

1 Chemical reaction mechanisms:
Mechanism for bromine containing species:

Reaction	k [(molec. cm ⁻³) ¹⁻ⁿ s ⁻¹]	Reaction order n	Reference	Reaction No.
$O_3 + h\nu \rightarrow O(^1D) + O_2$	$4.70 \cdot 10^{-7}$	1	Lehrer et al. (2004)	(R1)
$O(^1D) + O_2 \rightarrow O_3$	$4.20 \cdot 10^{-11}$	2	Atkinson et al. (2006)	(R2)
$O(^1D) + H_2O \rightarrow 2OH$	$2.30 \cdot 10^{-10}$	2	Atkinson et al. (2006)	(R3)
$Br + O_3 \rightarrow BrO + O_2$	$7.65 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R4)
$Br_2 + h\nu \rightarrow 2Br$	0.021	1	Lehrer et al. (2004)	(R5)
$BrO + h\nu \xrightarrow{O_2} Br + O_3$	0.014	1	Lehrer et al. (2004)	(R6)
$BrO + BrO \rightarrow 2Br + O_2$	$1.92 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R7)
$BrO + BrO \rightarrow Br_2 + O_2$	$5.42 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R8)
$BrO + HO_2 \rightarrow HOBr + O_2$	$4.31 \cdot 10^{-11}$	2	Atkinson et al. (2006)	(R9)
$HOBr + h\nu \rightarrow Br + OH$	$3.00 \cdot 10^{-4}$	1	Lehrer et al. (2004)	(R10)
$CO + OH(+M) \xrightarrow{O_2} HO_2 + CO_2(+M)$	$2.40 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R11)
$Br + HO_2 \rightarrow HBr + O_2$	$1.42 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R12)
$HOBr + HBr \xrightarrow{\text{aerosol}} Br_2 + H_2O$	See text			(R13)
$HOBr + H^+ + Br^- \xrightarrow{\text{snow/ice}} Br_2 + H_2O$	See text			(R14)
$Br + HCHO \xrightarrow{O_2} HBr + CO + HO_2$	$7.65 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R15)
$Br + CH_3CHO \xrightarrow{O_2} HBr + CH_3CO_3$	$3.22 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R16)
$Br_2 + OH \rightarrow HOBr + Br$	$5.66 \cdot 10^{-11}$	2	Atkinson et al. (2006)	(R17)
$HBr + OH \rightarrow H_2O + Br$	$1.23 \cdot 10^{-11}$	2	Atkinson et al. (2006)	(R18)
$Br + C_2H_2 \xrightarrow{3O_2} 2CO + 2HO_2 + Br$	$4.20 \cdot 10^{-14}$	2	Borken (1996)	(R19)
$Br + C_2H_2 \xrightarrow{2O_2} 2CO + HO_2 + HBr$	$8.92 \cdot 10^{-14}$	2	Borken (1996)	(R20)
$Br + C_2H_4 \xrightarrow{3.5O_2} 2CO + 2HO_2 + Br + H_2O$	$2.53 \cdot 10^{-13}$	2	Barnes et al. (1993)	(R21)
$Br + C_2H_4 \xrightarrow{2.5O_2} 2CO + HO_2 + HBr + H_2O$	$5.34 \cdot 10^{-13}$	2	Barnes et al. (1993)	(R22)
$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O$	$2.46 \cdot 10^{-15}$	2	Atkinson et al. (2006)	(R23)
$BrO + CH_3O_2 \rightarrow Br + HCHO + HO_2$	$1.60 \cdot 10^{-12}$	2	Aranda et al. (1997)	(R24)
$BrO + CH_3O_2 \rightarrow HOBr + HCHO + 0.5O_2$	$4.10 \cdot 10^{-12}$	2	Aranda et al. (1997)	(R25)
$OH + O_3 \rightarrow HO_2 + O_2$	$3.94 \cdot 10^{-14}$	2	Atkinson et al. (2006)	(R26)
$OH + HO_2 \rightarrow H_2O + O_2$	$1.26 \cdot 10^{-10}$	2	Atkinson et al. (2006)	(R27)
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$1.56 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R28)
$OH + OH \xrightarrow{O_2} H_2O + O_3$	$2.12 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R29)
$HO_2 + O_3 \rightarrow OH + 2O_2$	$1.37 \cdot 10^{-15}$	2	Atkinson et al. (2006)	(R30)
$HO_2 + HO_2 \rightarrow O_2 + H_2O_2$	$4.65 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R31)
$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$1.46 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R32)
$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	$3.80 \cdot 10^{-15}$	2	Atkinson et al. (2006)	(R33)
$C_2H_5 + O_2(+M) \rightarrow C_2H_5O_2(+M)$	$7.12 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R34)
$C_2H_4 + OH(+M) \xrightarrow{1.5O_2} CH_3O_2 + CO + H_2O(+M)$	$8.20 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R35)
$C_2H_4 + O_3 \rightarrow HCHO + CO + H_2O$	$4.33 \cdot 10^{-19}$	2	Sander et al. (1997)	(R36)
$C_2H_2 + OH(+M) \xrightarrow{1.5O_2} HCHO + CO + HO_2(+M)$	$7.50 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R37)
$C_3H_8 + OH \xrightarrow{2O_2} C_2H_5O_2 + CO + 2H_2O$	$8.13 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R38)
$HCHO + OH \xrightarrow{O_2} CO + H_2O + HO_2$	$9.29 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R39)
$CH_3CHO + OH \xrightarrow{O_2} CH_3CO_3 + H_2O$	$1.86 \cdot 10^{-11}$	2	Atkinson et al. (2006)	(R40)
$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$	$7.81 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R41)
$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	$3.97 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R42)
$CH_3OOH + OH \rightarrow HCHO + OH + H_2O$	$2.09 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R43)
$CH_3OOH + Br \rightarrow CH_3O_2 + HBr$	$5.19 \cdot 10^{-15}$	2	Atkinson et al. (2006)	(R44)
$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$	$3.06 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R45)
$CH_3O_2 + CH_3O_2 \xrightarrow{O_2} 2HCHO + 2HO_2$	$1.50 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R46)
$CH_3OH + OH \xrightarrow{O_2} HCHO + HO_2 + H_2O$	$7.68 \cdot 10^{-13}$	2	Atkinson et al. (2006)	(R47)
$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5O + C_2H_5O + O_2$	$6.80 \cdot 10^{-14}$	2	Atkinson et al. (2006)	(R48)
$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	$7.44 \cdot 10^{-15}$	2	Sander et al. (1997)	(R49)
$C_2H_5O + O_2 \rightarrow CH_3O_2 + HCHO$	$7.51 \cdot 10^{-17}$	2	Sander et al. (1997)	(R50)
$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2$	$1.31 \cdot 10^{-11}$	2	Atkinson et al. (2006)	(R51)
$C_2H_5OOH + OH \rightarrow C_2H_5O_2 + H_2O$	$8.21 \cdot 10^{-12}$	2	Sander et al. (1997)	(R52)
$C_2H_5OOH + Br \rightarrow C_2H_5O_2 + HBr$	$5.19 \cdot 10^{-15}$	2	Sander et al. (1997)	(R53)
$OH + OH(+M) \rightarrow H_2O_2(+M)$	$5.21 \cdot 10^{-12}$	2	Atkinson et al. (2006)	(R54)
$H_2O_2 + h\nu \rightarrow 2OH$	$2.00 \cdot 10^{-6}$	1	Lehrer et al. (2004)	(R55)

Mechanism for nitrogen containing species:

Reaction	k [(molec. cm ⁻³) ¹⁻ⁿ s ⁻¹]	Reaction order n	Reference	Reaction No.
NO + O ₃ → NO ₂ + O ₂	8.89 10 ⁻¹⁵	2	Atkinson et al. (2006)	(R56)
NO + HO ₂ → NO ₂ + OH	9.38 10 ⁻¹²	2	Atkinson et al. (2006)	(R57)
NO ₂ + O ₃ → NO ₃ + O ₂	9.02 10 ⁻¹⁸	2	Atkinson et al. (2006)	(R58)
NO ₂ + OH(+M) → HNO ₃ (+M)	1.62 10 ⁻¹¹	2	Atkinson et al. (2006)	(R59)
NO + NO ₃ → 2NO ₂	2.76 10 ⁻¹¹	2	Atkinson et al. (2006)	(R60)
HONO + OH → NO ₂ + H ₂ O	7.40 10 ⁻¹²	2	Atkinson et al. (2006)	(R61)
HO ₂ + NO ₂ (+M) → HNO ₄ (+M)	1.61 10 ⁻¹²	2	Atkinson et al. (2006)	(R62)
HNO ₄ (+M) → NO ₂ + HO ₂ (+M)	4.02 10 ⁻⁴	1	Atkinson et al. (2006)	(R63)
HNO ₄ + OH → NO ₂ + H ₂ O + O ₂	6.05 10 ⁻¹²	2	Atkinson et al. (2006)	(R64)
NO + OH(+M) → HONO(+M)	1.36 10 ⁻¹¹	2	Atkinson et al. (2006)	(R65)
OH + NO ₃ → NO ₂ + HO ₂	2.00 10 ⁻¹¹	2	Atkinson et al. (2006)	(R66)
HNO ₃ + $h\nu$ → NO ₂ + OH	4.40 10 ⁻⁸	1	Lehrer et al. (2004)	(R67)
NO ₂ + $h\nu$ $\xrightarrow{O_2}$ NO + O ₃	3.50 10 ⁻³	1	Lehrer et al. (2004)	(R68)
NO ₃ + $h\nu$ $\xrightarrow{O_2}$ NO ₂ + O ₃	1.40 10 ⁻¹	1	Lehrer et al. (2004)	(R69)
NO ₃ + $h\nu$ → NO + O ₂	1.70 10 ⁻²	1	Lehrer et al. (2004)	(R70)
NO + CH ₃ O ₂ $\xrightarrow{O_2}$ HCHO + HO ₂ + NO ₂	8.44 10 ⁻¹²	2	Atkinson et al. (2006)	(R71)
NO ₃ + CH ₃ OH $\xrightarrow{O_2}$ HCHO + HO ₂ + HNO ₃	6.38 10 ⁻¹⁷	2	Atkinson et al. (2006)	(R72)
NO ₃ + HCHO $\xrightarrow{O_2}$ CO + HO ₂ + HNO ₃	5.80 10 ⁻¹⁶	2	Atkinson et al. (2006)	(R73)
NO + C ₂ H ₅ O ₂ $\xrightarrow{O_2}$ CH ₃ CHO + NO ₂ + HO ₂	8.70 10 ⁻¹²	2	Atkinson et al. (2006)	(R74)
NO + CH ₃ CO ₃ $\xrightarrow{O_2}$ CH ₃ O ₂ + NO ₂ + CO ₂	2.00 10 ⁻¹¹	2	Atkinson et al. (2006)	(R75)
NO ₂ + CH ₃ CO ₃ (+M) → PAN(+M)	1.33 10 ⁻¹²	2	Atkinson et al. (2006)	(R76)
Br + NO ₂ (+M) → BrNO ₂ (+M)	5.03 10 ⁻¹²	2	Atkinson et al. (2006)	(R77)
Br + NO ₃ (+M) → BrO + NO ₂ (+M)	1.60 10 ⁻¹¹	2	Atkinson et al. (2006)	(R78)
BrO + NO ₂ (+M) → BrONO ₂ (+M)	3.89 10 ⁻¹²	2	Atkinson et al. (2006)	(R79)
BrO + NO → Br + NO ₂	2.38 10 ⁻¹¹	2	Atkinson et al. (2006)	(R80)
BrONO ₂ + $h\nu$ → NO ₂ + BrO	3.40 10 ⁻⁴	1	Lehrer et al. (2004)	(R81)
BrNO ₂ + $h\nu$ → NO ₂ + Br	9.30 10 ⁻⁵	1	Lehrer et al. (2004)	(R82)
BrONO ₂ + H ₂ O $\xrightarrow{\text{aerosol}}$ HOBr + HNO ₃	See text			(R83)
PAN + $h\nu$ → NO ₂ + CH ₃ CO ₃	3.03 10 ⁻⁷	1	DeMore et al. (1997)	(R84)
HNO ₃ + $h\nu$ $\xrightarrow{\text{aerosol}}$ OH + NO ₂	See text			(R85)
BrONO ₂ + H ₂ O $\xrightarrow{\text{ice/snow}}$ HOBr + HNO ₃	See text			(R86)

Mechanism for chlorine containing species:

Reaction	k [(molec. cm ⁻³) ¹⁻ⁿ s ⁻¹]	Reaction order n	Reference	Reaction No.
CH ₃ OOH + Cl → CH ₃ O ₂ + HCl	5.70 10 ⁻¹¹	2	Atkinson et al. (2006)	(R87)
C ₂ H ₅ O ₂ H + Cl → C ₂ H ₅ O ₂ + HCl	5.70 10 ⁻¹¹	2	Sander et al. (1997)	(R88)
HO ₂ + Cl → O ₂ + HCl	3.48 10 ⁻¹¹	2	Atkinson et al. (2006)	(R89)
HO ₂ + Cl → OH + ClO	7.17 10 ⁻¹²	2	Atkinson et al. (2006)	(R90)
H ₂ O ₂ + Cl → HO ₂ + HCl	2.46 10 ⁻¹³	2	Atkinson et al. (2006)	(R91)
O ₃ + Cl → O ₂ + ClO	1.06 10 ⁻¹¹	2	Atkinson et al. (2006)	(R92)
CH ₄ + Cl $\xrightarrow{O_2}$ CH ₃ O ₂ + HCl	5.13 10 ⁻¹⁴	2	Atkinson et al. (2006)	(R93)
C ₂ H ₂ + Cl $\xrightarrow{3O_3}$ 2CO + 2HO ₂ + Cl	2.00 10 ⁻¹¹	2	Borken (1996)	(R94)
C ₂ H ₂ + Cl $\xrightarrow{2O_3}$ 2CO + HO ₂ + HCl	4.24 10 ⁻¹¹	2	Borken (1996)	(R95)
C ₂ H ₄ + Cl $\xrightarrow{3.5O_3}$ 2CO + 2HO ₂ + Cl + H ₂ O	3.92 10 ⁻¹¹	2	Atkinson et al. (2006)	(R96)
C ₂ H ₄ + Cl $\xrightarrow{2.5O_3}$ 2CO + HO ₂ + HCl + H ₂ O	8.32 10 ⁻¹¹	2	Atkinson et al. (2006)	(R97)
C ₂ H ₆ + Cl → C ₂ H ₅ + HCl	5.60 10 ⁻¹¹	2	Atkinson et al. (2006)	(R98)
C ₃ H ₈ + Cl $\xrightarrow{2.5O_3}$ C ₂ H ₅ O ₂ + CO ₂ + HCl + H ₂ O	1.40 10 ⁻¹⁰	2	Atkinson et al. (2006)	(R99)
HCHO + Cl $\xrightarrow{O_2}$ CO + HCl + HO ₂	7.19 10 ⁻¹¹	2	Atkinson et al. (2006)	(R100)
CH ₃ CHO + Cl $\xrightarrow{O_2}$ HCl + CH ₃ CO ₃	7.20 10 ⁻¹¹	2	Atkinson et al. (2006)	(R101)
OH + Cl ₂ → Cl + HOCl	4.28 10 ⁻¹⁴	2	Atkinson et al. (2006)	(R102)
OH + HCl → Cl + H ₂ O	6.68 10 ⁻¹³	2	Atkinson et al. (2006)	(R103)
OH + HOCl → ClO + H ₂ O	4.32 10 ⁻¹³	2	Atkinson et al. (2006)	(R104)
OH + ClO → Cl + HO ₂	1.72 10 ⁻¹¹	2	Atkinson et al. (2006)	(R105)
OH + ClO → HCl + O ₂	3.50 10 ⁻¹³	2	Atkinson et al. (2006)	(R106)
ClO + ClO → Cl ₂ + O ₂	2.11 10 ⁻¹⁵	2	Atkinson et al. (2006)	(R107)
ClO + ClO → 2Cl + O ₂	2.25 10 ⁻¹⁵	2	Atkinson et al. (2006)	(R108)
ClO + ClO → Cl + OCIO	1.73 10 ⁻¹⁵	2	Atkinson et al. (2006)	(R109)
ClO + ClO(+M) → Cl ₂ O ₂ (+M)	4.42 10 ⁻¹³	2	Atkinson et al. (2006)	(R110)
Cl ₂ O ₂ (+M) → ClO + ClO(+M)	4.81 10 ⁻¹	1	Atkinson et al. (2006)	(R111)
ClO + HO ₂ → HOCl + O ₂	7.21 10 ⁻¹²	2	Atkinson et al. (2006)	(R112)
ClO + CH ₃ O ₂ → Cl + HCHO + HO ₂	1.36 10 ⁻¹²	2	Atkinson et al. (2006)	(R113)
ClO + NO → Cl + NO ₂	1.94 10 ⁻¹¹	2	Atkinson et al. (2006)	(R114)
ClO + NO ₂ (+M) → ClONO ₂ (+M)	2.77 10 ⁻¹²	2	Atkinson et al. (2006)	(R115)
Cl + ClONO ₂ → Cl ₂ + NO ₃	1.26 10 ⁻¹¹	2	Atkinson et al. (2006)	(R116)
OCIO + NO → ClO + NO ₂	2.44 10 ⁻¹³	2	DeMore et al. (1997)	(R117)
ClONO ₂ + OH → HOCl + NO ₃	3.34 10 ⁻¹³	2	Atkinson et al. (2006)	(R118)
ClO + BrO → Br + OCIO	8.47 10 ⁻¹²	2	Atkinson et al. (2006)	(R119)
ClO + BrO → Br + Cl + O ₂	6.80 10 ⁻¹²	2	Atkinson et al. (2006)	(R120)
ClO + BrO → BrCl + O ₂	1.12 10 ⁻¹²	2	Atkinson et al. (2006)	(R121)
Br + OCIO → BrO + ClO	1.69 10 ⁻¹³	2	Atkinson et al. (2006)	(R122)
Br + Cl ₂ O ₂ → BrCl + ClOO	3.00 10 ⁻¹²	2	Atkinson et al. (2006)	(R123)
Br ₂ + Cl → BrCl + Br	1.20 10 ⁻¹⁰	2	Sander et al. (1997)	(R124)
BrCl + Br → Br ₂ + Cl	3.30 10 ⁻¹⁵	2	Sander et al. (1997)	(R125)
Br + Cl ₂ → BrCl + Cl	1.10 10 ⁻¹⁵	2	Sander et al. (1997)	(R126)
BrCl + Cl → Br + Cl ₂	1.50 10 ⁻¹¹	2	Sander et al. (1997)	(R127)
HOBr + HCl $\xrightarrow{\text{aerosol}}$ BrCl + H ₂ O	See text			(R128)
HOBr + H ⁺ + Cl ⁻ $\xrightarrow{\text{snow/ice}}$ BrCl + H ₂ O	See text			(R129)
BrCl + $h\nu$ → Br + Cl	5.70 10 ⁻³	1	Lehrer et al. (2004)	(R130)
Cl ₂ + $h\nu$ → 2Cl	8.50 10 ⁻⁴	1	Lehrer et al. (2004)	(R131)
ClO + $h\nu$ $\xrightarrow{O_2}$ Cl + O ₃	5.00 10 ⁻⁷	1	Lehrer et al. (2004)	(R132)
HOCl + $h\nu$ → Cl + OH	8.60 10 ⁻⁵	1	Lehrer et al. (2004)	(R133)
ClONO ₂ + $h\nu$ → Cl + NO ₃	1.30 10 ⁻²	1	Lehrer et al. (2004)	(R134)
OCIO + $h\nu$ $\xrightarrow{O_2}$ ClO + O ₃	3.60 10 ⁻²	1	Lehrer et al. (2004)	(R135)

2 Determination of the uptake coefficient for the heterogeneous reactions for aerosols

For reaction (R13), the production of Br₂ is limited by the absorption of both gaseous HOBr and HBr in the suspended aerosol particles. The HOBr uptake coefficient, γ to the bulk of liquid phase can be expressed according to Hanson et al. (1994)

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{v_{\text{therm}}}{4H^*RT\sqrt{k_{\text{liq}}^I D_{\text{liq}} f(q)}}. \quad (1)$$

Here, α is the accommodation coefficient taken to be unity in the present study. The effective Henry constant, H^* , is applied for the species, which can dissociate in the liquid solutions, and it has the value of $1.7 \times 10^4 \text{ mol (L atm)}^{-1}$ for HOBr. k_{liq}^I is the first order liquid reaction rate constant of reaction (R13), which can be calculated as $k_{\text{liq}}^I = k_{\text{liq}}^{II} [\text{HBr}]_{\text{liq}} = k_{\text{liq}}^{II} H_{\text{HBr}}^* P_{\text{HBr}}$. The value of the second order liquid reaction rate constant, k_{liq}^{II} is $5 \times 10^4 \text{ L (mol s)}^{-1}$. The effective Henry constant of HBr for reaction (R13) is assumed to have a value of $3 \times 10^8 \text{ mol (L atm)}^{-1}$. For 10 ppt HBr, the partial pressure of gaseous HBr, $P_{\text{HBr}} = 10^{-11} \text{ atm}$. D_{liq} in Eq. (1) denotes the liquid HOBr diffusion coefficient, which is taken to be $5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The function $f(q)$ is defined as $f(q) = \coth(q) - (1/q)$, where $q = a\sqrt{k_{\text{liq}}^I/D_{\text{liq}}}$, and a is the typical aerosol radius taken to be $0.45 \mu\text{m}$. Thus, $\gamma = 0.12$ is obtained for a gas mixing ratio of 10 ppt HBr.

Similarly, for reaction (R128), $\gamma = 0.0027$, if the mixing ratio of HCl is 10 ppt, $k_{\text{liq}}^{II} = 10^5 \text{ L (mol s)}^{-1}$, and $H^* = 3 \times 10^6 \text{ mol (L atm)}^{-1}$.

3 Determination of the photolysis reaction rates

The photolysis reaction rates J are evaluated by using a three-coefficient formula (R oth, 1992, 2002)

$$J = J_0 \exp(b[1 - \sec(c\chi)]). \quad (2)$$

χ is the Solar Zenith Angle (SZA). The values for the coefficients J_0 , b , c for different chemical species are listed in Tab. S1. At 80°N , SZA varies following the relation (Lehrer et al., 2004)

$$\chi = \chi_0 - 4.11 \times 10^{-6} t + 6.5 \cos(2\pi t/86,400), \quad (3)$$

where the time t is in seconds. χ_0 denotes the initial value of SZA, which is taken to be 85.5° , corresponding to the date April 1 at this location. The second term on the RHS represents the change of SZA for different days in April, and the third term is the daily change of the SZA. The temporal evolution of the mixing ratios of the chemical species with varying SZA in bromine only mechanism with 200 m boundary layer height is presented in Fig. S1.

Table S1. Coefficients for the photolysis reaction rates, Eq. (2).

Species	$J_0 [\text{s}^{-1}]$	b	c
O ₃	$6.85 \cdot 10^{-5}$	3.510	0.820
Br ₂	$1.07 \cdot 10^{-1}$	0.734	0.900
BrO	$1.27 \cdot 10^{-1}$	1.290	0.857
HOBr	$2.62 \cdot 10^{-3}$	1.216	0.861
H ₂ O ₂	$2.75 \cdot 10^{-5}$	1.595	0.848
HNO ₃	$1.39 \cdot 10^{-6}$	2.094	0.848
NO ₂	$2.62 \cdot 10^{-2}$	1.068	0.871
NO ₃ →NO ₂	$6.20 \cdot 10^{-1}$	0.608	0.915
NO ₃ →NO	$7.03 \cdot 10^{-2}$	0.583	0.917
BrONO ₂	$3.11 \cdot 10^{-3}$	1.270	0.859
BrNO ₂	$1.11 \cdot 10^{-3}$	1.479	0.851
BrCl	$3.41 \cdot 10^{-2}$	0.871	0.887
Cl ₂	$7.37 \cdot 10^{-3}$	1.204	0.863
ClO	$1.08 \cdot 10^{-4}$	3.876	0.816
HOCl	$7.47 \cdot 10^{-4}$	1.396	0.855
ClONO ₂	$1.29 \cdot 10^{-4}$	1.286	0.861
OCIO	$2.61 \cdot 10^{-1}$	1.058	0.872

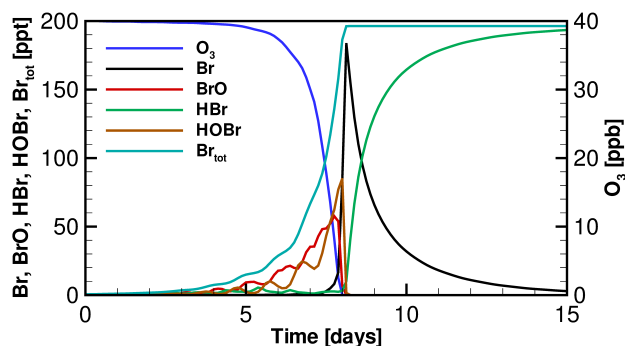


Fig. S1. Evolution of the mixing ratios of the chemical species with varying SZA using the bromine only mechanism for a 200 m boundary layer height.

4 Formation of Br during the ozone depletion stage

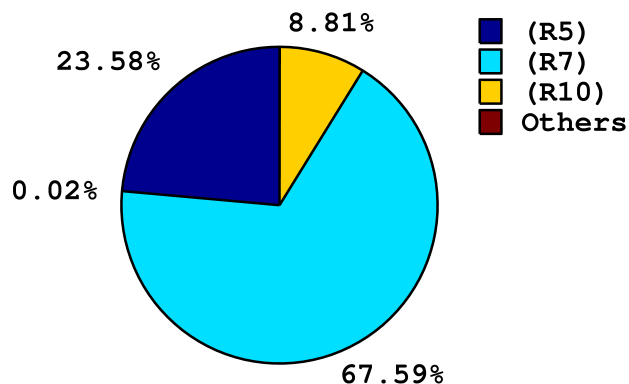
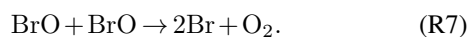


Fig. S2. Instantaneous contributions of various reactions to the Br formation at day 6 (depletion stage).

Figure S2 displays the different contributions to the formation of Br atoms at day 6, which is within the ozone depletion stage. The largest contribution to the formation of the bromine atoms comes from the BrO self-reaction



The reaction



contributes about 25% of the total formation of the Br atoms at this time.

However, it should be mentioned that the above values of the contributions by these reactions are different at other times.

5 Conversion of NO_x during the induction stage

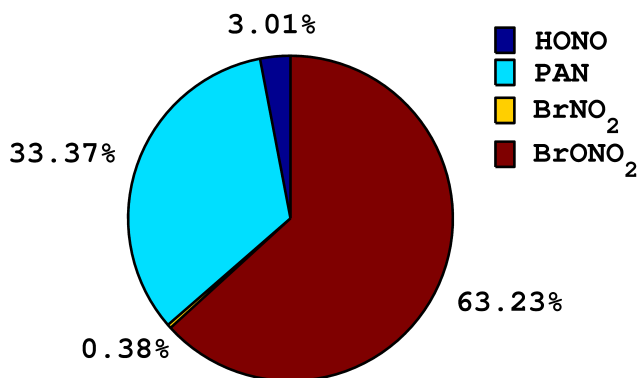
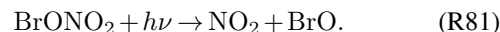


Fig. S3. Contributions to instantaneous conversion of NO_x at day 1 (induction stage).

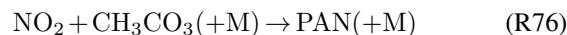
Concerning the instantaneous conversion of NO_x, a corresponding analysis is presented in Fig. S3 at day 1, which is in the induction stage. Most of the NO_x molecules are eventually converted to BrONO₂, which is caused by the combination of the reactions



and



The second product is PAN, which is produced through the combination of reactions



and



This results in an increase of the mixing ratios of both BrONO₂ and PAN, which makes the reactions associated with BrONO₂ and PAN become more important in the following ozone depletion stage.

6 Chlorine related chemical reaction mechanism

The mechanism including bromine, nitrogen and chlorine related species consists of 135 chemical reactions among 49 species. For the present computations, the reaction rate ratio $K_{\text{Br}_2/\text{BrCl}}$, of Br₂ and BrCl from the ice/snow surface, see Reactions (R14) and (R129), equals 1.0, which means that half of the deposited HOBr molecules are converted to Br₂, and the other half activate BrCl.

Figure S4 shows the profiles of the mixing ratios of the major chlorine containing species as well as ozone versus time for a boundary layer height of 200 m. The time lengths for the induction and the depletion stages using the chlorine containing mechanism are 7.4 days and 1.4 day, respectively. In the combined bromine and NO_x mechanism, these time scales are 3.4 and 1.0 days, so that the chlorine related mechanism hardly modifies the ozone depletion stage.

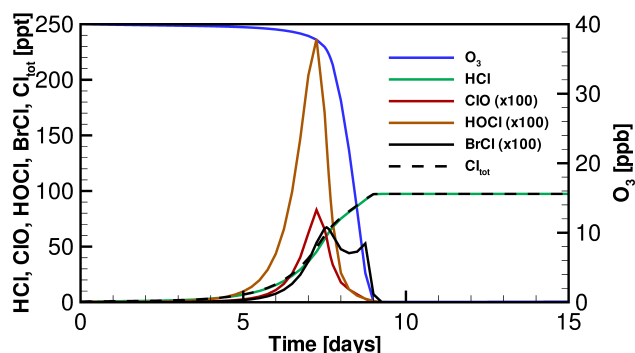


Fig. S4. Time evolution of ozone, chlorine containing species and total chlorine mixing ratios for a boundary layer height of 200 m.

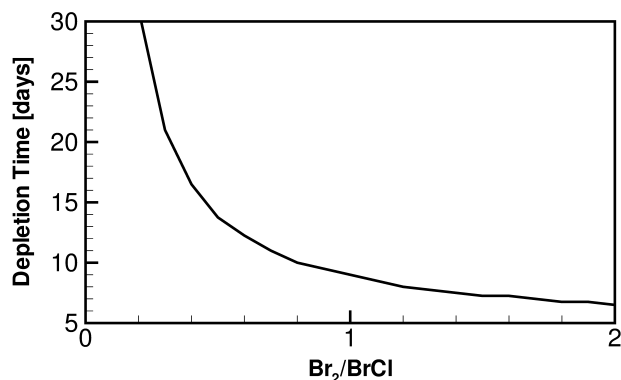


Fig. S5. Impact of the reaction rate ratio of (R14) and (R129), $K_{\text{Br}_2/\text{BrCl}}$, on the ozone depletion time.

The total chlorine mixing ratio is 100 ppt at the end of the event, mostly in the form of HCl. The mixing ratio of gaseous ClO is about 0.8 ppt, which is consistent with the measurements by Perner et al. (1999) at Ny-Ålesund, reporting the ClO mixing ratio to be less than 2 ppt.

A parameter study is performed for the influence of the reaction rate ratio $K_{\text{Br}_2/\text{BrCl}}$ from the ice/snow surface, cf. (R14) and (R129), on the total ozone depletion time. Figure S5 shows the total ozone depletion time to be about 6.5 days for $K_{\text{Br}_2/\text{BrCl}} = 2.0$. As the value of this ratio decreases, which means that less Br_2 is produced and more BrCl molecules are released from the ground surface, the ozone depletion event is retarded. When the ratio of the reaction rate ratio is less than 0.2, ozone depletion is hardly observed. This reveals that the ozone depletion time is strongly dependent on the reaction rate ratio $K_{\text{Br}_2/\text{BrCl}}$ for the formation of Br_2 and BrCl from the ice/snow surface. Adams et al. (2002) found in laboratory research that the major reaction product is Br_2 when the ice surface contains sufficient Br^- , whereas BrCl is released as the major product, if Br^- is significantly depleted in the ice or snow pack before ozone is consumed. Therefore, it can be concluded that the chemical composition of the ground surface may be important for the ozone depletion rate.

The change of bromine and chlorine atom concentrations with time versus ozone mixing ratio are plotted in Fig. S6. As the ozone depletes, an exponential increase of the bromine atom concentration is observed, whereas the enhancement of Cl is approximately steady. Thus, the destruction of ozone strongly depends on Br atoms and not on the Cl atoms. The calculated ratio of $[\text{Br}/\text{Cl}]$ during ozone depletion is of the order 10^3 , which means that more than 99% of the ozone is consumed directly by Br radicals. Previous experimental studies using the VOC decay measurement method suggest various values for the $[\text{Br}]/[\text{Cl}]$ ratio, ranging from tens to more than ten thousand (Jobson et al., 1994, Solberg et al., 1996, Ramacher et al., 1999, Boudries and Bottenheim,

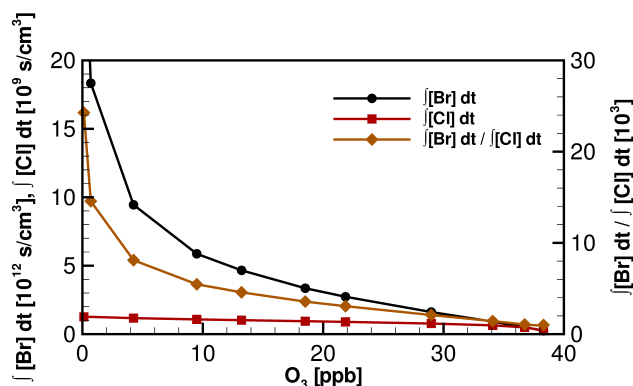


Fig. S6. Time integrated halogen atom concentration and the $[\text{Br}]/[\text{Cl}]$ ratio versus the ozone mixing ratio.

2000). However, most often, values in the order of some hundreds are found. Michalowski et al. (2000) suggested that the possible reason for the relatively high modeled value of the $[\text{Br}/\text{Cl}]$ ratio may be an underestimation of the Cl mixing ratio. In the present model, the gas phase Cl atom concentration is about $0.6 \cdot 10^4 \text{ molec. cm}^{-3}$, which is lower than the range from $2.0 \cdot 10^4 \text{ molec. cm}^{-3}$ to $1.0 \cdot 10^5 \text{ molec. cm}^{-3}$ proposed by Stephens et al. (2012) based on the data collected in spring of 2009 in Barrow, Alaska – this may also contribute to the high modeled value of $[\text{Br}/\text{Cl}]$. Spicer et al. (2002) recommend that an additional unknown Cl source should be assumed, which has not yet been considered in any study so far.

The present investigation of the influence of chlorine chemistry on ozone depletion shows that chlorine containing species have minor direct influence compared to NO_x and bromine chemistry.