

Halogen-catalyzed methane oxidation

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Abstract. This paper highlights the importance of halogen-catalyzed methane oxidation in the upper troposphere and lower stratosphere. The calculated rate of methane oxidation is increased by at least 20% in the upper troposphere when halogen catalysis is included. In the lower stratosphere, approximately 25% of methane oxidation can be initiated by chlorine; the precise fraction is very temperature dependent. Including halogen-catalyzed methane oxidation increases the HO_x and ClO_x concentrations and decreases the NO_x concentration. The calculated enhancement in the HO_x concentration due to halogen-catalyzed methane oxidation is around 10–15% in the lower stratosphere; and around 20% in the upper troposphere. The decrease in the NO_x concentration is around 10% in the upper troposphere. The enhancement in the ClO_x concentration is around 7–10% in the lower stratosphere. The increase in the calculated HO_x and ClO_x concentrations and the decrease in the NO_x concentration lead to an enhancement in the calculated O₃ loss. The additional O₃ loss calculated is most significant in the upper troposphere where over a 7-day simulation it was of the order of 0.1–1% for midlatitudes at equinox. As the atmospheric loading of chlorine drops the gross odd-oxygen production by NO + HO₂ will increase, so there will be an accelerated ozone recovery. On a per molecule basis, bromine-catalyzed methane oxidation is approximately 2 orders of magnitude faster than chlorine catalyzed methane oxidation. In the upper troposphere bromine-catalyzed methane oxidation destroys ozone at a rate which is approximately one third of that at which nitrogen-catalyzed methane oxidation is producing ozone. Therefore, with the increasing atmospheric bromine loading, bromine-catalyzed methane oxidation is set to become more important. It would be valuable to have kinetic studies of the reaction BrO with CH₃O₂ so that the role of bromine-catalyzed methane oxidation can be quantified more precisely.

Introduction

Methane oxidation is one of the most important atmospheric chemical processes. This paper shows that in the lower stratosphere and upper upper troposphere, halogen-catalyzed, and halogen-initiated, methane oxidation can be important at all latitudes.

Halogen-catalyzed methane oxidation can play a significant role in the production of HO_x (= H + OH + HO₂) radicals in just the region where it is usually accepted that nitrogen-catalyzed methane oxidation is one of the main sources of ozone, namely, the tropical lower stratosphere and upper upper troposphere [e.g., Law and Pyle 1993a b]. Since HO_x radicals play such an important part in atmospheric chemistry, this paper considers in detail halogen-catalyzed methane oxidation.

The numerical model used in this study was AUTOCHEM, a model described by Lary *et al.* [1995, 1996], Lary [1996], and Fisher and Lary [1995]. The model contains a description of 60 species and a total of 342 reactions.

Initiation of Methane Oxidation

Figure 1 schematically shows the reactions involved in methane oxidation. The whole process is usually initiated by hydrogen abstraction reactions such as



The rate at which hydrogen is abstracted from CH₄ by OH and Cl is a strong function of temperature, al-

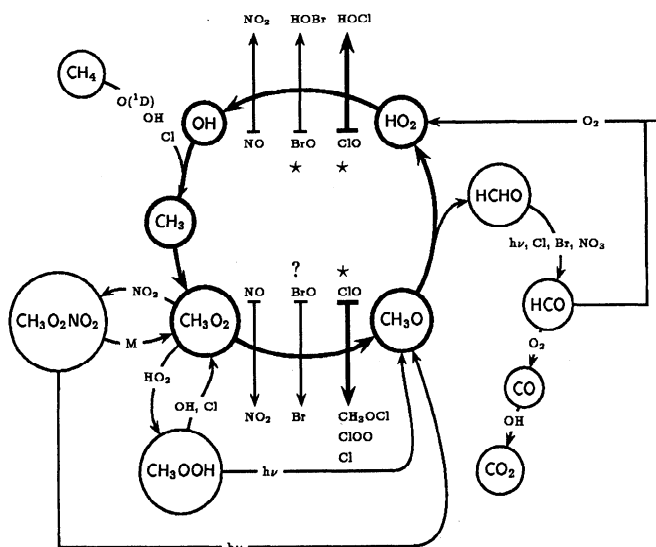


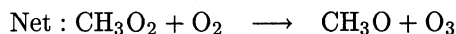
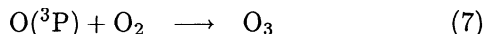
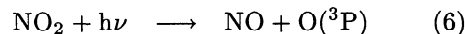
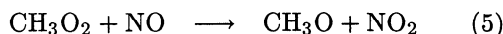
Figure 1. A schematic representation of methane oxidation. The thick arrows represent the key reactions of interest in this study. The question mark refers to a reaction whose kinetics need to be determined.

titude, and the total reactive chlorine loading ($\text{ClO}_y = 2\text{Cl}_2 + \text{Cl} + \text{ClO} + 2\text{Cl}_2\text{O}_2 + \text{HCl} + \text{HOCl} + \text{ClONO}_2$) and is not very sensitive to the aerosol loading. Although Br does react with CH_4 , it does so only very slowly. The extensive literature review of *Baulch et al.* [1981] quotes a rate constant which is very slow at stratospheric temperatures.

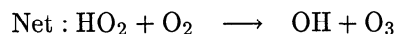
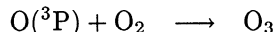
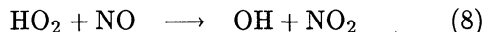
As can be seen in Figure 2, the reaction of CH_4 with OH is generally the main pathway for the initiation of methane oxidation in the troposphere and lower stratosphere. However, as the ClO_y concentration increases with altitude the reaction of CH_4 with Cl increases in importance, particularly in the upper troposphere and very low stratosphere. Initiation of methane oxidation by Cl is a very 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, Figure 2 shows that at 20 km over the equator approximately 40% of the initiation of methane oxidation is due to Cl. This increases up to 70% in the region close to the polar night boundary where chlorine activation has taken place, thus enhancing the amount of Cl atoms present. This obviously also produces HCl, which is a key factor in the deactivation of chlorine.

Halogen-catalyzed Methane Oxidation

When methane oxidation is discussed, it is usually with NO as the catalyst. However, ClO and BrO can also act as effective catalysts for methane oxidation (Figure 1). In addition, there is an important difference between the catalytic oxidation of methane by halogens and by nitrogen. When methane oxidation is catalyzed by NO, the conversion of CH_3O_2 to CH_3O results in the production of ozone due to:

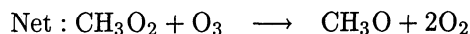


Once CH_3O has been formed it reacts with O_2 to form HO_2 and HCHO. The HO_2 can then be catalytically converted by NO into OH producing a further molecule of O_3 .

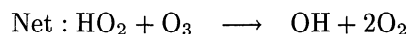
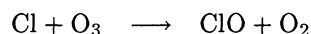
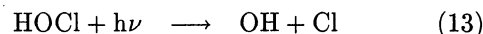
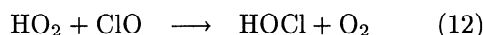


Therefore, for each completion of the nitrogen-catalyzed methane oxidation cycle, O_3 is produced.

In contrast, when methane oxidation is catalyzed by a halogen species such as ClO or BrO, the conversion of CH_3O_2 to CH_3O results in the destruction of ozone due to



If the products of the reaction of CH_3O_2 with ClO are CH_3OCl or ClOO instead of Cl the net effect of the cycle is the same, as CH_3OCl can be readily photolyzed to yield Cl [*Crowley et al.*, 1994; see also *DeMore, et al.*, 1994], and ClOO also quickly falls apart to yield Cl. Once HO_2 is formed, it can also be catalytically converted by ClO into OH destroying a further molecule of O_3 .



The rate limiting step of methane oxidation by nitrogen or halogens is the conversion of CH_3O_2 to CH_3O .

It should be noted that the rate limiting step is quite distinct from the initiation step, that is the reaction of CH_4 with radicals such as OH, $\text{O}(^1\text{D})$, and Cl, to give CH_3 which initiates the whole process of CH_4 oxidation. As CH_4 oxidation is catalytic, by definition the initiation step is slower than the rate of propagation, if it were not, the cycle would not be catalytic, and methane oxidation would not be such an important atmospheric process. This is because the definition of chain length, the number of times the cycle is executed before it is terminated, is simply the rate of propagation (namely, the slowest step, the rate of conversion of CH_3O_2 to CH_3O), divided by the rate of initiation (that is, the rate of reaction of CH_4 with OH, $\text{O}(^1\text{D})$, and Cl).

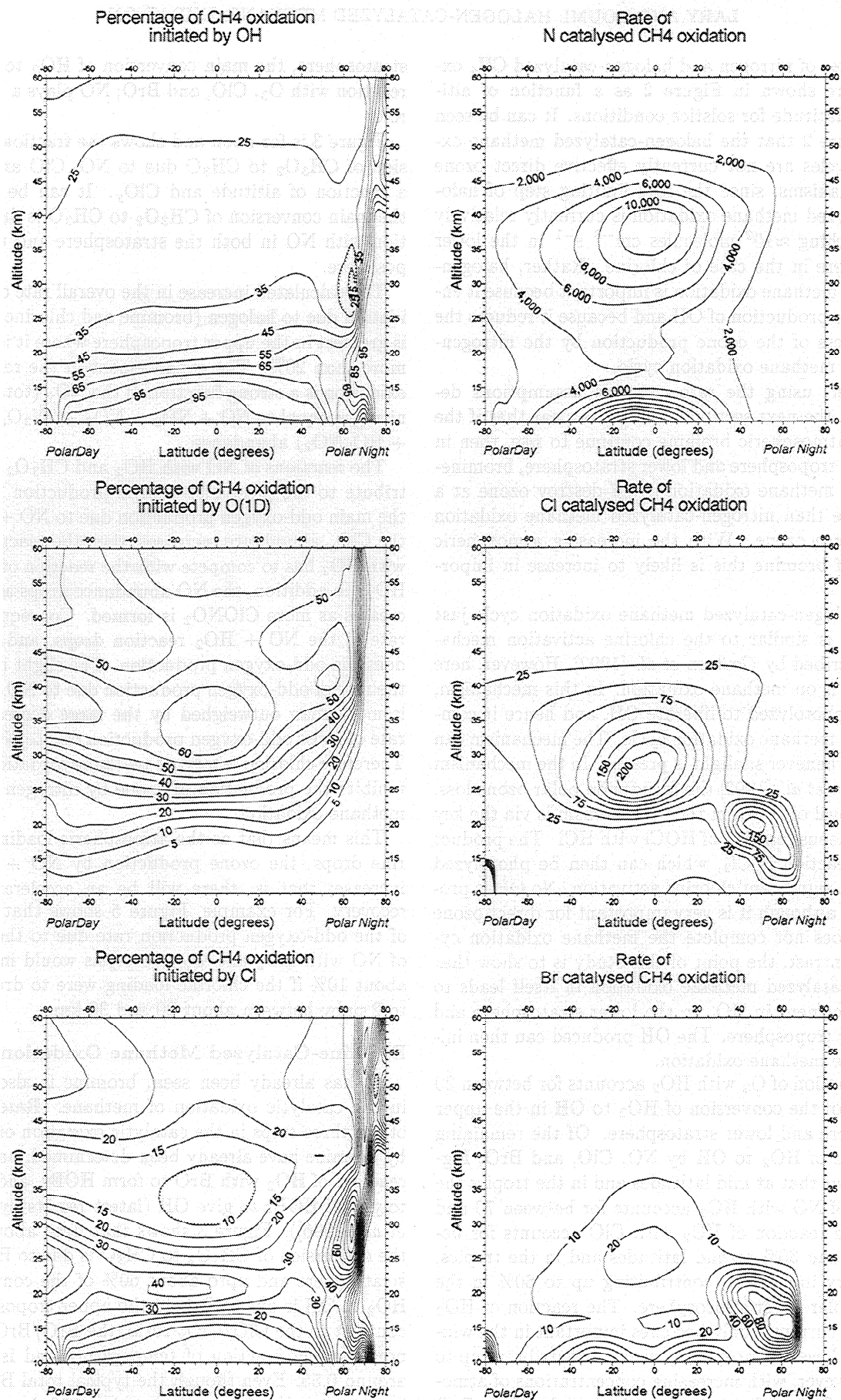


Figure 2. The percentage of initiation of CH₄ oxidation by OH, O(¹D), and Cl respectively, at noon on the left-hand side as a function of the altitude and latitude at the winter solstice and on the right-hand side as the rate of methane oxidation catalyzed by nitrogen, chlorine, and bromine in units of molecules cm⁻³ s⁻¹.

The rates of nitrogen and halogen-catalyzed CH_4 oxidation are shown in Figure 2 as a function of altitude and latitude for solstice conditions. It can be seen from Figure 2 that the halogen-catalyzed methane oxidation cycles are not currently effective direct ozone loss mechanisms, since the rate limiting step of halogen catalyzed methane oxidation is currently relatively slow, reaching $\approx 10^2$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ in the lower stratosphere in the case of chlorine. Rather, halogen-catalyzed methane oxidation is important because it enhances the production of OH and because it reduces the effectiveness of the ozone production by the nitrogen-catalyzed methane oxidation cycle.

However, using the rate constant assumptions described in the next section, it becomes clear that if the levels of atmospheric bromine continue to rise, then in the upper troposphere and lower stratosphere, bromine-catalyzed methane oxidation could destroy ozone at a faster rate than nitrogen-catalyzed methane oxidation can produce ozone. With the increasing atmospheric loading of bromine this is likely to increase in importance.

The halogen-catalyzed methane oxidation cycle just described is similar to the chlorine activation mechanism described by *Crutzen et al.* [1992]. However, here the focus is on methane oxidation. In this mechanism, HOCl is photolyzed to liberate OH, and hence it completes the methane oxidation cycle. The mechanism can proceed whenever sunlight is present. In the mechanism of *Crutzen et al.* [1992] the focus is on polar ozone loss. The removal of HOCl in their mechanism is via the key heterogeneous reaction of HOCl with HCl. The product of that reaction is Cl_2 , which can then be photolyzed leading to significant chlorine activation. No OH is produced, so although it is very important for direct ozone loss, it does not complete the methane oxidation cycle. In contrast, the point of this study is to show that halogen-catalyzed methane oxidation in itself leads to an enhancement in HO_x in the lower stratosphere and the upper troposphere. The OH produced can then initiate more methane oxidation.

The reaction of O_3 with HO_2 accounts for between 20 and 45% of the conversion of HO_2 to OH in the upper troposphere and lower stratosphere. Of the remaining conversion of HO_2 to OH by NO, ClO, and BrO, Figure 3 shows that at mid latitudes and in the tropics the reaction of NO with HO_2 accounts for between 70 and 95%. The reaction of HO_2 with ClO accounts for between 10 and 30% at mid latitudes and in the tropics, but is very important, contributing up to 60% in the winter, polar lower stratosphere. The reaction of HO_2 with BrO currently only becomes important in the winter, polar lower stratosphere, where it contributes up to 45%. However, with increasing concentrations of atmospheric BrO_y (total reactive bromine equal to $\text{Br} + \text{BrO} + 2\text{Br}_2 + \text{HBr} + \text{HOBr} + \text{BrCl} + \text{BrONO}_2$) it is likely to become important at midlatitudes and in the tropics also (Figure 4). Therefore, in the winter, polar lower

stratosphere, the main conversion of HO_2 to OH is by reaction with O_3 , ClO, and BrO; NO plays a very small role.

Figure 3 is for noon and shows the fractional conversion of CH_3O_2 to CH_3O due to NO, ClO and BrO as a function of altitude and ClO_y . It can be seen that the main conversion of CH_3O_2 to CH_3O is due to reaction with NO in both the stratosphere and upper troposphere.

The calculated increase in the overall rate of CH_4 oxidation due to halogen (bromine and chlorine) catalysis is greatest in the upper troposphere where it is typically more than 20%. The enhancement in the rate of CH_4 oxidation is a strong function of the NO_y (total reactive nitrogen equal to $\text{NO} + \text{NO}_2 + \text{NO}_3 + 2\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{HO}_2\text{NO}_2$) abundance.

The reactions of NO with HO_2 and CH_3O_2 both contribute to the gross odd-oxygen production rate, with the main odd-oxygen production due to $\text{NO} + \text{HO}_2$. As the ClO_y abundance increases, then the reaction of NO with HO_2 has to compete with the reaction of ClO with HO_2 . In addition, the NO abundance drops as ClO_y increases as more ClONO_2 is formed. Consequently, the rate of the $\text{NO} + \text{HO}_2$ reaction drops, and hence, so does the odd-oxygen production. The slight increase in the rate of odd-oxygen production due to $\text{NO} + \text{CH}_3\text{O}_2$ is more than outweighed by the large decrease in the rate of gross odd-oxygen production due to $\text{NO} + \text{HO}_2$. Therefore chlorine catalyzed methane oxidation slightly inhibits the production of ozone by nitrogen catalyzed methane oxidation.

This means that as the atmospheric loading of chlorine drops, the ozone production by $\text{NO} + \text{HO}_2$ will increase; that is, there will be an accelerated ozone recovery. For example, Figure 5 shows that the ratio of the odd-oxygen production rate due to the reaction of NO with HO_2 and O_2 photolysis would increase by about 10% if the chlorine loading were to drop from 3 to 2 ppbv between about 20 and 30 km.

Bromine-Catalyzed Methane Oxidation

As has already been seen, bromine is also involved in the catalytic oxidation of methane. Rates for two of the three steps in the catalytic oxidation of methane by bromine have already been determined, namely, the reaction of HO_2 with BrO to form HOBr, and the photolysis of HOBr to give OH (latest results by *Rattigan et al.* [1996]). Figure 3 shows that upto about 30% of the conversion of CH_3O_2 to CH_3O is due to BrO in the stratosphere and upto about 60% of the conversion of HO_2 to OH is due to BrO in the upper troposphere. In contrast to the ClO/ClO_y ratio, the BrO/BrO_y ratio is not a strong function of temperature and is typically around 0.55. Even though the typical total BrO_y loading is currently a factor of more than 150 times less than the typical total ClO_y , BrO and ClO convert similar amounts of HO_2 into OH in the polar and midlatitude lower stratosphere.

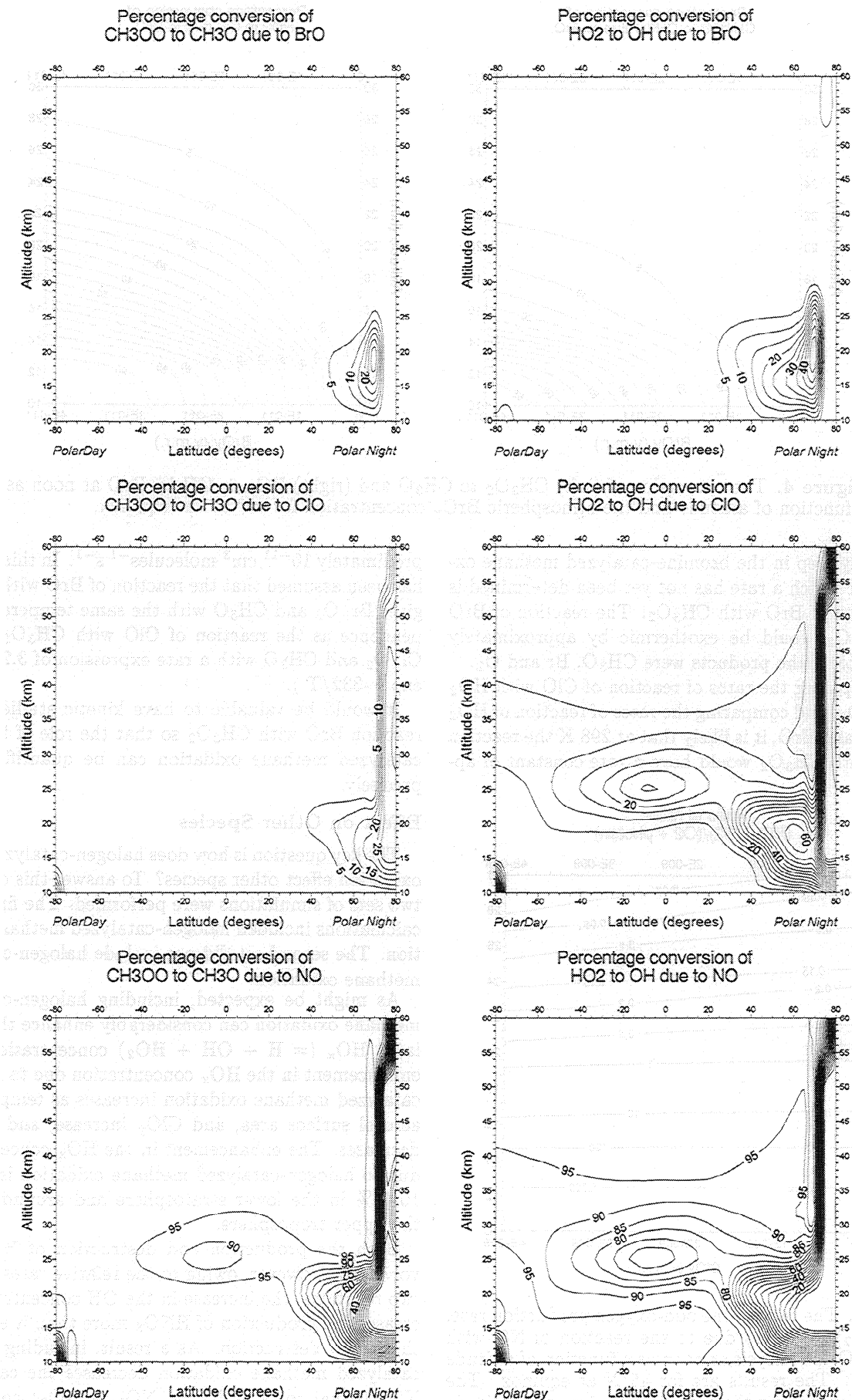


Figure 3. The conversion of (left) CH_3O_2 to CH_3O and (right) HO_2 to OH by BrO , ClO , and NO at noon as a function of altitude and latitude at the solstice.

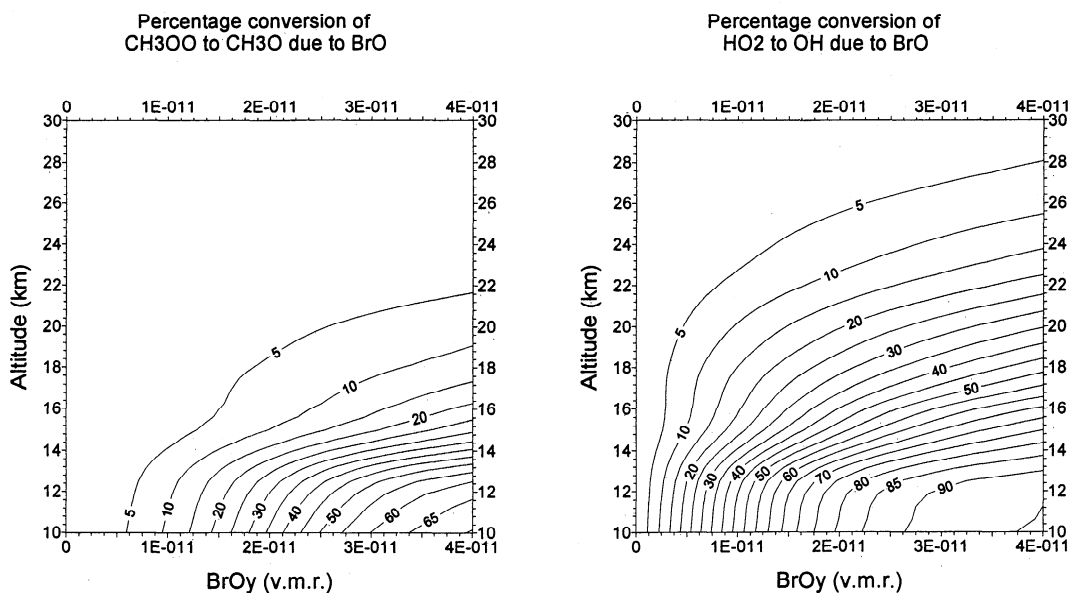


Figure 4. The conversion of (left) CH₃O₂ to CH₃O and (right) HO₂ to OH by BrO at noon as a function of altitude and the atmospheric BrO_y concentration for 45° at the equinox.

The only step in the bromine-catalyzed methane oxidation for which a rate has not yet been determined is the reaction of BrO with CH₃O₂. The reaction of BrO with CH₃O₂ would be exothermic by approximately -14 kJ/mole if the products were CH₃O, Br and O₂.

By comparing the rates of reaction of ClO with HO₂ and CH₃O₂, and comparing the rates of reaction of HO₂ with ClO and BrO, it is likely that at 298 K the reaction of BrO with CH₃O₂ would have a rate constant of ap-

proximately 10⁻¹¹ cm³ molecules⁻¹ s⁻¹. In this study it has been assumed that the reaction of BrO with CH₃O₂ gives Br, O₂ and CH₃O with the same temperature dependence as the reaction of ClO with CH₃O₂ to give Cl, O₂ and CH₃O with a rate expression of 3.23 × 10⁻¹¹ exp (-332/T).

It would be valuable to have kinetic studies of the reaction BrO with CH₃O₂ so that the role of bromine-catalyzed methane oxidation can be quantified more precisely.

Effect on Other Species

The key question is how does halogen-catalyzed methane oxidation effect other species? To answer this question, two sets of simulations were performed. The first set of calculations included halogen-catalyzed methane oxidation. The second set did not include halogen-catalyzed methane oxidation.

As might be expected, including halogen-catalyzed methane oxidation can considerably enhance the calculated HO_x (= H + OH + HO₂) concentration. The enhancement in the HO_x concentration due to halogen-catalyzed methane oxidation increases as temperature, aerosol surface area, and ClO_y increase, and as NO_y decreases. The enhancement in the HO_x concentration due to halogen-catalyzed methane oxidation is around 10-15% in the lower stratosphere and around 20% in the upper troposphere.

Both the production and destruction of HNO₃ involve OH. However, owing to the relative rates of these two reactions, the increase in the OH concentration increases the production of HNO₃ more than it enhances the HNO₃ destruction. As a result, including halogen catalyzed methane oxidation decreases the calculated NO_x (equal to N + NO + NO₂ + NO₃) concentration. The percentage decrease is greatest for low levels

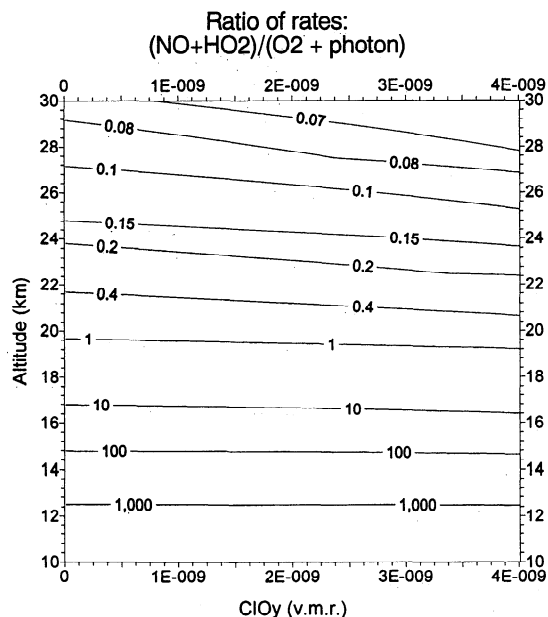


Figure 5. The ratio of the odd-oxygen production rate, (NO+HO₂)/(O₂+hν) due to the reaction of NO with HO₂ and O₂ photolysis at noon as a function of altitude and ClO_y. The results are for 45°N at equinox. The solid line overlaying the plots is a typical mid-latitude ClO_y vertical profile.

of NO_y . The decrease in the NO_x concentration due to halogen-catalyzed methane oxidation is around 1-5% in the lower stratosphere. The decrease in the NO_x concentration due to halogen catalyzed methane oxidation is around 10% in the upper troposphere for typical tropospheric ClO_y concentrations.

The main gas phase loss of HCl is its reaction with OH. Therefore the enhancement in the HO_x concentration due to including halogen catalyzed methane oxidation increases the calculated stratospheric ClO_x (equal to $\text{Cl} + \text{ClO} + 2\text{Cl}_2\text{O}_2$) concentration. The enhancement in the ClO_x concentration due to halogen-catalyzed methane oxidation increases with temperature and aerosol surface area, and the enhancement in the ClO_x concentration is greatest for low NO_y and ClO_y concentrations. The enhancement in the ClO_x concentration due to halogen-catalyzed methane oxidation is around 7-10% in the lower stratosphere. In the upper troposphere, halogen-catalyzed methane oxidation can lead to a decrease in the ClO_x concentration.

The increase in the calculated HO_x and ClO_x concentrations and the decrease in the NO_x concentration lead to a enhancement in the calculated O_3 loss. This enhancement is most significant in the upper troposphere. The calculated decrease in the O_3 concentration due to halogen-catalyzed methane oxidation over the 7-day simulation was of the order of 0.1-1% in the upper troposphere.

Summary

The rate of methane oxidation is increased by at least 20% in the upper troposphere when halogen catalysis is included. In the lower stratosphere, approximately 25% of methane oxidation can be initiated by chlorine; the precise fraction is very temperature dependent.

Including halogen-catalyzed methane oxidation increases the calculated HO_x and ClO_x concentrations and decreases the calculated NO_x concentration. The calculated enhancement in the HO_x concentration due to halogen-catalyzed methane oxidation is around 10-15% in the lower stratosphere and around 20% in the upper troposphere. The decrease in the NO_x concentration is around 10% in the upper troposphere. The enhancement in the ClO_x concentration is around 7-10% in the lower stratosphere. The increase in the calculated HO_x and ClO_x concentrations and the decrease in the NO_x concentration lead to a enhancement in the calculated O_3 loss. The additional O_3 loss calculated is most significant in the upper troposphere where over a 7-day simulation it was of the order of 0.1-1% for midlatitudes at equinox.

Apart from the reaction of O_3 with HO_2 which accounts for between 20 and 45% of the conversion of HO_2 to OH in the upper troposphere and lower stratosphere, the main conversion of HO_2 to OH occurs via reaction with NO, whereas in the upper troposphere the main conversion of HO_2 to OH is due to reaction with BrO. The main conversion of CH_3O_2 to CH_3O is due to

reaction with NO in both the stratosphere and upper troposphere.

As the atmospheric loading of chlorine drops, the gross odd-oxygen production by $\text{NO} + \text{HO}_2$ will increase, so there will be an accelerated ozone recovery. For example, the ratio of the odd-oxygen production rate due to the reaction of NO with HO_2 and O_2 photolysis would increase by about 10% if the chlorine loading were to drop from 3 to 2 ppbv in the lower stratosphere.

On a per molecule basis, bromine-catalyzed methane oxidation is approximately 2 orders of magnitude faster than chlorine catalyzed methane oxidation. In the upper troposphere, bromine-catalyzed methane oxidation destroys ozone at a rate which is approximately one third of that at which nitrogen-catalyzed methane oxidation is producing ozone. Therefore, with the increasing atmospheric bromine loading, bromine catalyzed methane oxidation is set to become more important. It would be valuable to have kinetic studies of the reaction BrO with CH_3O_2 so that the role of bromine-catalyzed methane oxidation can quantified more precisely.

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