldehyde mixing ratios. Formaldehyde mixing ratios observed during ozone depletion episodes agree with those calculated from time integrated halogen atom concentrations. Formaldehyde is the most important loss mechanism for active bromine and at the same time an important source for HO_x radicals. Via these reactions formaldehyde will indirectly influence chlorine chemistry and thus feedback mechanisms involving halogen atom concentrations and formaldehyde are likely to play a major role in the development of tropospheric ozone depletion episodes during polar sunrise.

Introduction

There are strong indications that ozone loss in the Arctic troposphere during spring is primarily due to Br-atom catalyzed reaction cycles (Barrie et al., 1988; Hausmann and Platt, 1994; Jobson et al., 1994; Sanders et al., 1997; Ariya et al., 1997, 1998, and 1999; Ramacher et al, 1997, and 1998). Very recently Sumner and Shepson (1999) reported measurements of formaldehyde during the Polar Sunrise Experiment 1998 (PSE 98). They conclude that photolysis of formaldehyde very likely is the most important primary source for odd oxygen radicals (HO_2, OH, RO_2) under the conditions of tropospheric polar sunrise. The reaction of HO_2 with BrO forms HOBr, which, based on our current understanding, is the source for heterogeneous formation of reactive halogens. Based on ambient measurements and budget considerations Sumner and Shepson (1999) inferred substantial production of formaldehyde in the snow pack. However, formaldehyde is also formed via the reaction of Cl-atoms with methane. In this paper we will use halogen atom concentrations derived from hydrocarbon measurements to study the impact of halogen chemistry on formaldehyde mixing ratios during polar tropospheric ozone depletion episodes.

Experiment

About 180 whole air samples were collected at the Canadian Forces station Alert, Nunavut, Canada (82.5° N,

62.3° W) between February 18 and May 13, 1998 in electropolished stainless steel canisters. The samples were pressurized with a metal bellows pump to a pressure of roughly 2000 hPa above ambient. The samples were analyzed at York University by gas chromatography for a broad range of volatile organic compounds.

The 3 σ detection limits for NMHC are in the range of 1-3 ppt, reproducibility is 5-10% for mixing ratios exceeding the detection limit by a factor of ten or more. The accuracy of the calibration is estimated to be better than 10%. Tests of the metal bellows pump and the stainless steel inlet line both with zero air and ambient air showed no change in hydrocarbon concentrations exceeding the reproducibility of the measurements.

Ozone was measured by a TECO Model 49 UV photometric ozone analyzer. It was calibrated before and during the study by means of a DASIBI model 1008 transfer standard which, in turn, had been calibrated directly against the NIST standard (National Institute of Standards and Technology, Gaithersburgh, Maryland, USA). To determine the zero of the instrument, zero air was supplied every second day for a period of 45 minutes at midnight. For 1 min averages detection limit is about 0.5 ppb and accuracy is estimated to be 2% or 0.5 ppb, whichever is greater.

Determination of Time Integrated Br- and Cl-Atom Concentrations

Changes in measured concentrations of NMHC during polar sunrise have been used to derive time integrated Cl- and Br- atom concentrations (Jobson et al., 1994; Solberg et al., 1996; Ariya et al., 1997, 1998, and 1999; Ramacher et al, 1997, and 1998). In order to minimize uncertainties due to hydrocarbon reactions with OH-radicals and mixing of air masses, we use hydrocarbons with very similar reaction rate constants for OH-radicals, but very different rate constants for their reaction with Cl- and Br- atoms. The set of compounds we use is given in Table 1 together with the relevant rate constants.

Calculated time integrated Cl- and Br- atom concentrations are shown in Figure 1 as a function of ozone mixing ratio. The statistical uncertainty of these results is about 10^{12} atoms s cm^{-3} and 10^9 atoms s cm^{-3} for the time integrated Br- and Cl-atom concentrations, respectively. The uncertainties of the reaction rate constants contribute a systematic error in the range of 15%-40%. Cl-atom concentrations show a linear relationship with the ozone mixing ratios, whereas the Br-

Table 1. Rate constants for reaction of selected hydrocarbons with OH-radicals, Cl- and Br- atoms (values are in 10^{-13} $cm^3 s^{-1}$ molecules^{-1} and for 250 K unless otherwise indicated).

Compounds	k_{OH}	$k_{Cl\bullet}$	$k_{Br\bullet}$
Propane	7.56 (a)	$1.41*10^3$ (b)	$4.3*10^{-4}$ [†](c)
Acetylene	5.33 (c)	$7.35*10^2$ (c)	1.54 [†](d)
Benzene	9.1 (d)	0.09 [†](e)	<0.1 [†](c)

(a) Atkinson et al., 1992; (b) DeMore et al, 1997; (c) Bierbach et al., 1996; (d), Barnes et al., 1993; (d) Atkinson, 1986; (e) Ariya, 1996. † rate constant for 298 K

ozone dependence can best be described by an exponential function. Similar observations were made by Ramacher et al. (1999), although at low ozone mixing ratios our observations show a steeper gradient for the Br-ozone relation.

Halogen Atom Chemistry and Formaldehyde Concentrations

Based on the time integrated Cl-atom concentration, an average methane mixing ratio of 1.8 ppm and the rate constant for the reaction of methane with Cl-atoms (Atkinson et
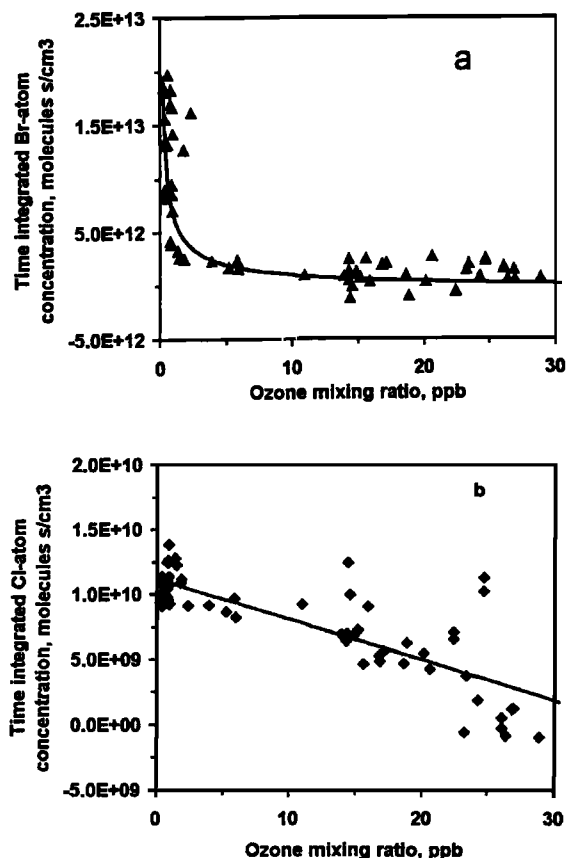

Figure 1. Time integrated Br-atom concentration (a) and Cl-atom concentration (b) as function of ozone mixing ratio. The solid curves are least square fits to the data, an exponential function has been used for 1a, and a linear fit for 1b.

al., 1992) we calculate a time integrated formaldehyde production of $3-4*10^{10}$ molecules cm^{-3} for periods of complete ozone depletion. The actual time for ozone depletion episodes to proceed to completion is not well established, but several estimates suggest that a duration of 2-3 days is reasonable (e.g. Sanders et al., 1997). From this we deduce an average formaldehyde formation rate of around $1-1.3*10^5$ molecules cm^{-3} s^{-1}. This is about 25%-50% higher than the postulated snow pack emissions derived by Sumner and Shepson (1999).

The rate constant for the reaction of formaldehyde with Br-atoms is relatively fast ($1.7*10^{-11}$ exp(-800/T), Atkinson et al., 1992). This reaction consequently can significantly reduce both the Br-atom and the formaldehyde concentrations. Indeed, the observed dependence between ozone and formaldehyde mixing ratios (Figure 2) derived from the time series of formaldehyde measured by Sumner and Shepson (1999) and ozone measurements during PSE98 shows that formaldehyde mixing ratios decrease for low ozone concentrations when the time integrated Br-atom concentrations are very high.

Development of Formaldehyde Concentration During Ozone Depletion Episodes

We can use the time integrated halogen atom concentrations to test whether gas phase chemistry can explain the observed dependence between ozone and formaldehyde concentrations (Figure 2). Our observations do not necessarily give a correct picture of the temporal development of the studied air masses and therefore we have to make certain assumptions about the time dependence of the ozone and halogen atom concentrations. We use three different relative ozone depletion rates, 7% h^{-1}, 5% h^{-1} and 3.5% h^{-1}, corresponding to a duration of 2, 3 and 4 days, respectively, for an ozone depletion to proceed to completion. Furthermore we assume that the observed dependence between time integrated halogen atom concentrations and ozone mixing ratio describes the actual development of the halogen concentrations during ozone depletion events. The resulting Cl- and Br- atom concentrations are in the range of $10^3 - 10^5$ atoms cm^{-3} and $10^6 - 10^8$ atoms cm^{-3}, respectively. To reduce random variability and to de-
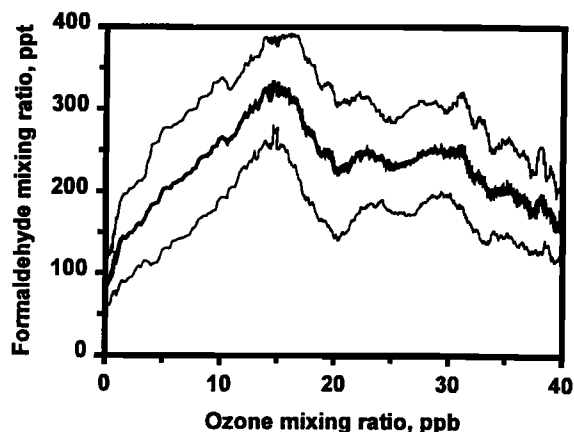

Figure 2. Formaldehyde mixing ratio as function of ozone mixing ratio derived from the formaldehyde measurements of Sumner and Shepson (1999) made during PSE 98. The thick solid line represents the 20-point running average, and the thin lines denote the ± 1 σ ranges.

scribe average conditions, we use the fitted curves (see Figure 1) to determine the dependence between ozone mixing ratios and time integrated halogen atom concentrations. Initial formaldehyde concentration is 160 ppt (the average of the mixing ratios outside ozone depletion episodes observed by Sumner and Shepson, 1999); OH- radical concentration is $4*10^5$ molecules cm^{-3}, compatible with the model calculations by Sander et al. (1997). For clear sky conditions and an average solar zenith angle of 85° the formaldehyde loss rate due to photolysis is $1.3*10^{-5}$ s^{-1}. The reaction rate constants for methane and formaldehyde with OH-radicals and halogen atoms were taken from Atkinson et al. (1989, 1992) and the calculations were made for a temperature of 250 K. The resulting dependence between formaldehyde and ozone concentration is shown in Figure 3.

Discussion and conclusions

The halogen atom levels we derived from hydrocarbon measurements have a substantial impact on the temporal development of formaldehyde concentrations during ozone depletion episodes. Specifically, the different halogen-ozone dependencies for Br- and Cl-atoms explain the formaldehyde concentration maximum observed for ozone mixing ratios of about 15 ppb. Within the uncertainties calculations and observations are in agreement. During PSE 98 both observed and calculated formaldehyde levels were always well below the steady state between formation via reaction of Cl-atoms with methane and its loss due to reaction with Cl-atoms. Consequently the presence of Cl-atoms always results in an increase of formaldehyde concentrations. The depletion episodes can be divided into two phases. For periods of moderate ozone loss (i.e. ozone above roughly 20 ppb), formaldehyde levels are increasing as a consequence of formaldehyde formation from methane oxidation by Cl-atoms. For ozone levels below about 10 ppb, the formaldehyde concentrations decrease substantially; in this regime the removal of formaldehyde by Br-atoms exceeds the formaldehyde formation due to methane oxidation. This explains the observations of Sumner and Shepson (1999) that formaldehyde mixing ratios increase for periods of partial ozone depletion, but decrease for periods with very low ozone levels. Formaldehyde levels calculated for ozone concentrations of less than 15 ppb are essentially independent of the initial formaldehyde concentration. The temporal dependence of both Cl- and Br-atom concentrations are essential in determining the development of formaldehyde concentration. Below about 10 ppb there seems to be very strong feedback between formaldehyde and Br-atom concentrations and ozone mixing ratios. The low formaldehyde concentrations favors the build-up of high Br-atom levels, which are the driving force behind efficient ozone depletions. Considering the dual role of formaldehyde as scavenger for Br-atoms and source of HO$_x$ radicals the Cl-atoms most likely have, via the formation of formaldehyde, a major impact on the development of ozone depletion episode during polar sunrise.

The origin of the high formaldehyde levels outside ozone depletion episodes remains uncertain. There is no independent estimate of the magnitude of the postulated formaldehyde formation in the snowpack. Present emission rates are based on the assumption that they balance atmospheric removal (Sumner and Shepson, 1999). It can also be speculated that the snowpack acts as a reservoir. If formaldehyde in the snow
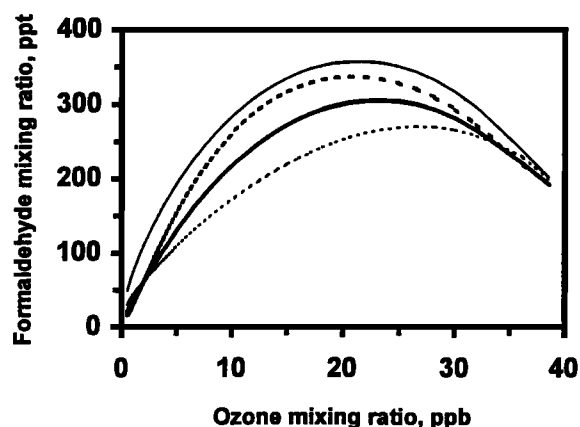

Figure 3. Formaldehyde mixing ratios calculated as function of ozone mixing ratios (for details see text). Thick broken line: relative ozone loss rates of 7% h^{-1}, thick solid line: 5% h^{-1}, and thin broken line: 3.5% h^{-1}. Thin solid line: same as thick solid line except for the inclusion of a formaldehyde source of $5.7*10^4$ molecules cm^{-3} s^{-1}.

phase is in equilibrium with the gas phase, formaldehyde could accumulate in the snow during partial ozone depletion episodes when chlorine chemistry causes high formaldehyde mixing ratios. This formaldehyde then could be released during periods of low formaldehyde concentrations.

Cl-atom concentrations of a few 10^4 atoms/cm^3 would be sufficient to maintain formaldehyde levels of 100-200 ppt. Such relatively low Cl-atom levels have to persist for at least a day or two before the time integrated Cl-atom concentration would have an obvious impact on NMHC mixing ratios. Our results indicate that at moderate time integrated Cl-atom levels the Br-atom concentrations are very small and consequently ozone depletion under these conditions may be marginal. This may result in a systematic underestimate of time integrated Cl-atom levels since these are based on the assumption that there is no impact of halogen chemistry during periods of normal ozone levels, that is above roughly 35 ppb. The presently available information does not allow conclusions about the existence or absence of Cl-atom concentrations in the range of 10^4 atoms/cm^3 at normal ozone levels during polar sunrise nor are there presently established methods or techniques that might be readily applied to answer this question.

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