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To cite this article: A. Mannan Zafar, Rolf Müller, Jens-Uwe Grooss, Sabine Robrecht, Bärbel Vogel & Ralph Lehmann (2018) The relevance of reactions of the methyl peroxy radical ( $\text{CH}_3\text{O}_2$ ) and methylhypochlorite ( $\text{CH}_3\text{OCl}$ ) for Antarctic chlorine activation and ozone loss, Tellus B: Chemical and Physical Meteorology, 70:1, 1-18, DOI: [10.1080/16000889.2018.1507391](https://doi.org/10.1080/16000889.2018.1507391)

To link to this article: <https://doi.org/10.1080/16000889.2018.1507391>



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# The relevance of reactions of the methyl peroxy radical ( $\text{CH}_3\text{O}_2$ ) and methylhypochlorite ( $\text{CH}_3\text{OCl}$ ) for Antarctic chlorine activation and ozone loss

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(Manuscript received 22 March 2018; in final form 24 July 2018)

## ABSTRACT

The maintenance of large concentrations of active chlorine in Antarctic spring allows strong chemical ozone destruction to occur. In the lower stratosphere (approximately 16–18 km, 85–55 hPa, 390–430 K) in the core of the polar vortex, high levels of active chlorine are maintained, although rapid gas-phase production of HCl occurs. The maintenance is achieved through HCl null cycles in which the HCl production is balanced by immediate reactivation. The chemistry of the methyl peroxy radical ( $\text{CH}_3\text{O}_2$ ) is essential for these HCl null cycles and thus for Antarctic chlorine and ozone loss chemistry in the lower stratosphere in the core of the polar vortex. The key reaction here is the reaction  $\text{CH}_3\text{O}_2 + \text{ClO} \rightarrow \text{products}$ ; this reaction should not be neglected in simulations of polar ozone loss. Here we investigate the full chemistry of  $\text{CH}_3\text{O}_2$  in box-model simulations representative for the conditions in the core of the polar vortex in the lower stratosphere. These simulations include the reaction  $\text{CH}_3\text{O}_2 + \text{Cl}$ , the product methylhypochlorite ( $\text{CH}_3\text{OCl}$ ) of the reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$ , and the subsequent chemical decomposition of  $\text{CH}_3\text{OCl}$ . We find that when the formation of  $\text{CH}_3\text{OCl}$  is taken into account, it is important that also the main loss channels for  $\text{CH}_3\text{OCl}$ , namely photolysis and reaction with Cl are considered. Provided that this is the case, there is only a moderate impact of the formation of  $\text{CH}_3\text{OCl}$  in the reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$  on polar chlorine chemistry in our simulations. Simulated peak mixing ratios of  $\text{CH}_3\text{OCl}$  ( $\approx 0.25$  ppb) occur at the time of the lowest ozone mixing ratios. Further, our model simulations indicate that the reaction  $\text{CH}_3\text{O}_2 + \text{Cl}$  does not have a strong impact on polar chlorine chemistry. During the period of the lowest ozone concentrations in late September, enhanced values of  $\text{CH}_3\text{O}_2$  are simulated and, as a consequence, also enhanced values of formaldehyde (about 100 ppt) and methanol (about 5 ppt).

*Keywords:* Antarctic Ozone, Antarctic chlorine chemistry, ozone hole, HCl null cycles

## 1. Introduction

Severe chemical ozone loss in Antarctic spring (e.g. Solomon, 1999; Tilmes et al., 2006; Tripathi et al., 2007; Parrondo et al., 2014) leads to extremely low ozone column values, which are referred to as the ozone hole. This phenomenon has been clearly observed each Antarctic spring since the early 1980s until today (e.g. Müller et al., 2008; WMO, 2014; Kuttippurath and Nair, 2017; Bernhard et al., 2017). In spite of the success of the

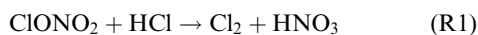
Montreal protocol and its amendments and adjustments in reducing atmospheric halogen levels and in limiting the growth of the Antarctic ozone hole (Chipperfield et al., 2015), the ozone hole will continue to occur each austral spring for decades to come (e.g. WMO, 2014; Oman et al., 2016; Hossaini et al., 2017; Fernandez et al., 2017).

The main chemical processes causing rapid chemical ozone destruction in the Antarctic polar vortex are well established, in particular heterogeneous chlorine activation through reactions driven by the occurrence of particles in the stratosphere at low temperatures and

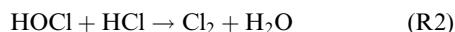
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catalytic ozone loss cycles involving chlorine and bromine radicals (Solomon, 1999; von Clarmann, 2013). These catalytic cycles (Solomon, 1999; Canty et al., 2016; Wohltmann et al., 2017) only run efficiently when large concentrations of ‘active chlorine’ are available; active chlorine is commonly referred to as  $\text{ClO}_x$  ( $\text{ClO}_x = \text{ClO} + 2 \times \text{Cl}_2\text{O}_2 + \text{Cl}$ ). Large concentrations of active chlorine have indeed been observed by a variety of measurements in late winter and spring in both the Arctic and Antarctic for different years and over a range of altitudes and time periods (e.g. Tuck, 1989; Solomon et al., 1987; Anderson et al., 1991; Toohey et al., 1993; Jaeglé et al., 1997; Kühl et al., 2004; Vogel et al., 2003; Santee et al., 2003; 2008; Sumińska-Ebersoldt et al., 2012; Wetzell et al., 2015).

The conversion of the main chlorine reservoir species ( $\text{HCl}$  and  $\text{ClONO}_2$ ) to active chlorine ( $\text{ClO}_x$ ) occurs through heterogeneous reactions on polar stratospheric clouds (PSCs) and stratospheric aerosol at low temperatures (Solomon, 1999; Drdla and Müller, 2012). The initial step in winter proceeds mainly via the heterogeneous reaction



(Solomon et al., 1986). The heterogeneous reaction

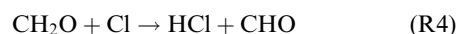


(Prather, 1992; Crutzen et al., 1992; Müller et al., 1994) substantially contributes to further chlorine activation after the initial step, in particular in the Antarctic (Grooß et al., 2011; Wohltmann et al., 2017; Müller et al., 2018). For the conditions in the polar vortex in winter and spring, the formation of  $\text{ClONO}_2$  and  $\text{HOCl}$  requires large concentrations of  $\text{ClO}$ ,  $\text{HO}_2$ , and  $\text{OH}$  (and thus sunlight), so that further activation of  $\text{HCl}$  is not expected to occur during polar night (with the exception of some radical formation in polar night due to galactic cosmic rays, Müller and Crutzen, 1993). However, a recent study (Grooß et al., 2018) suggests that an unknown chemical process is active at very low sun elevation, which depletes  $\text{HCl}$  more rapidly than can be reproduced in current model simulations.

In spring, when most of the chemical ozone destruction occurs (e.g. Hoppel et al., 2005; Livesey et al., 2015), also reactions converting active chlorine back to chlorine reservoir species (mainly  $\text{HCl}$  and  $\text{ClONO}_2$ ) proceed increasingly rapidly. In Antarctic spring, with declining ozone concentrations the  $\text{Cl}/\text{ClO}$  ratio is shifted increasingly in favour of  $\text{Cl}$  so that the rate of  $\text{HCl}$  production through the reaction



(Douglass et al., 1995; Grooß et al., 1997; Grooß et al., 2011) and, about in late September, also through the reaction

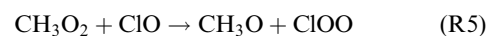


(Grooß et al., 2011; Müller et al., 2018) increases by more than an order of magnitude. Thus, for very low ozone concentrations (below 0.5 ppm), as they are regularly observed in the Antarctic lower stratosphere in polar spring (Hoppel et al., 2005; Solomon et al., 2007), the formation of  $\text{HCl}$  via the reactions R3 and R4 constitutes a potentially important chlorine deactivation mechanism. This deactivation mechanism, if not balanced by other chemical processes, would stop chlorine activation (and thus chemical ozone destruction) within days (Müller et al., 2018).

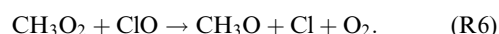
Therefore, it is an important question how the large concentrations of active chlorine, which cause chemical ozone loss can be maintained in Antarctic spring. The maintenance of active chlorine in spring has been clearly observed (e.g. Tuck, 1989; Anderson et al., 1991; Santee et al., 2003, 2008), the question of the responsible chemical mechanism has, however, received relatively little attention (Portmann et al., 1996; Solomon et al., 2015; Müller et al., 2018).

In a recent study, it was proposed that in the core of the Antarctic vortex in the lowermost stratosphere (approximately 16–18 km, 85–55 hPa, 390–430 K potential temperature), high levels of active chlorine are maintained through so-called  $\text{HCl}$  null cycles (cycles C1 and C2 in Müller et al., 2018, see also appendix). The key feature of these two  $\text{HCl}$  null cycles is that  $\text{HO}_2$  and thus  $\text{HOCl}$  is produced at the same rate as  $\text{HCl}$ , which further reacts via reaction R2, so that there is no net production of  $\text{HCl}$  in the cycles in spite of the strongly increasing rates of reactions R3 and R4 in Antarctic spring (Müller et al., 2018). At the same rate means that, within these cycles, the formation of an  $\text{HCl}$  molecule directly leads to the formation of an  $\text{HO}_2$  radical (and thus an  $\text{HOCl}$  molecule). Thus, although the rate limiting step of the  $\text{HCl}$  null cycles is the formation of  $\text{HCl}$  via reactions R3 and R4, the net effect of these cycles is *not* the formation of  $\text{HCl}$ .

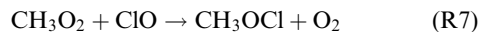
For the efficiency of the  $\text{HCl}$  null cycle that balances  $\text{HCl}$  formation in reaction R3 (C1, see appendix), the gas-phase reaction



is essential (Crutzen et al., 1992; Müller et al., 1994, 2018). Assuming that the product  $\text{ClOO}$  decomposes rapidly into  $\text{Cl} + \text{O}_2$ , this reaction may be written as

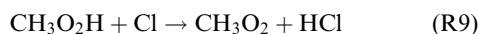
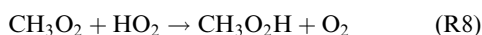


However, there is an alternative product channel for reaction R6 with methylhypochlorite ( $\text{CH}_3\text{OCl}$ ) as a product

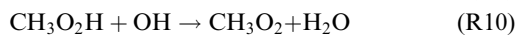
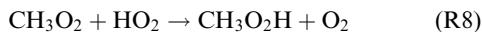


which has hitherto only been explored to a very limited extent (Helleis et al., 1994; Crowley et al., 1994; Carl et al., 1996; Müller et al., 1996).

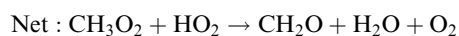
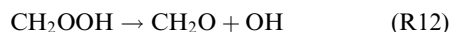
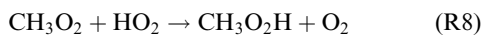
Without considering reaction R6, the formation of the observed extremely low ozone concentrations in Antarctic spring cannot be explained (Crutzen et al., 1992; Grooß et al., 2011; Müller et al., 2018). Reaction R6 constitutes the dominant sink of  $\text{CH}_3\text{O}_2$  under conditions of ozone hole chemistry. The  $\text{CH}_3\text{O}_2$  radical would otherwise participate to a much larger extent in the following cycles (Müller and Crutzen, 1994):



and

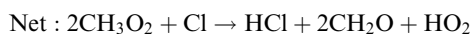
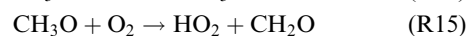


Reaction R10 has a minor channel (30%, Sander et al., 2011) in which  $\text{CH}_2\text{OOH}$  is produced; however  $\text{CH}_2\text{OOH}$  decomposes spontaneously into  $\text{CH}_2\text{O} + \text{OH}$  (Vaghjiani and Ravishankara, 1989; Vereecken et al., 2004). The net effect of this channel is thus



The net result of the three cycles above is a loss of  $\text{HO}_x$ , methyl peroxy, and active chlorine radicals. If these reactions occurred at a large rate in the polar spring stratosphere, they would lead to a reduced rate of activation of HCl and a loss of active chlorine radicals.

Moreover, also the methyl peroxy self-reaction could be important, which proceeds at stratospheric temperatures mainly via reaction R13 (Tyndall et al., 2001):



The net result of reactions R13–R15 is a loss of an active chlorine radical (Cl) but also the formation of an  $\text{HO}_2$  radical (which in turn results in the production of an active chlorine radical, Crutzen et al., 1992; Müller et al., 2018), so that the impact on active chlorine will be moderate.

Because of the importance of reactions of  $\text{CH}_3\text{O}_2$  for Antarctic stratospheric chemistry we consider here the

complete  $\text{CH}_3\text{O}_2$  chemistry including reactions of methylhypochlorite ( $\text{CH}_3\text{OCl}$ ) and take into account recent laboratory studies of the rate constant of R6 (Leather et al., 2012; Ward and Rowley, 2016). We further consider the impact of the reaction of the methyl peroxy radical with Cl on polar ozone chemistry, which has hitherto been neglected. We use a current chemical scheme of heterogeneous and gas-phase chemistry (Grooß et al., 2011; Zafar, 2016; Müller et al., 2018) focusing on the conditions in the core of the polar vortex in the lowermost stratosphere, where minimum ozone mixing ratios are reached in Antarctic spring (Hoppel et al., 2005; Solomon et al., 2007).

## 2. Model description

The simulations presented here were performed with a chemical box-model version of the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002; Grooß et al., 2011, 2014, 2018) in the same set-up as used in a previous study (Zafar, 2016; Müller et al., 2018).

The model simulations discussed here were conducted for a typical air parcel (Grooß et al., 2011; Müller et al., 2018) in the lower stratosphere circulating and descending from 430 to 390 K potential temperature (this range of potential temperatures corresponds approximately to 16–18 km or 55–85 hPa). The air parcel is representative for the conditions in the core of the polar vortex according to trajectory calculations; i.e. fluctuations in temperature and solar illumination (solar zenith angle) are realistic (Müller et al., 2018). Further, the diabatic descent (by about 35 K) prescribed based on calculations using a radiation model (Grooß et al., 2011; Müller et al., 2018) will also be realistic.

Stratospheric chemistry is calculated for air parcels along trajectories driven by meteorological information from operational analyses from the European Centre for Medium-range Weather Forecasts (ECMWF). The kinetics of the chemistry simulated along the trajectories is based on the recommendations by Sander et al. (2011). The photolysis rates are calculated for spherical geometry (Becker et al., 2000) and heterogeneous chemistry is calculated on ice, nitric acid trihydrate (NAT), liquid ternary particles ( $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HNO}_3$ ), and cold liquid binary aerosols (for details see Müller et al., 2018).

The initial values at the start of the simulation at 430 K potential temperature are based on observations by MIPAS-Envisat (ozone,  $\text{N}_2\text{O}$ ,  $\text{HNO}_3$ ) and tracer correlations with  $\text{N}_2\text{O}$  ( $\text{Cl}_y$ ,  $\text{Br}_y$ , and  $\text{NO}_y$ ), see Grooß et al. (2011) for more details. The initial values are the same as used by Müller et al. (2018), but are listed here again for reference:  $\text{O}_3 = 2.2$  ppm,  $\text{H}_2\text{O} = 4.1$  ppm,  $\text{CH}_4 = 1.2$  ppm,

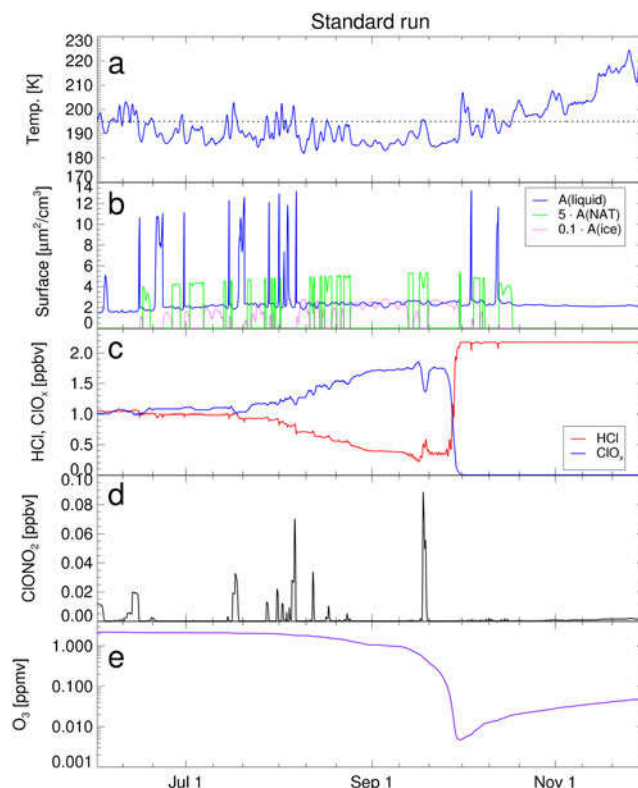


Fig. 1. Box-model simulations along a trajectory passing through the location of an ozone sonde observation of 14 ppb on 74 hPa (391 K potential temperature) at South Pole on 24 September 2003 (Grooß et al., 2011; Müller et al., 2018). The different panels show a time series of the most important parameters: (a) temperature of the air parcel, (b) PSCs: surface area density of ice (magenta, scaled by 0.1), NAT (green, scaled by 5) and liquid aerosol particles (blue), (c)  $\text{ClO}_x$  (blue), and HCl (red), (d)  $\text{ClONO}_2$ , and (e) ozone (note the logarithmic y-axis). Ozone and  $\text{ClO}_x$  mixing ratios are shown as 24 hour averages.

$\text{HNO}_3 = 4.5$  ppb,  $\text{HCl} = 1.05$  ppb,  $\text{ClO}_x = 1.01$  ppb,  $\text{ClONO}_2 = 12$  ppt,  $\text{HOCl} = 5$  ppt,  $\text{Br}_y = 17$  ppt,  $\text{CO} = 16$  ppb. (The initial value of  $\text{HNO}_3$  is chosen to account for denitrification, Müller et al., 2018.)

### 3. Results

The results of the reference case (standard run) have been presented in a previous publication (Müller et al., 2018) and will be briefly summarised here (Fig. 1) to provide the information relevant for the discussion of the chemistry of  $\text{CH}_3\text{O}_2$  and the sensitivity studies presented below. The air parcel descends from above 430 K potential temperature in June to close to 390 K in late October; the development of temperature and PSCs (ice, NAT, and liquid PSCs) along the trajectory employed here is shown in Fig. 1 (panels a and b).

The model simulation starts with about 1 ppb of  $\text{ClO}_x$  and with near zero values of  $\text{ClONO}_2$  due to the initial titration between HCl and  $\text{ClONO}_2$  in May. During polar night, there is a period of ‘sleeping chemistry’, which is followed by further HCl decrease (Grooß et al., 2011;

Müller et al., 2018). During polar night and during the period of decreasing HCl, HOCl mixing ratios (not shown) are somewhat variable but low (with peak values below about 0.2 ppb) in general agreement with observations (von Clarmann et al., 2012). Mixing ratios of  $\text{ClONO}_2$  likewise are extremely low, mostly below about 0.01 ppb and even peak values below 0.1 ppb (Fig. 1, panel d). These very low  $\text{ClONO}_2$  values are due to very low gas-phase concentrations of  $\text{HNO}_3$ , which in turn are caused by the uptake of  $\text{HNO}_3$  in PSC particles (note that PSCs are practically continuously present in the simulation until early October).

The decreasing HCl mixing ratios result in increasing  $\text{ClO}_x$  and thus in chemical ozone destruction increasing in strength. The ozone depletion ends abruptly with chlorine deactivation into HCl in late September (Fig. 1, panel e).

Compared to the study by Grooß et al. (2011), there are different assumptions here on the number densities of NAT particles. Grooß et al. (2011) assumed a NAT particle density of  $1 \text{ cm}^{-3}$ , while we assume a lower value of  $3 \cdot 10^{-3} \text{ cm}^{-3}$ . There is a large variability in observed



Table 1. Sensitivity simulations on the impact of the gas-phase reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$  and the heterogeneous reaction  $\text{HOCl} + \text{HCl}$  on ozone loss.

	$\text{HOCl} + \text{HCl}$ (R2)	$\text{CH}_3\text{O}_2 + \text{ClO}$ (R6)
Case A	Yes	Yes
Case B	Yes	No
Case C	No	Yes
Case D	No	No

NAT number densities (e.g. Pitts et al., 2011; Spang et al., 2018; Pitts et al., 2018) and choosing a particular number constitutes a simplification. However, assuming higher number densities for NAT leads to larger NAT surface areas (Drdla and Müller, 2012) and thus to a larger heterogeneous reactivity on NAT. Thus, in the simulations reported by Grooß et al. (2011) heterogeneous reactivity on NAT dominated the reactivity on STS. Here heterogeneous reactions on STS have a stronger impact than in the earlier study (Grooß et al., 2011), which should be more realistic. Nonetheless, in spite of these differences, the results for the standard run (Fig. 1) are very close to those reported for the same trajectory by Grooß et al. (2011).

### 3.1. Impact of the gas-phase reaction $\text{CH}_3\text{O}_2 + \text{ClO}$ and the heterogeneous reaction $\text{HOCl} + \text{HCl}$ on ozone loss

Müller et al. (2018) argued that in the lowermost stratosphere, in the core of the vortex, reactions R2 and R6 are essential for the efficacy of the HCl null cycles, which allow high levels of active chlorine to be maintained in polar spring. In the standard run, we assume here that the product of reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$  (R6) is only  $\text{CH}_3\text{O} + \text{Cl} + \text{O}_2$ . In a set of sensitivity tests, we neglected reaction R2, neglected R6, and neglected both R2 and R6 (Table 1). The results confirm the conclusions of the early study by Crutzen et al. (1992) and the recent analysis by Müller et al. (2018). Substantial depletion of HCl beyond the initial titration of  $\text{ClONO}_2$  against HCl is only achieved by including both R2 and R6 (Fig. 2).

Reaction R2 is taken into account in state-of-the-art models; if it were neglected, a steady increase of HCl over late August and early September (by about 0.5 ppb) would be simulated (case C, green line in Fig. 2). If the gas-phase reaction R6 is neglected, the picture is similar, but the increase of HCl in late August, early September is slower (case B, blue line). The increase in HCl in late August and early September is strongest if both R2 and R6 are neglected (case D, orange line in Fig. 2). An increase in HCl corresponds to a decrease in  $\text{ClO}_x$  and thus to slower ozone loss rates. Without reaction R2 and

R6 (cases B–D), the observed decline of ozone mixing ratios to extremely low values end of September cannot be explained (Grooß et al., 2011).

We also show the impact of taking into account reaction R6 on simulated  $\text{HO}_2$ , formaldehyde ( $\text{CH}_2\text{O}$ ), and  $\text{CH}_3\text{O}_2$  mixing ratios (Fig. 3). The  $\text{HO}_2$  radical is important for the effectiveness of cycle C1. Throughout the period of high levels of active chlorine, its concentrations are strongly suppressed although there is rapid formation of  $\text{HO}_2$  in cycle C1 (through R15, see appendix). The low  $\text{HO}_2$  concentrations occur because of the consumption of  $\text{HO}_2$  in cycle C1 caused by the heterogeneous reaction R2 (Crutzen et al., 1992; Müller and Crutzen, 1994; Jaeglé et al., 1997; Müller et al., 2018). Concentrations of  $\text{CH}_2\text{O}$  are somewhat higher when reaction R6 is taken into account, with peak values in late September more than a factor of three higher with reaction R6 (Fig. 3, top panel). Without reaction R6, simulated mixing ratios of  $\text{CH}_3\text{O}_2$  are much higher than when reaction R6 is taken into account (Fig. 3, bottom panel). Thus, reaction R6 strongly suppresses mixing ratios of  $\text{CH}_3\text{O}_2$ , with the exception of a peak in  $\text{CH}_3\text{O}_2$  in late September, when the minimum ozone concentration occurs.

### 3.2. Sensitivity on the rate constant of $\text{CH}_3\text{O}_2 + \text{ClO}$

Reaction R6 is essential for the efficacy of the HCl null cycles that allow active chlorine levels to be maintained in polar spring (Müller et al., 2018, see also appendix). In the standard run, for the overall rate constant for reaction R6, we employed the recommended value  $k(T) = 3.3 \times 10^{-12} \exp(-115/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (where  $T$  is temperature in Kelvin), which is based on Helleis et al. (1993). More recent laboratory studies report different rate constants of  $k(T) = 1.96 \times 10^{-11} \exp(-626/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Leather et al., 2012) and  $k(T) = 2.20 \times 10^{-11} \exp(-642/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Ward and Rowley, 2016), which lead to a smaller reaction rate at low temperatures. For a temperature of 190 K, the recommended rate constant (Sander et al., 2011) corresponds to  $1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the rate reported by Leather et al. (2012) to  $0.73 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the rate reported by Ward and Rowley (2016) to  $0.75 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; the study by Crutzen et al. (1992) assumed the constant value  $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the rate constant. Leather et al. (2012) concluded that the new data might reduce the effectiveness of ozone loss cycles involving reaction R6, but support the importance of this reaction in the late winter and spring time polar vortex region.

We tested the impact of the recently reported rate constants for reaction R6 (Leather et al., 2012; Ward and Rowley, 2016) and their temperature dependence in a

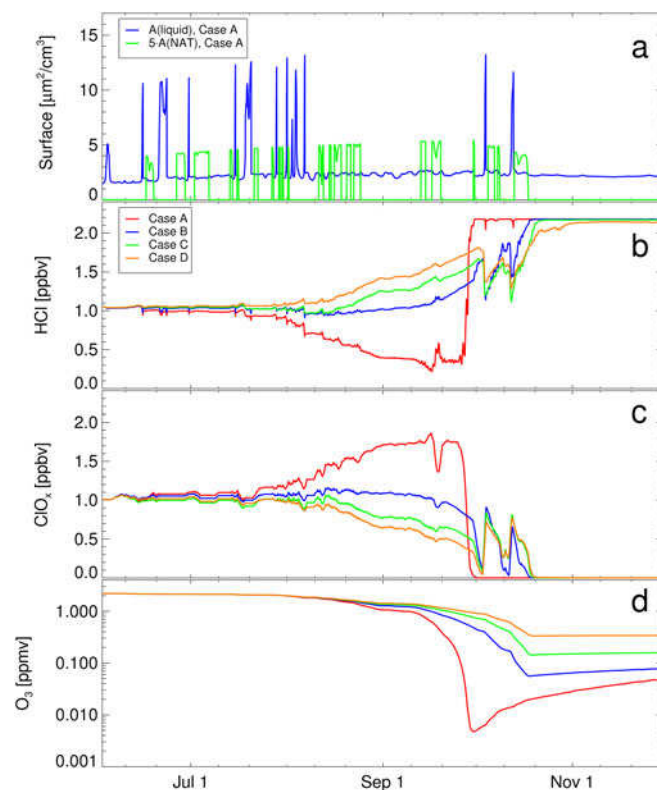


Fig. 2. Sensitivity simulations on the impact of the gas-phase reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$  (R6) and the heterogeneous reaction  $\text{HOCl} + \text{HCl}$  (R2) on ozone loss. Top panel shows the simulated surface areas of NAT and liquid particles (also shown in Fig. 1). The panels below show HCl (b), active chlorine ( $\text{ClO}_x$ , c), and ozone (d). Red line is the standard run (case A), blue line a run neglecting R6 (case B), green line a run neglecting R2 (case C), and orange line a case neglecting both R2 and R6 (case D). Ozone and  $\text{ClO}_x$  mixing ratios are shown as 24 hour averages.

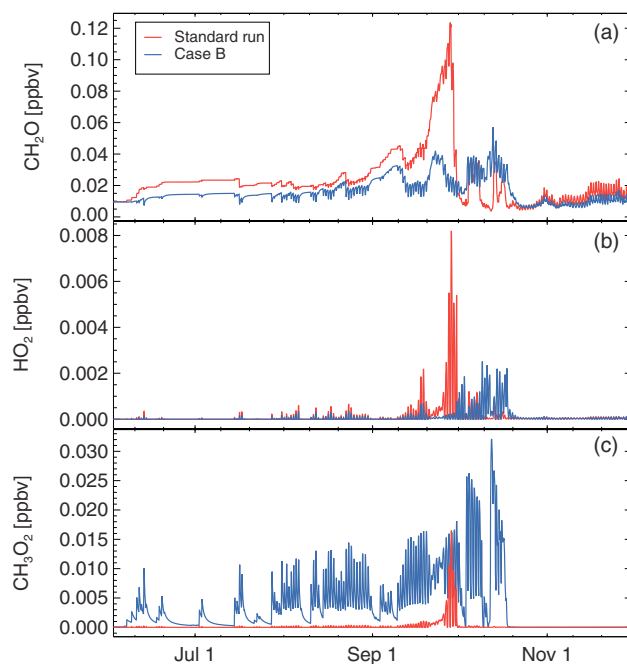


Fig. 3. The temporal development of  $\text{CH}_2\text{O}$  (panel a),  $\text{HO}_2$  (panel b), and  $\text{CH}_3\text{O}_2$  (panel c) for the standard run (case A, red lines) and for case B (blue lines) neglecting R6.

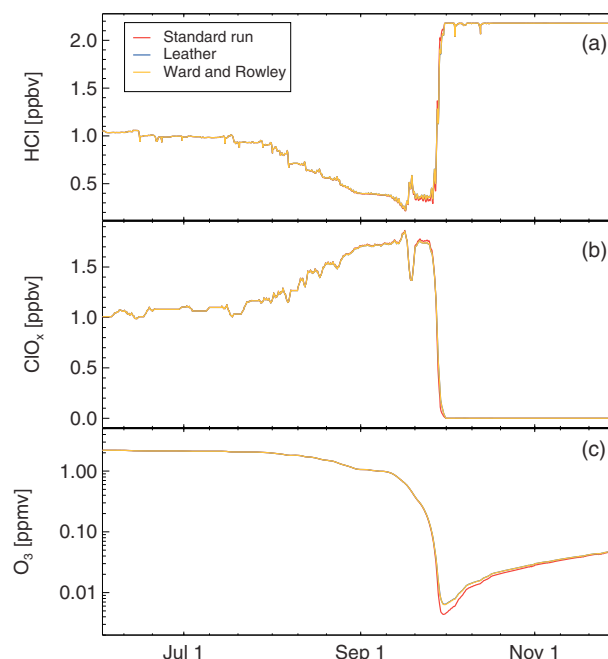


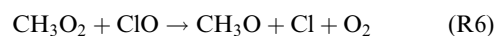
Fig. 4. Sensitivity simulations on the rate constant of reaction R6 ( $\text{CH}_3\text{O}_2 + \text{ClO}$ ). The panels show HCl (a), active chlorine ( $\text{ClO}_x$ , b), and ozone (c). Red line shows the standard run using the recommended value (Sander et al., 2011) for R6, blue line shows a run assuming the overall rate constant for R6 reported by Leather et al. (2012) and the yellow line indicates the rate constant for R6 reported by Ward and Rowley (2016). (The blue and the yellow lines are almost identical.) Ozone and  $\text{ClO}_x$  mixing ratios are shown as 24 hour averages.

sensitivity simulation (Fig. 4). A significant impact of the recently reported rate constants by Leather et al. (2012) and Ward and Rowley (2016) on the results is not noticeable in the simulation.

This result is expected, as moderate changes of the rate constant of reaction R6 do not affect the efficacy of the first HCl null cycle, which is rather controlled by the rate constant of reaction R3 (see appendix). Only if the rate of reaction R6 dropped to values that would make other reactions that remove  $\text{CH}_3\text{O}_2$  (R8 and R13) competitive in rate to reaction R6, the rate constant of reaction R6 would become relevant.

### 3.3. Reactions involving methylhypochlorite ( $\text{CH}_3\text{OCl}$ )

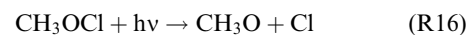
In laboratory experiments (Helleis et al., 1994; Biggs et al., 1995; Tyndall et al., 1998), two reaction channels have been identified for the reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$ :



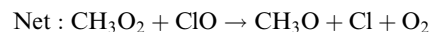
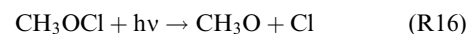
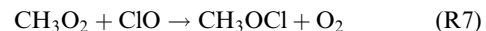
That means that for reaction R6 not only the products  $\text{CH}_3\text{O} + \text{Cl} + \text{O}_2$  are possible (as assumed for cycle C1, Müller et al., 2018, see also appendix), but also the formation of methylhypochlorite ( $\text{CH}_3\text{OCl}$ ). Thus, for a

complete picture of the impact of the methane oxidation cycle on polar stratospheric chemistry, the chemistry of methylhypochlorite has to be taken into account.

**3.3.1 Loss of  $\text{CH}_3\text{OCl}$  through photolysis.** In the polar stratosphere, photolysis constitutes an important removal process for  $\text{CH}_3\text{OCl}$



(Crowley et al., 1994; Krisch et al., 2004), whereas the reaction of  $\text{CH}_3\text{OCl}$  with OH is negligible (Crowley et al., 1996). The net result of reactions R7 and R16



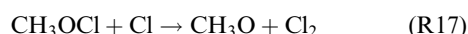
is the same as reaction R6, so that cycle C1 should remain unaltered.

This is indeed the outcome of a sensitivity study, where the production of  $\text{CH}_3\text{OCl}$  in reaction R7 was assumed to occur with 100% efficiency and photolysis is assumed as the only loss process (R16) (see blue line in Fig. 5). The simulated development of HCl, active chlorine and ozone in this sensitivity simulation is very close to the standard run, with the only exception of a somewhat stronger HCl activation in early August in the standard

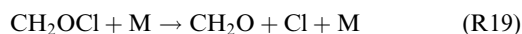


run. This stronger activation in the standard run does not occur continuously, but rather in steps; at these steps somewhat more HCl depletion occurs in the standard run (Fig. 5). The HCl activation in these steps occurs because of short-term fluctuations to higher temperatures (Fig. 1, panel a), resulting in the release of  $\text{HNO}_3$  to the gas-phase and the subsequent formation of  $\text{NO}_x$  and (consequently) the formation of  $\text{ClONO}_2$  (Fig. 1, panel d). When  $\text{CH}_3\text{OCl}$  is considered in the model, somewhat less ClO is available in the (short) higher temperature periods, so that somewhat less  $\text{ClONO}_2$  is formed and therefore the heterogeneous activation of HCl (via reaction R1) is less.

**3.3.2 Reaction of  $\text{CH}_3\text{OCl}$  with Cl.** Carl et al. (1996) and Kukui et al. (1997) pointed out a further relevant reaction for methylhypochlorite ( $\text{CH}_3\text{OCl}$ ), namely the reaction with Cl and reported rate constants and reaction products:

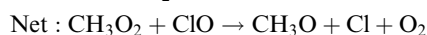
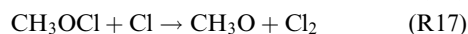
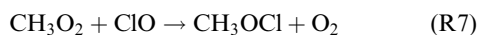


where  $\text{CH}_2\text{OCl}$  rapidly reacts further via



(Carl et al., 1996).

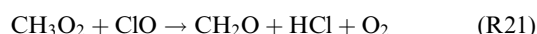
Reaction R17 constitutes the dominant pathway (about 80–85%, Carl et al., 1996; Kukui et al., 1997; He et al., 2005) and leads to the following reaction sequence:



Thus, the net effect of this cycle again should be the same as reaction R6.

This is indeed borne out by the results of a sensitivity simulation, where in addition to a 100% efficiency for the production of  $\text{CH}_3\text{OCl}$  in the branching ratio of R6/R7 and loss of  $\text{CH}_3\text{OCl}$  by photolysis (R16) the loss of  $\text{CH}_3\text{OCl}$  via reaction with Cl (R17) was added. The results (green line in Fig. 5) are very close to the results without reaction R17 (blue line in Fig. 5).

The minor reaction pathway R7 and R18 together with R19 leads to the net reaction



and thus to a deactivation of chlorine. In a sensitivity study (orange line in Fig. 5), we added reactions R18 and R19 assuming a 100% production channel of HCl and  $\text{CH}_2\text{O}$ , assumed 100% production efficiency of  $\text{CH}_3\text{OCl}$  in the branching ratio of R6/R7, and included the major gas-phase loss of  $\text{CH}_3\text{OCl}$ , namely photolysis (R16). (For

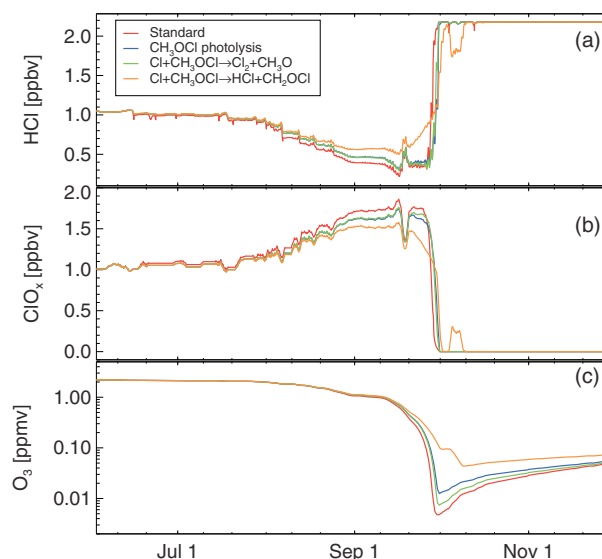


Fig. 5. Sensitivity simulations including  $\text{CH}_3\text{OCl}$  chemistry. The panels show HCl (a), active chlorine ( $\text{ClO}_x$ , b), and ozone ( $\text{O}_3$ , c). Red line shows the standard run. The blue, green, and orange lines show runs assuming 100% efficiency for the production of  $\text{CH}_3\text{OCl}$  in the branching ratio of R6/R7. The blue line shows results from a run assuming loss of  $\text{CH}_3\text{OCl}$  only through photolysis, the green line results assuming in addition loss through the reaction of  $\text{CH}_3\text{OCl} + \text{Cl}$  with the products  $\text{Cl}_2 + \text{CH}_3\text{O}$  and the orange line assuming in addition loss through the reaction of  $\text{CH}_3\text{OCl} + \text{Cl}$ , but with the products  $\text{HCl} + \text{CH}_2\text{OCl}$ . Ozone and  $\text{ClO}_x$  mixing ratios are shown as 24 hour averages.

example, on 10 September, the rate of loss of  $\text{CH}_3\text{OCl}$  through photolysis is  $1.65 \cdot 10^{-2}$  ppb/day and the loss through reaction with Cl is  $0.51 \cdot 10^{-2}$  ppb/day). Indeed, adding reaction R21 leads to a shift towards higher values of HCl in the simulation and the importance of this effect increases towards end of September with increasing values of Cl, i.e. with decreasing values of ozone (orange line in Fig. 5).

However, assuming a 100% efficiency for the production of  $\text{CH}_3\text{OCl}$  in the branching ratio of R6/R7, as it was done in the sensitivity studies shown in Fig. 5, is not realistic. Therefore, we conducted a study assuming more realistic chemical parameters, namely an efficiency for  $\text{CH}_3\text{OCl}$  formation in the branching ratio of R6/R7 of 23% (i.e. a branching ratio of R6/R7 77%:23% Helleis et al., 1994) and a branching ratio between reactions 17 and 18 of 80–20% (Carl et al., 1996; Kukui et al., 1997; He et al., 2005). In Fig. 6, the results of this sensitivity test (blue line) are compared against the standard run (red line). There is very little difference to the standard run under these assumptions, except for slightly more activation of HCl in the standard run.

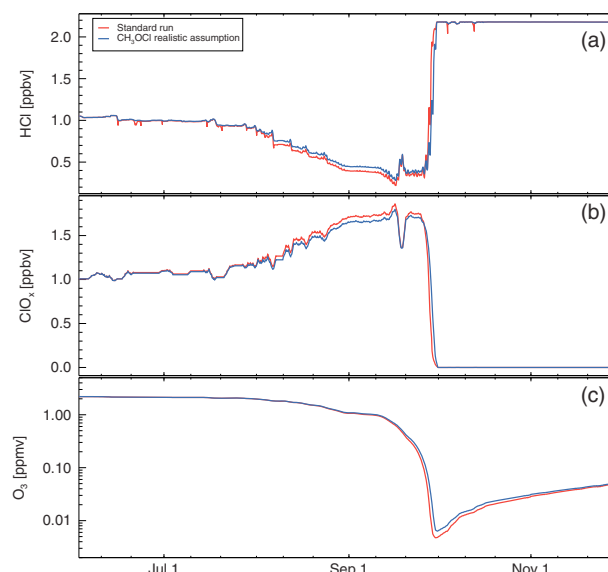
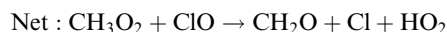
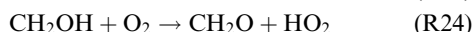
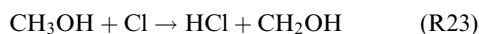
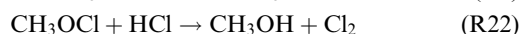
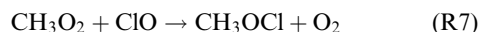


Fig. 6. Sensitivity simulations including  $\text{CH}_3\text{OCl}$  chemistry. The panels show HCl (a), active chlorine ( $\text{ClO}_x$ , b), and ozone (c). Red line shows results for the standard run. Blue line shows results for a run assuming realistic branching ratios for  $\text{CH}_3\text{OCl}$  production in R7 and for HCl production in R18 (see text). Ozone and  $\text{ClO}_x$  mixing ratios are shown as 24 hour averages.

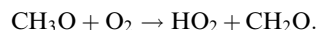
3.3.3 *The heterogeneous reaction  $\text{CH}_3\text{OCl} + \text{HCl}$ .* Kenner et al. (1993) and Crowley et al. (1994) suggested that the heterogeneous reaction



might take place in analogy with the heterogeneous reaction R2. However, there is no study of this reaction based on laboratory measurements. If reaction R22 occurred in the polar stratosphere, it would constitute a significant source of methanol ( $\text{CH}_3\text{OH}$ ) and should lead to the following reaction sequence:



Thus, the net effect of this cycle is identical to the effect of reaction R6 followed by reaction R15



We tested the possible impact of the heterogeneous reaction R22 by assuming it to occur on ice, NAT and STS particles with the same rate as the heterogeneous reaction R2. Moreover, we have assumed a 100% efficiency for the production of  $\text{CH}_3\text{OCl}$  in the branching ratio R6/R7 and loss of  $\text{CH}_3\text{OCl}$  through the main gas-phase loss (photolysis, reaction R16). In Fig. 7, the

results of this sensitivity run (blue line) are compared with the standard run (red line). As expected from the net result of the cycle shown above, there is only a minor impact of the hypothetical heterogeneous reaction R22 on chemical ozone loss. Further, if the hypothetical heterogeneous reaction R22 is taken into account, there are somewhat higher concentrations of  $\text{CH}_3\text{OH}$  and much lower concentrations of  $\text{CH}_3\text{OCl}$  (Fig. 8, black lines).

3.3.4 *Formation of methanol in the antarctic stratosphere.* In the standard run, with reaction R6 taken into account (constituting a major loss pathway for  $\text{CH}_3\text{O}_2$ ), mixing ratios of  $\text{CH}_3\text{O}_2$  are suppressed for most of the simulation period (Fig. 3). Nonetheless, for very low ozone concentrations in the polar lower stratosphere, because of the strongly increasing speed of reaction cycle C1 (Müller et al., 2018), enhanced values of  $\text{CH}_3\text{O}_2$  (compared to the period before and after late September) are simulated (Fig. 3). Consequently, because of reaction R13, also enhanced values of  $\text{CH}_3\text{OH}$  are projected (Fig. 3). If detectable, these enhanced values would constitute an indication of the relevance of the chemistry of  $\text{CH}_3\text{O}_2$  for polar ozone loss.

Moreover, the formation of methylhypochlorite in reaction R7 is mostly neglected in formulations of polar chemistry, if taken into account, mixing ratios of methylhypochlorite range between 10–250 ppt, with peak values occurring for the lowest ozone mixing ratios (Fig. 8). The

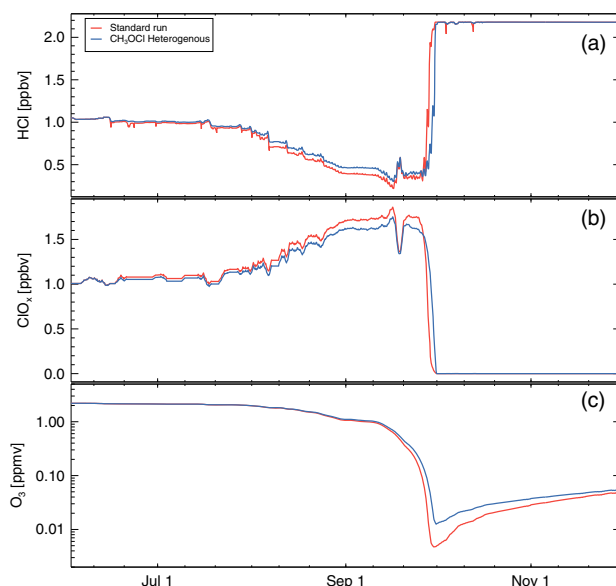


Fig. 7. Simulations assuming the hypothetical heterogeneous reaction  $\text{CH}_3\text{OCl} + \text{HCl} \rightarrow \text{CH}_3\text{OH} + \text{Cl}_2$  (Kenner et al., 1993; Crowley et al., 1994); the sensitivity run assuming that this reaction occurs on ice, NAT and STS is shown in blue and the standard run is shown in red. The panels show HCl (a), active chlorine ( $\text{ClO}_x$ , b), and ozone (c). Ozone and  $\text{ClO}_x$  mixing ratios are shown as 24 hour averages.

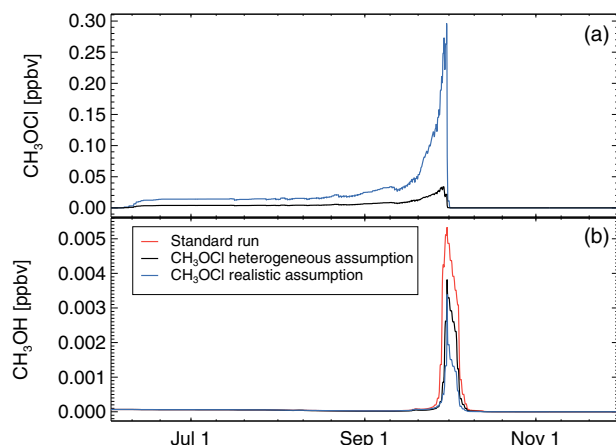


Fig. 8. Results of the temporal development of methylhypochlorite ( $\text{CH}_3\text{OCl}$ , panel a) and methanol ( $\text{CH}_3\text{OH}$ , panel b). Shown are results for a case (blue line) with a realistic formation rate of  $\text{CH}_3\text{OCl}$  in reaction R7 and a realistic branching ratio for the reaction  $\text{CH}_3\text{OCl} + \text{Cl}$  (reactions R17 and R18). Also shown are results for a run with realistic assumptions for  $\text{CH}_3\text{OCl}$  chemistry and, in addition, assuming that the hypothetical heterogeneous reaction R22 occurs in the polar stratosphere (black lines). The methanol mixing ratios for the standard run are shown as the red line in panel b.

simulated pattern of the temporal development of  $\text{CH}_3\text{OCl}$  (Fig. 8) is consistent with the first estimate of  $\text{CH}_3\text{OCl}$  mixing ratios in the Antarctic stratosphere (Carl et al., 1996), although this first estimate predicted much lower concentrations.

During the period of very low ozone concentrations, also a substantial enhancement of methanol ( $\text{CH}_3\text{OH}$ ) is simulated with peak values of about 5 ppt for the standard case (Fig. 8). The methanol is formed in the self-

reaction of  $\text{CH}_3\text{O}_2$  (reaction R13). Because during the period of very low ozone concentrations the  $\text{CH}_3\text{O}_2$  mixing ratios are lower when methylhypochlorite formation is taken into account, also the simulated methanol (peak values of about 3 ppt) is lower in this case. Assuming that the hypothetical heterogeneous reaction of methylhypochlorite with HCl (R22) takes place, results again in higher methanol concentrations due to the additional methanol source from reaction R22 (Fig. 8).

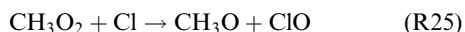
Table 2. The set of additional reactions taken into account to describe the chemistry of  $\text{CH}_3\text{O}_2 + \text{Cl} \rightarrow$  products.

Reaction	Rate constant	
$\text{CH}_3\text{O}_2 + \text{Cl} \rightarrow \text{products}$	$1.6 \cdot 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Sander et al. (2011)
$\text{CH}_2\text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$	$6.0 \cdot 10^4 \text{ s}^{-1}$	Maricq et al. (1994)
$\text{CH}_2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}$	$1.7 \cdot 10^4 \text{ s}^{-1}$	Maricq et al. (1994)
$\text{CH}_2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2$	$2.3 \cdot 10^4 \text{ s}^{-1}$	Maricq et al. (1994)
Reaction	Rate constant (0.5/0.5)	Rate constant (0.2/0.8)
$\text{CH}_3\text{O}_2 + \text{Cl} \rightarrow \text{CH}_3\text{O} + \text{ClO}$	$0.80 \cdot 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$0.32 \cdot 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$\text{CH}_3\text{O}_2 + \text{Cl} \rightarrow \text{CO} + \text{H}_2\text{O} + \text{HCl}$	$0.48 \cdot 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$7.68 \cdot 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$\text{CH}_3\text{O}_2 + \text{Cl} \rightarrow \text{CO}_2 + 2\text{H} + \text{HCl}$	$1.36 \cdot 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$2.18 \cdot 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$\text{CH}_3\text{O}_2 + \text{Cl} \rightarrow \text{CO}_2 + \text{H}_2 + \text{HCl}$	$1.84 \cdot 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$2.94 \cdot 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Top part shows the reactions and the reported rate constants from the literature, bottom part shows the reactions and rate constants as implemented (both for the 50:50 and the 20:80 branching ratio of R25 and R26) in the chemistry scheme employed here (Maricq et al., 1994).

### 3.4. The relevance of the reaction $\text{CH}_3\text{O}_2 + \text{Cl}$

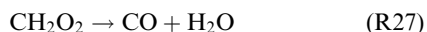
The main reaction pathway of  $\text{CH}_3\text{O}_2$  for the conditions in the polar lower stratosphere considered here so far is the reaction with ClO via reaction R6. Nonetheless, there is also a reaction of  $\text{CH}_3\text{O}_2$  with the Cl radical (Maricq et al., 1994; Jungkamp et al., 1995; Daële and Poulet, 1996; Sander et al., 2011)



with a recommended rate constant of  $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Sander et al., 2011). The branching ratio between reactions R25 and R26 is uncertain (Maricq et al., 1994; Jungkamp et al., 1995; Daële and Poulet, 1996) and no recommendation is given (Sander et al., 2011).

Before 26 September, when the Cl/ClO ratio remains clearly below  $10^{-3}$ , reaction R6 will dominate over reactions R25 and R26. In late September, the reaction of  $\text{CH}_3\text{O}_2$  with the Cl radical increases in importance with decreasing ozone (and the associated increase in the Cl/ClO ratio). The impact of reactions R25 and R26 on stratospheric chlorine chemistry has hitherto not been investigated although under conditions of activated chlorine and low ozone reaction R26 constitutes a source of HCl.

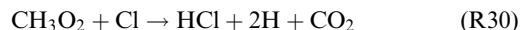
In addition to HCl, the Criegee intermediate ( $\text{CH}_2\text{O}_2$ ) is a product of reaction R26, which decays very rapidly; it has a lifetime of  $\approx 10 \mu\text{s}$  (see Table 2 and Maricq et al., 1994).



(see Table 2 for the decay rates of  $\text{CH}_2\text{O}_2$ ).

The reaction pathway via reaction R25 has the same impact on polar chlorine chemistry as reaction R6

because of the product  $\text{CH}_3\text{O}$ , which leads to formation of  $\text{HO}_2$ . The same is true for reaction R26 followed by the decay of  $\text{CH}_2\text{O}_2$  via R28 with the net reaction



The two H radicals are rapidly converted into two  $\text{HO}_2$  radicals, one of which may serve to compensate the formation of HCl in reaction R26. Thus, the impact of the net reaction R30 on polar chlorine chemistry is again very similar to reaction R6. However, a decay of  $\text{CH}_2\text{O}_2$  via reactions R27 and R29, the main decay pathways of  $\text{CH}_2\text{O}_2$  (Table 2) does not lead to the formation of radicals so that the HCl production in R26 is not compensated and thus there is a net production of HCl.

We have implemented reactions R25 and R26 in our model simulations using the recommended rate constant (Sander et al., 2011). Because the branching ratio between reactions R25 and R26 is uncertain; we use here both branching ratios which are reported in the literature, namely 0.5/0.5 and 0.2/0.8 (Maricq et al., 1994; Jungkamp et al., 1995; Daële and Poulet, 1996; Sander et al., 2011). We have also implemented the decay of the Criegee intermediate  $\text{CH}_2\text{O}_2$  (see Table 2) according to R27, R28, and R29 using the rates reported by Maricq et al. (1994). In the model formulation, we have not introduced  $\text{CH}_2\text{O}_2$  explicitly but have rather employed the relative decay pathways of  $\text{CH}_2\text{O}_2$  (R27, R28, and R29) together with the rate of reaction R26 (see Table 2, bottom for the effective rate constants implemented in the chemistry scheme).

The results of the simulations including reactions R25 and R26 and the decay of the Criegee intermediate  $\text{CH}_2\text{O}_2$  are shown in Fig. 9. As expected, the impact of reactions R25 and R26 on Antarctic stratospheric chlorine and ozone chemistry (including the branching ratio between the two reactions) can be neglected for most of the simulation period for which the Cl/ClO ratio remains low. Solely, in late September, when the Cl/ClO ratio

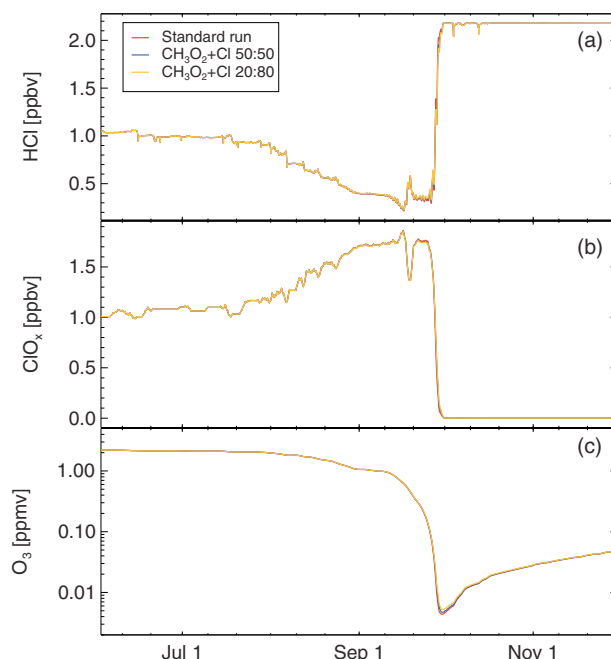
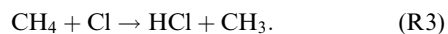


Fig. 9. Simulations including the reaction  $\text{CH}_3\text{O}_2 + \text{Cl} \rightarrow \text{products}$ . The panels show HCl (a), active chlorine ( $\text{ClO}_x$ , b), and ozone (c). The two branching ratios of this reaction and three decay channels for  $\text{CH}_3\text{O}_2$  are taken into account (see Table 2 for the details of the reactions implemented in the chemistry scheme). Ozone and  $\text{ClO}_x$  mixing ratios are shown as 24 hour averages.

increases strongly with decreasing ozone, a very slight impact of additional HCl formation (and thus less ozone depletion) is noticeable when the reaction  $\text{CH}_3\text{O}_2 + \text{Cl}$  is included, in particular when assuming a 0.2/0.8 branching ratio in favour of reaction R26.

#### 4. Discussion

The importance of methane oxidation and  $\text{HO}_x$  chemistry for ozone loss in polar spring has been recognised for some time (Crutzen et al., 1992; Müller and Crutzen, 1994; Müller et al., 1994; Carl et al., 1996; Portmann et al., 1996; Jaeglé et al., 1997). In particular in the Antarctic, declining ozone concentrations lead to a strong increase in Cl and therefore to an increasingly rapid rate of the reaction



This rapid rate of formation of HCl, however, does not lead to deactivation because of the action of the HCl null cycle C1 (see appendix); only when eventually an imbalance of gas phase HCl production and heterogeneous HCl destruction develops, a very rapid, irreversible conversion of active chlorine into HCl (i.e. deactivation) occurs (e.g. Crutzen et al., 1992; Douglass et al., 1995; Carl et al., 1996; Grooß et al., 2011; Müller et al., 2018). The rapid conversion of active chlorine to HCl in the Antarctic is obvious in observations (Grooß et al., 1997;

Santee et al., 2003, 2008; Sugita et al., 2013). A very rapid rate for reaction R3 in the lowermost stratosphere in late austral winter and in spring could also be observed as a signature in carbon isotope measurements in the lowermost stratosphere. Brenninkmeijer et al. (1996) measured isotopically very light CO ( $\delta^{13}\text{C}$  CO down to  $-47\text{‰}$ ), which may only be explained by the dominant production of isotopically light CO in the reaction of Cl with  $\text{CH}_4$  (reaction R3) and thus through extremely high Cl concentrations in austral spring (Müller et al., 1996).

A rapid rate of reaction R3 in the polar stratosphere with the associated formation of  $\text{CH}_3\text{O}_2$  radicals followed by the reaction of  $\text{CH}_3\text{O}_2 + \text{ClO}$  (reaction R6) leads to an enhanced production of  $\text{HO}_x$  radicals, as noted already in the first study on reaction R6 (Simon et al., 1989). For cold conditions in the polar regions, when heterogeneous reactions and uptake of  $\text{HNO}_3$  in the particle phase may occur, this enhanced production of  $\text{HO}_x$  radicals will lead to formation of HOCl followed by the heterogeneous reaction  $\text{HCl} + \text{HOCl}$  (reaction R2) (Crutzen et al., 1992; Müller and Crutzen, 1994; Müller et al., 1994; Jaeglé et al., 1997). Further, Portmann et al. (1996) pointed out that for conditions of no uptake of  $\text{HNO}_3$  in the particle phase and no denitrification,  $\text{HO}_x$  radicals will also partly be lost through the reaction  $\text{HNO}_3 + \text{OH}$  (in addition to the  $\text{HO}_x$  loss by HOCl). Lary and Toumi (1997) reported that halogen-catalysed methane oxidation chemistry including reaction R6 may also be important for the



ozone chemistry in the lower stratosphere outside of the polar regions.

The importance of the HCl null cycles (Müller et al., 2018, see also appendix), which has been corroborated here by a detailed analysis of the chemistry of  $\text{CH}_3\text{O}_2$  for the conditions of the polar lower stratosphere in winter and spring has a bearing for the relevance of reaction rates, both heterogeneous and gas-phase, in the polar stratosphere. As long as reactions are sufficiently fast to sustain cycles C1 and C2 and faster than potential competitive reactions, the exact values of rate constants do not matter. Thus, the fate of  $\text{CH}_3\text{O}_2$  is not sensitive here to the exact value of the rate constant of reaction R6 because the competitive reactions that would remove  $\text{CH}_3\text{O}_2$  otherwise (i.e. the self-reaction R13 and the  $\text{HO}_2$  reaction R8) are too slow to compete with reaction R6 for any realistic value of the rate constant for reaction R6 (see Section 3.2). The same argument applies to the reaction  $\text{CH}_3\text{O}_2 + \text{Cl}$  (reactions R25 and R26, see Section 3.4).

Similarly, the exact value of the rate of the heterogeneous reaction R2 (and other heterogeneous reactions) does not matter, as (for the conditions considered here) it will very likely be always fast enough to sustain cycles C1 and C2. This is consistent with studies, which find very little impact of the nature of heterogeneous reactions (i.e. liquid particles, NAT, and ice) on stratospheric polar chlorine and ozone chemistry (Wegner et al., 2012; Drdla and Müller, 2012; Wohltmann et al., 2013; Kirner et al., 2015). In particular, Kirner et al. (2015) find that for Antarctic chlorine and ozone loss chemistry even the impact of the substantial increase in heterogeneous reactivity through the formation of ice particles has very little effect on the simulated polar ozone loss; they report that in their simulations for high southern latitudes, heterogeneous chemistry on ice particles causes only up to 5 DU of additional ozone depletion.

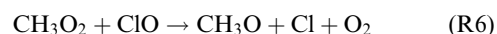
In our model simulations, we find evidence for an enhanced production of formaldehyde ( $\text{CH}_2\text{O}$ ) when including reaction R6 into the chemical scheme, with peak values more than a factor of three higher (Fig. 3) than without reaction R6. For the time period 8 September to 1 December 2003 indications of enhanced values of  $\text{CH}_2\text{O}$  have been found in remote sensing measurements of the MIPAS instrument (Fig. 7 in Steck et al., 2008) and other remote sensing measurements of  $\text{CH}_2\text{O}$  in the atmosphere are available (Ricaud et al., 2007; Dufour et al., 2009). For a more quantitative comparison, the averaging strategy for the remote sensing measurements should be tailored better to the conditions in the core of the Antarctic polar vortex in the lower stratosphere.

The same arguments apply to methanol. There are space borne measurements of methanol in the upper troposphere and lower stratosphere, albeit for much higher mixing ratios (Dufour et al., 2006; Santee et al., 2017). In-situ measurements of methanol in the remote free troposphere (5–10 km) range between 0.3 and 1.0 ppb (Singh et al., 1995) and measurements in the lower stratosphere are very variable with a mean value of  $\approx 100$  ppt (Singh et al., 2000). Measuring the low concentrations of methanol to be expected in the lower Antarctic stratosphere in spring (Fig. 8), will likely require selecting profiles showing extremely low ozone concentrations for an averaging procedure in remote sensing measurements.

The trajectory set-up used here, including a diabatic descent by about 35 K over the period of simulation, allows the chemical mechanisms to be analysed in detail. In contrast, analyses of chemical mechanisms over a polar winter and spring period on surfaces of a three-dimensional model, which are defined on isentropic or pressure surfaces will compare air volumes that are quite different over the period of interest (e.g. the air in the core of the polar vortex in the lower stratosphere between mid June and mid July descends by about 20 K). However, in our simulations mixing is entirely neglected. Although some mixing will certainly occur in reality, there is evidence that the core of the Antarctic vortex constitutes an air mass that is relatively unaffected by mixing with air from the edge of the polar vortex (Michelsen et al., 1999; Lee et al., 2001; Solomon et al., 2015). Furthermore, mixing across the vortex edge is likely overestimated in state-of-the-art models even when employing sophisticated Lagrangian or Eulerian transport schemes (Hoppe et al., 2014).

## 5. Conclusions

The box-model studies for the lowermost stratosphere (390–430 K potential temperature) in the core of the Antarctic vortex presented here corroborate and extend conclusions reported earlier (e.g. Crutzen et al., 1992; Grooß et al., 2011; Müller et al., 2018), namely that the reaction



is a key reaction for polar ozone loss. Recent new measurements of the rate constant (Leather et al., 2012; Ward and Rowley, 2016) do not alter this picture and have very little influence on the results of the box-model simulations reported here. The importance of reaction R6 stems from the supply of  $\text{HO}_2$  that leads to formation of  $\text{HOCl}$  and thus ultimately to a depletion of HCl. In this way, reaction R6 leads to an HCl null cycle that allows the maintenance of high levels of active chlorine in spring

when the rate of chlorine deactivation through HCl formation is high (Müller et al., 2018). The action of these null cycles allows the concentrations of active chlorine to remain high and thus ozone depletion to proceed. During the period of the lowest ozone concentrations enhanced values of  $\text{CH}_3\text{O}_2$  are simulated and, as a consequence, enhanced values of formaldehyde (about 100 ppt) and methanol (about 5 ppt).

Reaction R6 has an alternative product channel, namely formation of methylhypochlorite



which has hitherto only received very limited consideration in studies of polar ozone loss (Helleis et al., 1994; Crowley et al., 1994; Carl et al., 1996; Müller et al., 1996). Here, because of the importance of  $\text{CH}_3\text{O}_2$  for Antarctic chlorine chemistry and ozone loss, we have conducted a study employing the full polar chemistry of  $\text{CH}_3\text{O}_2$  including both reactions R6 and R7 and the reaction  $\text{CH}_3\text{O}_2 + \text{Cl}$ . First, we find very little impact of the reaction  $\text{CH}_3\text{O}_2 + \text{Cl}$  on polar chlorine chemistry. Second, we find that formation of  $\text{CH}_3\text{OCl}$  in the reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$  (R7) does not constitute a substantial change to the relevance of the reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$  for polar ozone loss in the core of the vortex in the lower stratosphere, provided that the main loss channels for  $\text{CH}_3\text{OCl}$ , namely photolysis and reaction with Cl are taken into account. In our simulations,  $\text{CH}_3\text{OCl}$  mixing ratios in the lowermost Antarctic stratosphere range between 10 and 250 ppt and peak at the time when the lowest ozone mixing ratios are reached. We have also investigated the possible impact of the hypothetical heterogeneous reaction of  $\text{CH}_3\text{OCl}$  with HCl (Kenner et al., 1993; Crowley et al., 1994), which however does not significantly alter the chemical processes that determine active chlorine concentrations and polar ozone loss.

In summary, the reaction  $\text{CH}_3\text{O}_2 + \text{ClO}$  is important for polar ozone loss because it allows effective HCl null cycles to proceed which are responsible for the maintenance of high levels of active chlorine in polar spring when ozone is chemically destroyed at a large rate. The relevance of this reaction for polar ozone chemistry is not changed by including the formation of methylhypochlorite ( $\text{CH}_3\text{OCl}$ ) in this reaction (Helleis et al., 1994; Biggs et al., 1995; Tyndall et al., 1998) into the chemical scheme.

## Acknowledgements

We thank John Crowley, Ines Tritscher, and Reinhold Spang for very helpful discussions. Part of this work was done in the frame of the master's thesis of A.M.Z at the Technische Universität Darmstadt; we thank Martin

Ebert for supervising the thesis. We thank the European Centre for Medium-Range Weather Forecasts (ECMWF) for providing meteorological data sets.

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

Part of this work was funded by the European Community's Seventh Framework Programme (FP7/2007–2013) as a contribution to “StratoClim” (grant agreement no. 603557).

## Supplemental data

Supplemental data for this article can be accessed [here](#).

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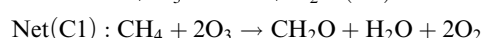
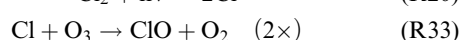
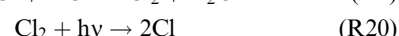
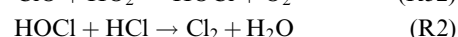
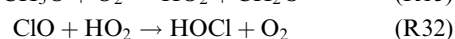
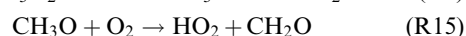
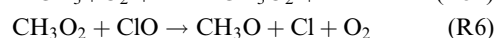
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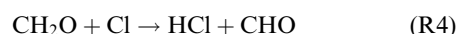
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## Appendix

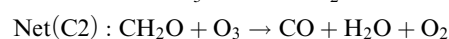
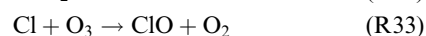
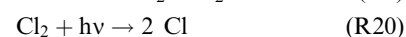
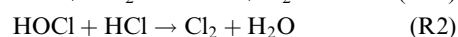
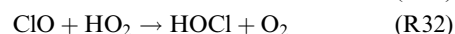
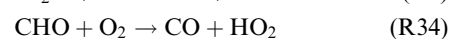
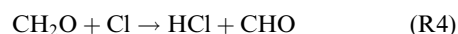
The HCl null cycles responsible for the maintenance of high levels of active chlorine throughout Antarctic spring have been formulated previously, but are repeated in this appendix for reference. Cycle C1 (Crutzen et al., 1992; Müller and Crutzen, 1994; Müller et al., 2018) starts with HCl production in the reaction  $\text{CH}_4 + \text{Cl}$



Further, the formation of HCl in the reaction



leads to the following cycle (C2, Müller et al., 2018):



In an earlier study (Müller et al., 2018), the efficiency of these cycles for maintaining high levels of active chlorine in polar spring was demonstrated based on the temporal development of the rates of the key chemical processes by applying a unique algorithm for the determination of chemical pathways (Lehmann, 2004). Müller et al. (2018) reported for the first days of September rates of HCl recycling of 88 ppt in 10 days through cycle C1 and of 26 ppt in 10 days through cycle C2. In contrast, for the last days of September (21–30), the rate of recycling of HCl in cycles C1 and C2 is reported to be much more rapid (rates of 3.7 ppb in 10 days and 2.9 ppb in 10 days respectively Müller et al., 2018).