

Supplement of Atmos. Chem. Phys. Discuss., 15, 8329–8360, 2015  
<http://www.atmos-chem-phys-discuss.net/15/8329/2015/>  
doi:10.5194/acpd-15-8329-2015-supplement  
© Author(s) 2015. CC Attribution 3.0 License.



*Supplement of*

## **The NO<sub>x</sub> dependence of bromine chemistry in the Arctic atmospheric boundary layer**

**K. D. Custard et al.**

*Correspondence to:* K. D. Custard (kdcustard@gmail.com)

**Table S1.** Gas-phase chemical reactions used in the model. All rate constants are calculated for a temperature of 248 K unless otherwise noted and are expressed in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Reaction	Rate Constant	Reference
$\text{O}(^1D) + \text{M} \rightarrow \text{O}(^3P)$	$3.34 \times 10^{-11}$	<i>Ravishankara et al.</i> [2002]
$\text{O}(^3P) + \text{O}_2 \rightarrow \text{O}_3$	$2.12 \times 10^{-14}$	<i>Atkinson et al.</i> [2004]
$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	$2.2 \times 10^{-10}$	<i>Atkinson et al.</i> [2004]
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2$	$3.84 \times 10^{-14}$	<i>Atkinson et al.</i> [2004]
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O}$	$1.34 \times 10^{-10}$	<i>Atkinson et al.</i> [2004]
$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$1.52 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
$\text{OH} + \text{O}(^3P) \rightarrow \text{O}_2$	$3.74 \times 10^{-11}$	<i>Atkinson et al.</i> [2004]
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}(^3P)$	$1.74 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	$1.86 \times 10^{-11}$	<i>Atkinson et al.</i> [2004]
$\text{OH} + \text{NO}_3 \rightarrow \text{HO}_2 + \text{NO}_2$	$2.0 \times 10^{-11}$	<i>Atkinson et al.</i> [2004]
$\text{HO}_2 + \text{NO}_3 \rightarrow \text{HNO}_3$	$4.0 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	$1.39 \times 10^{-15}$	<i>Atkinson et al.</i> [2004]
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$2.58 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
$\text{NO} + \text{OH} \rightarrow \text{HONO}$	$3.49 \times 10^{-11}$	<i>Atkinson et al.</i> [2004]
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	$9.59 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2$	$7.09 \times 10^{-15}$	<i>Sander et al.</i> [2006]
$\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$	$2.98 \times 10^{-11}$	<i>Sander et al.</i> [2006]
$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	$1.2 \times 10^{-10}$	<i>Atkinson et al.</i> [2004]
$\text{NO}_2 + \text{HO}_2 \leftrightarrow \text{HNO}_4$	f: $8.6 \times 10^{-12}$ r: $1.32 \times 10^{-4}$	<i>Atkinson et al.</i> [2004]
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3$	$6.15 \times 10^{-18}$	<i>Sander et al.</i> [2006]
$\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$	f: $1.83 \times 10^{-12}$ r: $3.76 \times 10^{-5}$	<i>Atkinson et al.</i> [2004]
$\text{NO}_2 + \text{CH}_3\text{COOO} \leftrightarrow \text{PAN}$	f: $1.4 \times 10^{-11}$ r: $3.1 \times 10^{-8}$	<i>Atkinson et al.</i> [2004]
$\text{NO}_3 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$	$4.36 \times 10^{-17}$	<i>Sander et al.</i> [2006]
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_3$	$2.6 \times 10^{-22}$	<i>Atkinson et al.</i> [2004]
$\text{HONO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	$3.74 \times 10^{-12}$	<i>Sander et al.</i> [2006]
$\text{HNO}_3 + \text{OH} \rightarrow \text{NO}_3 + \text{H}_2\text{O}$	$1.5 \times 10^{-13}$	<i>Atkinson et al.</i> [2004]
$\text{HNO}_4 + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	$6.2 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
$\text{CO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2$	$2.4 \times 10^{-13}$	<i>Atkinson et al.</i> [2004]
$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3\text{OO} + \text{H}_2\text{O}$	$1.87 \times 10^{-15}$	<i>Sander et al.</i> [2006]
$\text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{C}_2\text{H}_2\text{OH}$	$7.8 \times 10^{-13}$	<i>Atkinson et al.</i> [2004]
$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5\text{OO}$	$1.18 \times 10^{-13}$	<i>Lurmann et al.</i> [1986]
$\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{C}_2\text{H}_4\text{OH}$	$1.02 \times 10^{-11}$	<i>hahtin et al.</i> [2003]
$\text{C}_3\text{H}_8 + \text{OH} \rightarrow \text{nC}_3\text{H}_7\text{O}_2$	$1.56 \times 10^{-13}$	<i>Harris and Kerr</i> [1988]
$\text{C}_3\text{H}_8 + \text{OH} \rightarrow \text{iC}_3\text{H}_7\text{O}_2$	$6.64 \times 10^{-13}$	<i>Harris and Kerr</i> [1988]
$\text{C}_3\text{H}_6 + \text{OH} \rightarrow \text{C}_3\text{H}_6\text{OH}$	$3.63 \times 10^{-11}$	<i>Atkinson et al.</i> [2004]
$\text{C}_3\text{H}_6\text{O} + \text{OH} \rightarrow \text{Products}$	$2.51 \times 10^{-11}$	<i>Atkinson et al.</i> [2004]
$\text{nC}_3\text{H}_7\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{C}_3\text{H}_6\text{O} + \text{HO}_2$	$5.4 \times 10^{-11}$	<i>Eberhard et al.</i> [1996]
$\text{iC}_3\text{H}_7\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{COCH}_3 + \text{HO}_2$	$1.2 \times 10^{-11}$	<i>Eberhard and Howard</i> [1996]
$\text{nC}_4\text{H}_{10} + \text{OH} \rightarrow \text{nC}_4\text{H}_9\text{OO}$	$1.64 \times 10^{-12}$	<i>Donahue et al.</i> [1998]
$\text{iC}_4\text{H}_{10} + \text{OH} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{OO}$	$1.65 \times 10^{-12}$	<i>Donahue et al.</i> [1998]
$\text{nC}_4\text{H}_9\text{OO} + \text{NO} \rightarrow \text{n-Butanal} + \text{NO}_2 + \text{HO}_2$	$5.4 \times 10^{-11}$	<i>Michalowski et al.</i> [2000]
$\text{nC}_4\text{H}_9\text{OO} + \text{CH}_3\text{OO} \rightarrow \text{n-Butanal} + \text{HCHO} + \text{HO}_2 + \text{HO}_2$	$6.7 \times 10^{-13}$	<i>Michalowski et al.</i> [2000]
$\text{nC}_4\text{H}_9\text{OO} + \text{CH}_3\text{OO} \rightarrow \text{n-Butanal} + \text{CH}_3\text{OH}$	$2.3 \times 10^{-13}$	<i>Michalowski et al.</i> [2000]
$\text{nC}_4\text{H}_9\text{OO} + \text{CH}_3\text{OO} \rightarrow \text{nC}_4\text{H}_9\text{OH} + \text{HCHO}$	$2.3 \times 10^{-13}$	<i>Michalowski et al.</i> [2000]
$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{O}$	$7.09 \times 10^{-13}$	<i>Atkinson et al.</i> [2004]
$\text{n-Butanal} + \text{OH} \rightarrow \text{Products}$	$2.0 \times 10^{-11}$	<i>Michalowski et al.</i> [2000]
$\text{CH}_3\text{OO} + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH}$	$8.82 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
$\text{C}_2\text{H}_5\text{OO} + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5\text{OOH}$	$1.12 \times 10^{-11}$	<i>Atkinson et al.</i> [2004]
$\text{CH}_3\text{COOO} + \text{HO}_2 \rightarrow \text{CH}_3\text{COOOH}$	$2.54 \times 10^{-11}$	<i>DeMore et al.</i> [1997]

58	$C_2H_5OOH + OH \rightarrow C_2H_5OO$	$6.0 \times 10^{-12}$	Atkinson et al. [2004]
59	$CH_3OO + CH_3OO \rightarrow HCHO + HO_2$	$3.64 \times 10^{-13}$	Lurmann et al. [1986]
60	$CH_3OOH + OH \rightarrow HCHO + H_2O + OH$	$2.54 \times 10^{-12}$	Sander and Crutzen [1996]
61	$CH_3OOH + OH \rightarrow CH_3OO + H_2O$	$6.01 \times 10^{-12}$	Sander and Crutzen [1996]
62	$CH_3OO + HO_2 \rightarrow CH_3OOH$	$1.01 \times 10^{-11}$	Atkinson et al. [2004]
63	$CH_3OO + NO \rightarrow HCHO + HO_2 + NO_2$	$8.76 \times 10^{-12}$	Atkinson et al. [2004]
64	$CH_3OO + NO_2 \rightarrow CH_3OONO_2$	$9.63 \times 10^{-12}$	DeMore et al. [1997]
65	$CH_3OO + nC_3H_7O_2 \rightarrow HCHO + C_3H_6O + HO_2 + HO_2$	$6.70 \times 10^{-13}$	Lightfoot et al. [1992]
66	$CH_3OO + nC_3H_7O_2 \rightarrow C_3H_6O + CH_3OH$	$2.3 \times 10^{-13}$	Lightfoot et al. [1992]
67	$CH_3OO + nC_3H_7O_2 \rightarrow HCHO + nC_3H_7OH$	$2.3 \times 10^{-13}$	Lightfoot et al. [1992]
68	$CH_3OO + iC_3H_7O_2 \rightarrow HCHO + CH_3COCH_3 + HO_2 + HO_2$	$1.2 \times 10^{-14}$	Lightfoot et al. [1992]
69	$CH_3OO + iC_3H_7O_2 \rightarrow CH_3COCH_3 + CH_3OH$	$4.1 \times 10^{-15}$	Lightfoot et al. [1992]
70	$CH_3OO + iC_3H_7O_2 \rightarrow HCHO + iC_3H_7OH$	$4.1 \times 10^{-15}$	Lightfoot et al. [1992]
71	$CH_3OO + C_2H_5OO \rightarrow CH_3CHO + HCHO + HO_2 + HO_2$	$2.0 \times 10^{-13}$	Kirchner and Stockwell [1996]
72	$CH_3OO + CH_3COOO \rightarrow HCHO + CH_3OO + HO_2$	$1.58 \times 10^{-11}$	Kirchner and Stockwell [1996]
73	$C_2H_5OO + NO \rightarrow CH_3CHO + HO_2 + NO_2$	$8.68 \times 10^{-12}$	Lurmann et al. [1986]
74	$C_2H_5OO + NO_2 \rightarrow C_2H_5OONO_2$	$8.8 \times 10^{-12}$	Atkinson et al. [1997]
75	$C_2H_5OO + HO_2 \rightarrow C_2H_5OOH$	$9.23 \times 10^{-12}$	Atkinson et al. [2004]
76	$C_2H_5OO + CH_3COOO \rightarrow CH_3CHO + CH_3COO + HO_2$	$4.0 \times 10^{-12}$	Michalowski et al. [2000]
77	$iC_3H_7O_2 + HO_2 \rightarrow iPerox$	$9.23 \times 10^{-12}$	Michalowski et al. [2000]
78	$nC_3H_7O_2 + HO_2 \rightarrow nPerox$	$9.23 \times 10^{-12}$	Michalowski et al. [2000]
79	$HCHO + OH \rightarrow HO_2 + CO$	$9.3 \times 10^{-12}$	Atkinson et al. [2004]
80	$HCHO + HO_2 \rightarrow HOCH_2O_2$	$7.53 \times 10^{-14}$	Sander et al. [2006]
81	$HCHO + NO_3 \rightarrow HNO_3 + HO_2 + CO$	$5.8 \times 10^{-16}$	DeMore et al. [1997]
82	$CH_3CHO + OH \rightarrow CH_3COOO + H_2O$	$1.98 \times 10^{-11}$	Atkinson et al. [2004]
83	$CH_3CHO + NO_3 \rightarrow HNO_3 + CH_3COOO$	$1.4 \times 10^{-15}$	DeMore et al. [1997]
84	$CH_3COCH_3 + OH \rightarrow H_2O + CH_3COCH_2$	$1.37 \times 10^{-13}$	Atkinson et al. [2004]
85	$HOCH_2O_2 + NO \rightarrow HCOOH + HO_2 + NO_2$	$8.68 \times 10^{-12}$	Lurmann et al. [1986]
86	$HOCH_2O_2 + HO_2 \rightarrow HCOOH + H_2O$	$2.0 \times 10^{-12}$	Lurmann et al. [1986]
87	$HOCH_2O_2 + HOCH_2O_2 \rightarrow HCOOH + HCOOH + HO_2 + HO_2$	$1.0 \times 10^{-13}$	Lurmann et al. [1986]
88	$HCOOH + OH \rightarrow HO_2 + H_2O + CO_2$	$4.0 \times 10^{-13}$	DeMore et al. [1997]
89	$CH_3COOO + NO \rightarrow CH_3OO + NO_2 + CO_2$	$2.4 \times 10^{-11}$	Atkinson et al. [2004]
90	$CH_3COOO + HO_2 \rightarrow CH_3COOH + O_3$	$1.87 \times 10^{-11}$	Kirchner and Stockwell [1996]
91	$CH_3COOO + CH_3COOO \rightarrow CH_3COO + CH_3COO$	$2.5 \times 10^{-11}$	Kirchner and Stockwell [1996]
92	$C_2H_5OONO_2 \rightarrow C_2H_5OO + NO_2$	$3.2 \times 10^{-3}$	Atkinson et al. [1997]
93	$CH_3OONO_2 \rightarrow CH_3OO + NO_2$	$3.4 \times 10^{-3}$	Atkinson et al. [1997]
94			
95	$Cl_2 + OH \rightarrow HOCl + Cl$	$2.85 \times 10^{-14}$	Atkinson et al. [2004]
96	$Cl + O_3 \rightarrow ClO$	$1.02 \times 10^{-11}$	Atkinson et al. [2004]
97	$Cl + H_2 \rightarrow HCl$	$3.5 \times 10^{-15}$	Atkinson et al. [2004]
98	$Cl + HO_2 \rightarrow HCl$	$3.57 \times 10^{-11}$	Sander et al. [2006]
99	$Cl + HO_2 \rightarrow ClO + OH$	$6.68 \times 10^{-12}$	Sander et al. [2006]
100	$Cl + H_2O_2 \rightarrow HCl + HO_2$	$2.11 \times 10^{-13}$	Atkinson et al. [2004]
101	$Cl + NO_3 \rightarrow ClO + NO_2$	$2.4 \times 10^{-11}$	Atkinson et al. [2004]
102	$Cl + CH_4 \rightarrow HCl + CH_3OO$	$3.99 \times 10^{-14}$	Sander et al. [2006]
103	$Cl + C_2H_6 \rightarrow HCl + C_2H_5OO$	$5.36 \times 10^{-11}$	Sander et al. [2006]
104	$Cl + C_2H_4 \rightarrow HCl + C_2H_5OO$	$1.0 \times 10^{-10}$	Atkinson et al. [2004]
105	$Cl + MEK \rightarrow HCl$	$4.21 \times 10^{-11}$	Atkinson et al. [2004]
106	$Cl + C_2H_2 \rightarrow ClC_2CHO$	$2.5 \times 10^{-10}$	Atkinson et al. [2004]
107	$Cl + C_3H_6 \rightarrow HCl + C_3H_5Cl$	$2.7 \times 10^{-10}$	Keil and Shepson [2006]
108	$Cl + C_3H_8 \rightarrow HCl + iC_3H_7O_2$	$1.65 \times 10^{-10}$	DeMore et al. [1997]
109	$Cl + C_3H_8 \rightarrow HCl + nC_3H_7O_2$	$1.65 \times 10^{-10}$	DeMore et al. [1997]
110	$Cl + C_3H_6O \rightarrow HCl$	$1.1 \times 10^{-10}$	Wallington et al. [1988]
111	$Cl + iC_4H_{10} \rightarrow HCl + C_4H_9$	$1.3 \times 10^{-10}$	Hooshiyar and Niki [1995]
112	$Cl + nC_4H_{10} \rightarrow HCl + C_4H_9$	$2.15 \times 10^{-10}$	Tyndall et al. [1997]
113	$Cl + n\text{-Butanal} \rightarrow HCl + \text{Products}$	$1.1 \times 10^{-10}$	Michalowski et al. [2000]
114	$Cl + HCHO \rightarrow HCl + HO_2 + CO$	$7.18 \times 10^{-11}$	Sander et al. [2006]

115	$\text{Cl} + \text{CH}_3\text{CHO} \rightarrow \text{HCl} + \text{CH}_3\text{COOO}$	$8.08 \times 10^{-11}$	Atkinson et al. [2004]
116	$\text{Cl} + \text{CH}_3\text{COCH}_3 \rightarrow \text{HCl} + \text{CH}_3\text{COCH}_2$	$1.39 \times 10^{-12}$	Atkinson et al. [2004]
117	$\text{Cl} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{OO} + \text{HCl}$	$2.36 \times 10^{-11}$	Atkinson et al. [2004]
118	$\text{Cl} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_2\text{OOH} + \text{HCl}$	$3.54 \times 10^{-11}$	Atkinson et al. [2004]
119	$\text{Cl} + \text{CHBr}_3 \rightarrow \text{HCl} + \text{Br} + \text{CBr}_2\text{O}$	$2.9 \times 10^{-13}$ (at 298 K)	Kamboures et al. [2002]
120	$\text{Cl} + \text{OCIO} \rightarrow \text{ClO} + \text{ClO}$	$6.35 \times 10^{-11}$	Atkinson et al. [2004]
121	$\text{Cl} + \text{ClNO}_3 \rightarrow \text{Cl}_2 + \text{NO}_3$	$1.12 \times 10^{-11}$	Sander et al. [2006]
122	$\text{Cl} + \text{PAN} \rightarrow \text{HCl} + \text{HCHO} + \text{NO}_3$	$1.0 \times 10^{-14}$	Tsalkani et al. [1988]
123	$\text{Cl} + \text{HNO}_3 \rightarrow \text{HCl} + \text{NO}_3$	$1.0 \times 10^{-16}$	Wine et al. [1988]
124	$\text{Cl} + \text{NO}_2 \rightarrow \text{ClNO}_2$	$1.43 \times 10^{-12}$ (at 298 K)	Ravishankara et al. [1988]
125	$\text{Cl} + \text{HBr} \rightarrow \text{HCl} + \text{Br}$	$4.48 \times 10^{-12}$	Nicovich and Wine [1990]
126	$\text{ClO} + \text{O}(^3P) \rightarrow \text{Cl} + \text{O}_2$	$1.6 \times 10^{-11}$	Atkinson et al. [2004]
127	$\text{ClO} + \text{OH} \rightarrow \text{Cl} + \text{HO}_2$	$2.45 \times 10^{-11}$	Atkinson et al. [2004]
128	$\text{ClO} + \text{OH} \rightarrow \text{HCl}$	$2.37 \times 10^{-13}$	Sander et al. [2006]
129	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl}$	$8.67 \times 10^{-12}$	Atkinson et al. [2004]
130	$\text{ClO} + \text{CH}_3\text{OO} \rightarrow \text{Cl} + \text{HCHO} + \text{HO}_2$	$2.08 \times 10^{-12}$	Sander et al. [2006]
131	$\text{ClO} + \text{CH}_3\text{COOO} \rightarrow \text{Cl} + \text{CH}_3\text{OO} + \text{CO}_2$	$2.03 \times 10^{-12}$	Michalowski et al. [2000]
132	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$2.04 \times 10^{-11}$	Atkinson et al. [2004]
133	$\text{ClO} + \text{NO}_2 \rightarrow \text{ClNO}_3$	$7.1 \times 10^{-12}$	Atkinson et al. [2004]
134	$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2$	$1.64 \times 10^{-15}$	Atkinson et al. [2004]
135	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{Cl}$	$1.54 \times 10^{-15}$	Atkinson et al. [2004]
136	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OCIO}$	$1.40 \times 10^{-15}$	Atkinson et al. [2004]
137	$\text{OCIO} + \text{OH} \rightarrow \text{HOCl}$	$1.13 \times 10^{-11}$	Atkinson et al. [2004]
138	$\text{OCIO} + \text{NO} \rightarrow \text{ClO} + \text{H}_2\text{O}$	$1.51 \times 10^{-13}$	Atkinson et al. [2004]
139	$\text{HOCl} + \text{OH} \rightarrow \text{ClO} + \text{H}_2\text{O}$	$4.0 \times 10^{-13}$	Sander et al. [2006]
140	$\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}$	$6.84 \times 10^{-13}$	Atkinson et al. [2004]
141	$\text{ClNO}_3 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_3$	$3.17 \times 10^{-13}$	Atkinson et al. [2004]
142	$\text{HOCl} + \text{O}(^3P) \rightarrow \text{ClO} + \text{OH}$	$1.7 \times 10^{-13}$	Atkinson et al. [2004]
143			
144	$\text{Br} + \text{O}_3 \rightarrow \text{BrO}$	$6.75 \times 10^{-13}$	Atkinson et al. [2004]
145	$\text{Br}_2 + \text{OH} \rightarrow \text{HOBr}$	$5.0 \times 10^{-11}$	Atkinson et al. [2004]
146	$\text{Br} + \text{HO}_2 \rightarrow \text{HBr}$	$1.25 \times 10^{-12}$	Atkinson et al. [2004]
147	$\text{Br} + \text{C}_2\text{H}_2 \rightarrow \text{BrCH}_2\text{CHO}$	$3.7 \times 10^{-14}$	Atkinson et al. [2004]
148	$\text{Br} + \text{C}_2\text{H}_4 \rightarrow \text{HBr} + \text{C}_2\text{H}_5\text{OO}$	$1.3 \times 10^{-13}$	Atkinson et al. [2004]
149	$\text{Br} + \text{C}_3\text{H}_6 \rightarrow \text{HBr} + \text{C}_3\text{H}_5$	$1.60 \times 10^{-12}$	Atkinson et al. [2004]
150	$\text{Br} + \text{HCHO} \rightarrow \text{HBr} + \text{CO} + \text{HO}_2$	$6.75 \times 10^{-13}$	Sander et al. [2006]
151	$\text{Br} + \text{CH}_3\text{CHO} \rightarrow \text{HBr} + \text{CH}_3\text{COOO}$	$2.8 \times 10^{-12}$	Atkinson et al. [2004]
152	$\text{Br} + \text{C}_3\text{H}_6\text{O} \rightarrow \text{HBr}$	$9.7 \times 10^{-12}$	Wallington et al. [1989]
153	$\text{Br} + \text{nButanal} \rightarrow \text{HBr}$	$9.7 \times 10^{-12}$	Michalowski et al. [2000]
154	$\text{Br} + \text{CH}_3\text{OOH} \rightarrow \text{HBr} + \text{CH}_3\text{OO}$	$4.03 \times 10^{-15}$	Mallard et al. [1993]
155	$\text{Br} + \text{NO}_2 \rightarrow \text{BrNO}_2$	$6.3 \times 10^{-12}$	Atkinson et al. [2006]
156	$\text{Br} + \text{NO}_2 \leftrightarrow \text{BrONO}$	f: $6.3 \times 10^{-12}$ r: 0.02	Atkinson et al. [2006]
157			Orlando and Burkholder [2000]
158	$\text{Br} + \text{BrNO}_2 \rightarrow \text{Br}_2 + \text{NO}_2$	$5.0 \times 10^{-11}$	Orlando and Burkholder [2000]
159	$\text{Br} + \text{BrONO} \rightarrow \text{Br}_2 + \text{NO}_2$	$1.0 \times 10^{-12}$	Orlando and Burkholder [2000]
160	$\text{Br} + \text{BrNO}_3 \rightarrow \text{Br}_2 + \text{NO}_3$	$4.9 \times 10^{-11}$	Orlando and Tyndall [1997]
161	$\text{Br} + \text{OCIO} \rightarrow \text{BrO} + \text{ClO}$	$1.43 \times 10^{-13}$	Atkinson et al. [2004]
162	$\text{BrO} + \text{O}(^3P) \rightarrow \text{Br}$	$4.8 \times 10^{-11}$	Atkinson et al. [2004]
163	$\text{BrO} + \text{OH} \rightarrow \text{Br} + \text{HO}_2$	$4.93 \times 10^{-11}$	Atkinson et al. [2004]
164	$\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr}$	$3.38 \times 10^{-11}$	Atkinson et al. [2004]
165	$\text{BrO} + \text{CH}_3\text{OO} \rightarrow \text{HOBr} + \text{CH}_2\text{OO}$	$4.1 \times 10^{-12}$	Aranda et al. [1997]
166	$\text{BrO} + \text{CH}_3\text{OO} \rightarrow \text{Br} + \text{HCHO} + \text{HO}_2$	$1.6 \times 10^{-12}$	Aranda et al. [1997]
167	$\text{BrO} + \text{CH}_3\text{COOO} \rightarrow \text{Br} + \text{CH}_3\text{COO}$	$1.7 \times 10^{-12}$	Michalowski et al. [2000]
168	$\text{BrO} + \text{C}_3\text{H}_6\text{O} \rightarrow \text{HOBr}$	$1.5 \times 10^{-14}$	Michalowski et al. [2000]
169	$\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$	$2.48 \times 10^{-11}$	Atkinson et al. [2004]
170	$\text{BrO} + \text{NO}_2 \rightarrow \text{BrNO}_3$	$1.53 \times 10^{-11}$	Atkinson et al. [2004]
171	$\text{BrO} + \text{BrO} \rightarrow \text{Br} + \text{Br}$	$2.82 \times 10^{-12}$	Sander et al. [2006]

172	$\text{BrO} + \text{BrO} \rightarrow \text{Br}_2$	$9.3 \times 10^{-13}$	<i>Sander et al.</i> [2006]
173	$\text{BrO} + \text{HBr} \rightarrow \text{HOBr} + \text{Br}$	$2.1 \times 10^{-14}$	<i>Hansen et al.</i> [1999]
174	$\text{HBr} + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O}$	$1.26 \times 10^{-11}$	<i>Sander et al.</i> [2006]
175	$\text{CH}_3\text{Br} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Br}$	$1.27 \times 10^{-14}$	<i>Atkinson et al.</i> [2004]
176	$\text{CHBr}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Br}$	$1.2 \times 10^{-13}$	<i>Atkinson et al.</i> [2004]
177			
178	$\text{Cl} + \text{BrCl} \leftrightarrow \text{Br} + \text{Cl}_2$	f: $1.5 \times 10^{-11}$ r: $1.1 \times 10^{-15}$	<i>Clyne and Cruse</i> [1972]
179	$\text{Cl} + \text{Br}_2 \leftrightarrow \text{BrCl} + \text{Br}$	f: $1.2 \times 10^{-10}$ r: $3.3 \times 10^{-1}$	<i>Clyne and Cruse</i> [1972]
180	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl}$	$7.04 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
181	$\text{BrO} + \text{ClO} \rightarrow \text{BrCl}$	$1.15 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
182	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OClO}$	$9.06 \times 10^{-12}$	<i>Atkinson et al.</i> [2004]
183	$\text{HOBr} + \text{OH} \rightarrow \text{BrO} + \text{H}_2\text{O}$	$5.0 \times 10^{-13}$	<i>Kukui et al.</i> [1996]
184	$\text{HOBr} + \text{Cl} \rightarrow \text{BrCl} + \text{OH}$	$8.0 \times 10^{-11}$	<i>Kukui et al.</i> [1996]
185	$\text{HOBr} + \text{O}(^3P) \rightarrow \text{BrO} + \text{OH}$	$2.12 \times 10^{-11}$	<i>Atkinson et al.</i> [2004]
186			
187			
188			

189 **Table S2.** Photochemical reactions.  $J_{\max}$  values for 25 March are shown as an example.  $J$  coefficients  
 190 are expressed in units of  $s^{-1}$ .  
 191  
 192

193	Reaction	$J_{\max}$ 25 March	Lifetime	Source
194				
195	$O_3 + hv \rightarrow O_2 + O(^1D)$	$3.9 \times 10^{-6}$	3.0 days	calculated from OASIS data
196	$NO_2 + hv \rightarrow NO + O(^3P)$	$8.6 \times 10^{-3}$	1.9 min	calculated from OASIS data
197	$H_2O_2 + hv \rightarrow OH + OH$	$3.4 \times 10^{-6}$	3.4 days	calculated from OASIS data
198	$NO_3 + hv \rightarrow NO + O_2$	$4.5 \times 10^{-2}$	22 s	Michalowski et al. [2000]
199	$N_2O_5 + hv \rightarrow NO_2 + NO_3$	$1.5 \times 10^{-5}$	18 h	calculated from OASIS data
200	$HONO + hv \rightarrow OH + NO$	$1.8 \times 10^{-3}$	9.2 min	calculated from OASIS data
201	$HNO_3 + hv \rightarrow NO_2 + OH$	$1.5 \times 10^{-7}$	79 days	calculated from OASIS data
202	$HNO_4 + hv \rightarrow NO_2 + HO_2$	$7.3 \times 10^{-7}$	16 days	calculated from OASIS data
203	$HCHO + hv \rightarrow HO_2 + HO_2 + CO$	$1.5 \times 10^{-5}$	19 h	calculated from OASIS data
204	$HCHO + hv \rightarrow CO + H_2$	$3.1 \times 10^{-5}$	8.8 h	calculated from OASIS data
205	$CH_3CHO + hv \rightarrow CH_3OO + HO_2 + CO$	$1.1 \times 10^{-6}$	11 days	calculated from OASIS data
206	$CH_3OOH + hv \rightarrow HCHO + HO_2 + OH$	$3.2 \times 10^{-6}$	3.7 days	calculated from OASIS data
207	$C_3H_6O + hv \rightarrow HO_2 + C_2H_5OO + CO$	$1.4 \times 10^{-6}$	8.3 days	calculated from OASIS data
208	$PAN + hv \rightarrow CH_3COOO + NO_2$	$1.7 \times 10^{-7}$	66 days	calculated from OASIS data
209	$OCIO + hv \rightarrow O(^3P) + ClO$	0.12	8.1 s	estimate from Pöhler et al. [2010]
210	$Cl_2 + hv \rightarrow Cl + Cl$	$2.1 \times 10^{-3}$	8.1 min	calculated from OASIS data
211	$ClO + hv \rightarrow Cl + O(^3P)$	$2.4 \times 10^{-5}$	11 h	calculated from OASIS data
212	$HOCl + hv \rightarrow OH + Cl$	$1.4 \times 10^{-4}$	2 h	estimate from Lehrer et al. [2004]
213	$ClNO_3 + hv \rightarrow Cl + NO_3$	$2.9 \times 10^{-5}$	9.5 h	calculated from OASIS data
214	$ClNO_3 + hv \rightarrow ClO + NO_2$	$3.4 \times 10^{-6}$	3.4 days	calculated from OASIS data
215	$BrNO_3 + hv \rightarrow Br + NO_3$	$2.1 \times 10^{-4}$	1.3 h	calculated from OASIS data
216	$BrNO_3 + hv \rightarrow BrO + NO_2$	$1.2 \times 10^{-3}$	14.2 min	calculated from OASIS data
217	$BrO + hv \rightarrow Br + O(^3P)$	$3.0 \times 10^{-2}$	33 s	calculated from OASIS data
218	$Br_2 + hv \rightarrow Br + Br$	$4.4 \times 10^{-2}$	23 s	calculated from OASIS data
219	$HOBr + hv \rightarrow Br + OH$	$2.3 \times 10^{-3}$	7.2 min	calculated from OASIS data
220	$BrNO_2 + hv \rightarrow Br + NO_2$	$5.7 \times 10^{-3}$	2.9 min	estimate from Scheffler et al. [1997] &
221				Landgraf & Crutzen et al. [1998]
222	$ClNO_2 + hv \rightarrow Cl + NO_2$	$4.4 \times 10^{-5}$	6.3 h	estimate from Ganske et al. [1992]
223	$BrCl + hv \rightarrow Br + Cl$	$1.26 \times 10^{-2}$	1.3 min	calculated from OASIS data
224				

225

226

227

228

229

230

231

232

233

234

235

236

237

238

239

240 **Table S3.** Mass transfer reactions. All rate constants are expressed in units of s<sup>-1</sup>.

241

242

243	Reaction	<i>k</i> (forward)	<i>k</i> (reverse)
244			
245	<i>Particles</i>		
246	HCl <sub>(g)</sub> → H <sup>+</sup> <sub>(p)</sub> + Cl <sup>-</sup> <sub>(p)</sub>	2.58 × 10 <sup>-3</sup>	
247	HBr <sub>(g)</sub> → H <sup>+</sup> <sub>(p)</sub> + Br <sup>-</sup> <sub>(p)</sub>	1.80 × 10 <sup>-3</sup>	
248	HOCl <sub>(g)</sub> → HOCl <sub>(p)</sub>	2.16 × 10 <sup>-3</sup>	
249	HOBr <sub>(g)</sub> → HOBr <sub>(p)</sub>	1.26 × 10 <sup>-3</sup>	
250	HOI <sub>(g)</sub> → HOI <sub>(p)</sub>	5.42 × 10 <sup>-4</sup>	
251	OH <sub>(g)</sub> → OH <sub>(p)</sub>	3.26 × 10 <sup>-5</sup>	
252	O <sub>3(g)</sub> ↔ O <sub>3(p)</sub>	6.54 × 10 <sup>-6</sup>	8.76 × 10 <sup>5</sup>
253	Cl <sub>2(g)</sub> ↔ Cl <sub>2(p)</sub>	2.69 × 10 <sup>-5</sup>	2.96 × 10 <sup>7</sup>
254	Br <sub>2(g)</sub> ↔ Br <sub>2(p)</sub>	1.78 × 10 <sup>-5</sup>	2.97 × 10 <sup>8</sup>
255	BrCl <sub>(g)</sub> ↔ BrCl <sub>(p)</sub>	6.60 × 10 <sup>-4</sup>	1.91 × 10 <sup>10</sup>
256	HNO <sub>3(g)</sub> → HNO <sub>3(p)</sub>	5.50 × 10 <sup>-4</sup>	
257	N <sub>2</sub> O <sub>5(g)</sub> → N <sub>2</sub> O <sub>5(p)</sub>	1.08 × 10 <sup>-4</sup>	
258	HONO <sub>(g)</sub> → HONO <sub>(p)</sub>	1.63 × 10 <sup>-4</sup>	
259	PAN <sub>(g)</sub> → PAN <sub>(p)</sub>	2.05 × 10 <sup>-5</sup>	
260	HNO <sub>4(g)</sub> → HNO <sub>4(p)</sub>	4.89 × 10 <sup>-4</sup>	
261	ClNO <sub>2(g)</sub> → ClNO <sub>2(p)</sub>	1.26 × 10 <sup>-3</sup>	
262	BrNO <sub>2(g)</sub> → BrNO <sub>2(p)</sub>	1.26 × 10 <sup>-3</sup>	
263	ClNO <sub>3(g)</sub> → ClNO <sub>3(p)</sub>	1.26 × 10 <sup>-3</sup>	
264	BrNO <sub>3(g)</sub> → BrNO <sub>3(p)</sub>	1.26 × 10 <sup>-3</sup>	
265			
266	<i>Snow</i>		
267	HBr <sub>(g)</sub> → H <sup>+</sup> <sub>(s)</sub> + Br <sup>-</sup> <sub>(s)</sub>	1.67 × 10 <sup>-5</sup>	
268	HCl <sub>(g)</sub> → H <sup>+</sup> <sub>(s)</sub> + Cl <sup>-</sup> <sub>(s)</sub>	1.67 × 10 <sup>-5</sup>	
269	HOBr <sub>(g)</sub> → HOBr <sub>(s)</sub>	1.67 × 10 <sup>-5</sup>	
270	HOCl <sub>(g)</sub> → HOCl <sub>(s)</sub>	1.67 × 10 <sup>-5</sup>	
271	OH <sub>(g)</sub> → OH <sub>(s)</sub>	1.67 × 10 <sup>-6</sup>	
272	O <sub>3(g)</sub> → O <sub>3(s)</sub>	1.67 × 10 <sup>-6</sup>	
273	Cl <sub>2(g)</sub> ↔ Cl <sub>2(s)</sub>	8.0 × 10 <sup>-6</sup>	7.71 × 10 <sup>-2</sup>
274	Br <sub>2(g)</sub> ↔ Br <sub>2(s)</sub>	1.0 × 10 <sup>-5</sup>	7.71 × 10 <sup>-2</sup>
275	BrCl <sub>(g)</sub> ↔ BrCl <sub>(s)</sub>	1.25 × 10 <sup>-5</sup>	7.71 × 10 <sup>-2</sup>
276	HNO <sub>3(g)</sub> → HNO <sub>3(s)</sub>	1.67 × 10 <sup>-5</sup>	
277	N <sub>2</sub> O <sub>5(g)</sub> → N <sub>2</sub> O <sub>5(s)</sub>	1.67 × 10 <sup>-5</sup>	
278	HONO <sub>(g)</sub> → HONO <sub>(s)</sub>	1.67 × 10 <sup>-5</sup>	
279	PAN <sub>(g)</sub> → PAN <sub>(s)</sub>	1.67 × 10 <sup>-5</sup>	
280	HNO <sub>4(g)</sub> → HNO <sub>4(s)</sub>	1.67 × 10 <sup>-5</sup>	
281	ClNO <sub>2(g)</sub> → ClNO <sub>2(s)</sub>	1.67 × 10 <sup>-4</sup>	
282	BrNO <sub>2(g)</sub> → BrNO <sub>2(s)</sub>	1.67 × 10 <sup>-4</sup>	
283	ClNO <sub>3(g)</sub> → ClNO <sub>3(s)</sub>	1.67 × 10 <sup>-4</sup>	
284	BrNO <sub>3(g)</sub> → BrNO <sub>3(s)</sub>	1.67 × 10 <sup>-4</sup>	

285

286 **Table S4.** Aqueous-phase reactions in the model. All aqueous reaction rate constants are converted to  
 287 units consistent to the gas-phase reactions to be read by the modeling program.

288 \* Third order rate constant, expressed in units of  $\text{cm}^6 \cdot \text{molecule}^{-2} \cdot \text{s}^{-1}$

289 † second order rate constant, expressed in units of  $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$

290 ‡ first order rate constant, expressed in units of  $\text{s}^{-1}$

291

Reaction	k (actual)	k (particle)	k (snow)	Reference
$\text{Cl}^- + \text{HOBr} + \text{H}^+ \rightarrow \text{BrCl}^*$	$1.55 \times 10^{-32}$	$5.17 \times 10^{-21}$	$9.30 \times 10^{-26}$	(Wang et al., 1994)
$\text{Br}^- + \text{HOCl} + \text{H}^+ \rightarrow \text{BrCl}^*$	$3.59 \times 10^{-36}$	$1.2 \times 10^{-24}$	$2.15 \times 10^{-29}$	(Sander et al., 1997)
$\text{Br}^- + \text{HOBr} + \text{H}^+ \rightarrow \text{Br}_2^*$	$4.41 \times 10^{-32}$	$1.47 \times 10^{-20}$	$2.64 \times 10^{-25}$	(Beckwith et al., 1996)
$\text{Cl}^- + \text{HOCl} + \text{H}^+ \rightarrow \text{Cl}_2^*$	$6.07 \times 10^{-38}$	$2.02 \times 10^{-26}$	$3.63 \times 10^{-31}$	(Wang and Margerum, 1994)
$\text{BrCl} + \text{Cl}^- \rightarrow \text{BrCl}_2^- \dagger$	$1 \times 10^{-11}$	3.3	$5.99 \times 10^{-5}$	(Michalowski et al., 2000)
$\text{BrCl}_2^- \rightarrow \text{BrCl} + \text{Cl}^- \ddagger$	$1.58 \times 10^9$	$1.58 \times 10^9$	$1.58 \times 10^9$	(Michalowski et al., 2000)
$\text{BrCl} + \text{Br}^- \rightarrow \text{Br}_2\text{Cl}^- \dagger$	$1 \times 10^{-11}$	3.3	$5.99 \times 10^{-5}$	(Michalowski et al., 2000)
$\text{Br}_2\text{Cl}^- \rightarrow \text{BrCl} + \text{Br}^- \ddagger$	$3.34 \times 10^5$	$3.34 \times 10^5$	$3.34 \times 10^5$	(Michalowski et al., 2000; Wang et al., 1994)
$\text{Cl}_2 + \text{Br}^- \rightarrow \text{BrCl}_2^- \dagger$	$1.28 \times 10^{-11}$	4.27	$7.66 \times 10^{-5}$	(Michalowski et al., 2000; Beckwith et al., 1996; Wang et al., 1994)
$\text{BrCl}_2^- \rightarrow \text{Cl}_2 + \text{Br}^- \ddagger$	$6.94 \times 10^2$	$6.94 \times 10^2$	$6.94 \times 10^2$	(Michalowski et al., 2000; Wang et al., 1994)
$\text{O}_3 + \text{Br}^- \rightarrow \text{HOBr} \dagger$	$1.35 \times 10^{-20}$	$4.5 \times 10^{-9}$	$8.08 \times 10^{-14}$	(Michalowski et al., 2000)
$\text{OH} + \text{Cl}^- \rightarrow \text{HOCl} \dagger$	$1.35 \times 10^{-20}$	$4.5 \times 10^{-9}$	$8.08 \times 10^{-14}$	assumed same as $\text{O}_3 + \text{Br}^-$
$\text{N}_2\text{O}_5 + \text{Cl}^- \rightarrow \text{ClNO}_2 \dagger$	$1.66 \times 10^{-12}$	$5.5 \times 10^{-1}$	$9.94 \times 10^{-5}$	assume diffusion limited
$\text{ClNO}_2 + \text{H}^+ + \text{Cl}^- \rightarrow \text{Cl}_2 \dagger$	$1.66 \times 10^{-14}$	$5.5 \times 10^{-3}$	$9.94 \times 10^{-8}$	estimated from (Roberts et al., 2008)
$\text{N}_2\text{O}_5 + \text{Br}^- \rightarrow \text{BrNO}_2 \dagger$	$1.66 \times 10^{-12}$	$5.5 \times 10^{-1}$	$9.94 \times 10^{-5}$	assume diffusion limited
$\text{BrNO}_2 + \text{H}^+ + \text{Br}^- \rightarrow \text{Br}_2 \dagger$	$7.31 \times 10^{-17}$	$2.44 \times 10^{-5}$	$4.38 \times 10^{-10}$	estimated from (Schweitzer et al., 1998)

292

293

294

295

296

297

298

299

300

301

302

303

304

305

306

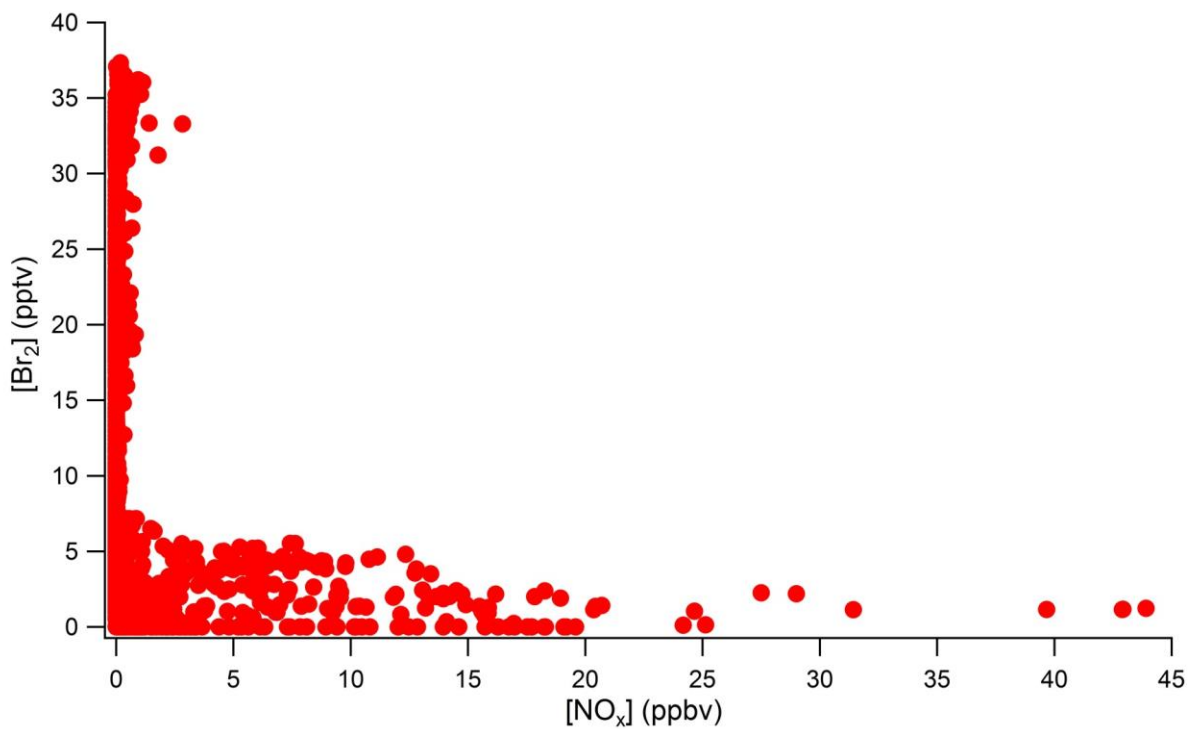


307

308 **Table S5.** Summary of the ambient measurements from OASIS that were used to constrain the model  
309 and the instrumental method used. Constrained parameters were input into the model at 10 minute  
310 intervals.

311

312	<u>Measured Species</u>	<u>Method</u>	<u>Method Reference</u>
313	O <sub>3</sub> and NO <sub>x</sub>	Chemiluminescence	<i>Ridley et al.</i> [1992];
314			<i>Ryerson et al.</i> [2000];
315			<i>Weinheimer et al.</i> , [1998]
316	HONO	Long Path Absorption Photometer	<i>Villena et al.</i> , [2011]
317	CO	CO Monitor	
318	Cl <sub>2</sub> and Br <sub>2</sub>	CIMS	<i>Liao et al.</i> [2011, 2012]
319	HCHO	Tunable Diode Laser Absorption	<i>Fried et al.</i> , [2003];
320		Spectroscopy	<i>Lancaster et al.</i> [2000]
321	CH <sub>3</sub> CHO, CH <sub>3</sub> COCH <sub>3</sub> , MEK,	Online GC-MS	<i>Apel et al.</i> [2010]
322	<i>n</i> -C <sub>4</sub> H <sub>10</sub> , <i>i</i> -C <sub>4</sub> H <sub>10</sub>		
323	C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , C <sub>3</sub> H <sub>6</sub> ,	Canister samples, offline GC-MS	<i>Russo et al.</i> [2010]
324	<i>n</i> -C <sub>4</sub> H <sub>10</sub> , <i>i</i> -C <sub>4</sub> H <sub>10</sub>		
325	Photolysis Frequencies	Spectral Actinic Flux Density	<i>Shetter and Muller et al.</i> [1999]
326			



327

328 Figure S1. 5 minute averages of observed concentrations of  $\text{Br}_2$  and  $\text{NO}_x$  from OASIS 2009. It  
329 should be noted that the  $\text{Br}_2$  axis has pptv units and the  $\text{NO}_x$  axis has ppbv units.

330

331

332

333

334

335

336

337

338

339

340

341

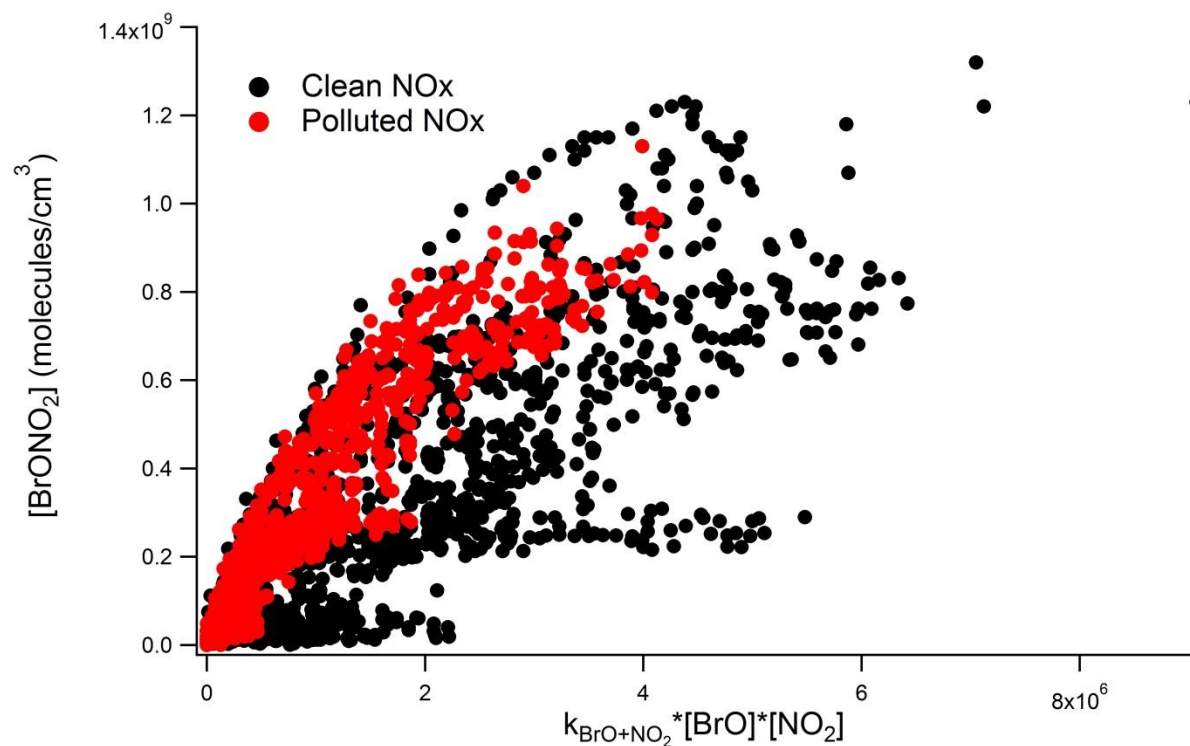
342

343

344

345

346  
347  
348  
349  
350  
351



352  
353  
354  
355  
356

Figure S2. Simulated BrONO<sub>2</sub> mole ratio (low NO<sub>x</sub> & high NO<sub>x</sub> cases) plotted against the production rate of BrONO<sub>2</sub>.

357 Apel, E. C., Emmons, L. K., Karl, T., Flocke, F., Hills, A. J., Madronich, S., Lee-Taylor, J.,  
358 Fried, A., Weibring, P., Walega, J., Richter, D., Tie, X., Mauldin, L., Campos, T., Weinheimer,  
359 A., Knapp, D., Sive, B., Kleinman, L., Springston, S., Zaveri, R., Ortega, J., Voss, P., Blake, D.,  
360 Baker, A., Warneke, C., Welsh-Bon, D., de Gouw, J., Zheng, J., Zhang, R., Rudolph, J.,  
361 Junkermann, W., and Riemer, D. D.: Chemical evolution of volatile organic compounds in the  
362 outflow of the Mexico City Metropolitan area, Atmospheric Chemistry and Physics, 10, 2353-  
363 2375, 2010.

364 Aranda, A., LeBras, G., LaVerdet, G., and Poulet, G.: The BrO+Ch3O2 reaction: Kinetics and  
365 role in the atmospheric ozone budget, *Geophysical Research Letters*, 24, 2745-2748,  
366 10.1029/97gl02686, 1997.

367 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin,  
368 M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric  
369 chemistry: Volume I - gas phase reactions of O-x, HOx, NOx and SOx species, *Atmospheric  
370 Chemistry and Physics*, 4, 1461-1738, 2004.

371 Beckwith, R. C., Wang, T. X., and Margerum, D. W.: Equilibrium and kinetics of bromine  
372 hydrolysis, *Inorganic Chemistry*, 35, 995-1000, 10.1021/ic950909w, 1996.

373 Clyne, M. A. A., and Cruse, H. W.: Atomic resonance fluorescence spectrometry for rate  
374 constants of rapid bimolecular reactions .1. Reactions O+NO2, Cl+CINO,Br+CINO, *Journal of  
375 the Chemical Society-Faraday Transactions II*, 68, 1281-&, 10.1039/f29726801281, 1972.

376 DeMore, W. B., Sander, S., Golden, D., Hampson, R., Kurylo, M., Howard, C., Ravishankara,  
377 A., Kolb, C., Molina, M., and T, C. I. o.: Jet Propulsion Lab., Pasadena (1997), *Chemical  
378 kinetics and photochemical data for use in stratospheric modeling*, Jet Propulsion Lab.,  
379 California Inst. of Tech., Pasadena, CA 1997.

380 Donahue, N. M., Anderson, J. G., and Demerjian, K. L.: New rate constants for ten OH alkane  
381 reactions from 300 to 400 K: An assessment of accuracy, *Journal of Physical Chemistry A*, 102,  
382 3121-3126, 10.1021/jp980532q, 1998.

383 Eberhard, J., and Howard, C. J.: Temperature-dependent kinetics studies of the reactions of  
384 C2H5O2 and n-C3H7O2 radicals with NO, *International Journal of Chemical Kinetics*, 28, 731-  
385 740, 10.1002/(sici)1097-4601(1996)28:10<731::aid-kin3>3.0.co;2-o, 1996.

386 Eberhard, J., Villalta, P. W., and Howard, C. J.: Reaction of isopropyl peroxy radicals with NO  
387 over the temperature range 201-401 K, *Journal of Physical Chemistry*, 100, 993-997,  
388 10.1021/jp951824j, 1996.

389 Fried, A., Crawford, J., Olson, J., Walega, J., Potter, W., Wert, B., Jordan, C., Anderson, B.,  
390 Shetter, R., Lefer, B., Blake, D., Blake, N., Meinardi, S., Heikes, B., O'Sullivan, D., Snow, J.,  
391 Fuelberg, H., Kiley, C. M., Sandholm, S., Tan, D., Sachse, G., Singh, H., Faloon, I., Harward,  
392 C. N., and Carmichael, G. R.: Airborne tunable diode laser measurements of formaldehyde  
393 during TRACE-P: Distributions and box model comparisons, *Journal of Geophysical Research-  
394 Atmospheres*, 108, 23, 10.1029/2003jd003451, 2003.

395 Ganske, J. A., Berko, H. N., and Finlaysonpitts, B. J.: Absorption cross-section for gaseous  
396 ClNO2 and Cl2 at 298-K - potential organic oxidant source in the marine troposphere, *Journal of  
397 Geophysical Research-Atmospheres*, 97, 7651-7656, 1992.

398 Hansen, J. C., Li, Y. M., Li, Z. J., and Francisco, J. S.: On the mechanism of the BrO plus HBr  
399 reaction, *Chemical Physics Letters*, 314, 341-346, 10.1016/s0009-2614(99)01093-3, 1999.

400 Harris, S. J., and Kerr, J. A.: Relative rate measurements of some reactions of hydroxyl radicals  
401 with alkanes studied under atmospheric conditions, *International Journal of Chemical Kinetics*,  
402 20, 939-955, 10.1002/kin.550201203, 1988.

403 Hooshiyar, P. A., and Niki, H.: Rate constants for the gas-phase reactions of Cl-atoms with C<sub>2</sub>-  
404 C<sub>8</sub> alkanes at T=296 +/-2K, *International Journal of Chemical Kinetics*, 27, 1197-1206,  
405 10.1002/kin.550271206, 1995.

406 Kamboures, M. A., Hansen, J. C., and Francisco, J. S.: A study of the kinetics and mechanisms  
407 involved in the atmospheric degradation of bromoform by atomic chlorine, *Chemical Physics*  
408 *Letters*, 353, 335-344, 10.1016/s0009-2614(01)01439-7, 2002.

409 Keil, A. D., and Shepson, P. B.: Chlorine and bromine atom ratios in the springtime Arctic  
410 troposphere as determined from measurements of halogenated volatile organic compounds,  
411 *Journal of Geophysical Research-Atmospheres*, 111, 11, 10.1029/2006jd007119, 2006.

412 Kirchner, F., and Stockwell, W. R.: Effect of peroxy radical reactions on the predicted  
413 concentrations of ozone, nitrogenous compounds, and radicals, *Journal of Geophysical Research-*  
414 *Atmospheres*, 101, 21007-21022, 10.1029/96jd01519, 1996.

415 Kukui, A., Kirchner, U., Benter, T., and Schindler, R. N.: A gaskinetic investigation of HOBr  
416 reactions with Cl(P-2), O(P-3) and OH((2)Pi). The reaction of BrCl with OH((2)Pi), *Berichte*  
417 *Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, 100, 455-461, 1996.

418 Lancaster, D. G., Fried, A., Wert, B., Henry, B., and Tittel, F. K.: Difference-frequency-based  
419 tunable absorption spectrometer for detection of atmospheric formaldehyde, *Applied Optics*, 39,  
420 4436-4443, 10.1364/ao.39.004436, 2000.

421 Landgraf, J., and Crutzen, P. J.: An efficient method for online calculations of photolysis and  
422 heating rates, *Journal of the Atmospheric Sciences*, 55, 863-878, 10.1175/1520-  
423 0469(1998)055<0863:aemfoc>2.0.co;2, 1998.

424 Lehrer, E., Honninger, G., and Platt, U.: A one dimensional model study of the mechanism of  
425 halogen liberation and vertical transport in the polar troposphere, *Atmospheric Chemistry and*  
426 *Physics*, 4, 2427-2440, 2004.

427 Liao, J., Sihler, H., Huey, L., Neuman, J., Tanner, D., Friess, U., Platt, U., Flocke, F., Orlando,  
428 J., Shepson, P., Beine, H., Weinheimer, A., Sjostedt, S., Nowak, J., Knapp, D., Staebler, R.,  
429 Zheng, W., Sander, R., Hall, S., and Ullmann, K.: A comparison of Arctic BrO measurements by  
430 chemical ionization mass spectrometry and long path-differential optical absorption  
431 spectroscopy, *Journal of Geophysical Research-Atmospheres*, 116, 10.1029/2010JD014788,  
432 2011.

433 Liao, J., Huey, L., Tanner, D., Flocke, F., Orlando, J., Neuman, J., Nowak, J., Weinheimer, A.,  
434 Hall, S., Smith, J., Fried, A., Staebler, R., Wang, Y., Koo, J., Cantrell, C., Weibring, P., Walega,  
435 J., Knapp, D., Shepson, P., and Stephens, C.: Observations of inorganic bromine (HOBr, BrO,  
436 and Br-2) speciation at Barrow, Alaska, in spring 2009, *Journal of Geophysical Research-*  
437 *Atmospheres*, 117, 10.1029/2011JD016641, 2012.

438 Lightfoot, P. D., Cox, R. A., Crowley, J. N., Destriau, M., Hayman, G. D., Jenkin, M. E.,  
439 Moortgat, G. K., and Zabel, F.: Organic peroxy-radicals - kinetics, spectroscopy and  
440 tropospheric chemistry, *Atmospheric Environment Part a-General Topics*, 26, 1805-1961,  
441 10.1016/0960-1686(92)90423-i, 1992.

442 Lurmann, F. W., Lloyd, A. C., and Atkinson, R.: A chemical mechanism for use in long-range  
443 transport acid deposition computer modeling, *Journal of Geophysical Research-Atmospheres*, 91,  
444 905-936, 10.1029/JD091iD10p10905, 1986.

445 Mallard, W. G., Westley, F., Herron, J. T., Hampson, R. F., and Frizzel, D. H.: NIST Chemical  
446 Kinetics Database: Version 5.0 National Institute of Standards and Technology, Gaithersburg,  
447 MD. , 1993.

448 Michalowski, B., Francisco, J., Li, S., Barrie, L., Bottenheim, J., and Shepson, P.: A computer  
449 model study of multiphase chemistry in the Arctic boundary layer during polar sunrise, *Journal*  
450 *of Geophysical Research-Atmospheres*, 105, 15131-15145, 10.1029/2000JD900004, 2000.

451 Nicovich, J. M., and Wine, P. H.: Kinetics of the reactions of O(3P) and Cl(2P) with HBr and  
452 Br<sub>2</sub>, *International Journal of Chemical Kinetics*, 22, 379-397, 10.1002/kin.550220406, 1990.

453 Orlando, J. J., and Tyndall, G. S.: Rate coefficients for the thermal decomposition of BrONO<sub>2</sub>  
454 and the heat of formation of BrONO<sub>2</sub>, *Journal of Physical Chemistry*, 100, 19398-19405,  
455 10.1021/jp9620274, 1996.

456 Orlando, J. J., and Burkholder, J. B.: Identification of BrONO as the major product in the gas-  
457 phase reaction of Br with NO<sub>2</sub>, *Journal of Physical Chemistry A*, 104, 2048-2053,  
458 10.1021/jp993713g, 2000.

459 Pohler, D., Vogel, L., Friess, U., and Platt, U.: Observation of halogen species in the Amundsen  
460 Gulf, Arctic, by active long-path differential optical absorption spectroscopy, *Proceedings of the*  
461 *National Academy of Sciences of the United States of America*, 107, 6582-6587,  
462 10.1073/pnas.0912231107, 2010.

463 Ravishankara, A. R., Smith, G. J., and Davis, D. D.: A kinetics study of the reaction of Cl with  
464 NO<sub>2</sub>, *International Journal of Chemical Kinetics*, 20, 811-814, 10.1002/kin.550201005, 1988.

465 Ravishankara, A. R., Dunlea, E. J., Blitz, M. A., Dillon, T. J., Heard, D. E., Pilling, M. J.,  
466 Strekowski, R. S., Nicovich, J. M., and Wine, P. H.: Redetermination of the rate coefficient for  
467 the reaction of O(D-1) with N<sub>2</sub>, *Geophysical Research Letters*, 29, 4, 10.1029/2002gl014850,  
468 2002.

469 Ridley, B. A., Grahek, F. E., and Walega, J. G.: A small, high-sensitivity, medium-response  
470 ozone detector suitable for measurements from light aircraft, *Journal of Atmospheric and*  
471 *Oceanic Technology*, 9, 142-148, 10.1175/1520-0426(1992)009<0142:ashsmr>2.0.co;2, 1992.

472 Roberts, J. M., Osthoff, H. D., Brown, S. S., and Ravishankara, A. R.: N<sub>2</sub>O<sub>5</sub> oxidizes chloride to  
473 Cl<sup>-</sup> in acidic atmospheric aerosol, *Science*, 321, 1059-1059, 10.1126/science.1158777, 2008.

474 Russo, R. S., Zhou, Y., White, M. L., Mao, H., Talbot, R., and Sive, B. C.: Multi-year (2004-  
475 2008) record of nonmethane hydrocarbons and halocarbons in New England: seasonal variations  
476 and regional sources, *Atmospheric Chemistry and Physics*, 10, 4909-4929, 10.5194/acp-10-  
477 4909-2010, 2010.

478 Ryerson, T. B., Williams, E. J., and Fehsenfeld, F. C.: An efficient photolysis system for fast-  
479 response NO<sub>2</sub> measurements, *Journal of Geophysical Research-Atmospheres*, 105, 26447-  
480 26461, 10.1029/2000jd900389, 2000.

481 Sander, R., and Crutzen, P. J.: Model study indicating halogen activation and ozone destruction  
482 in polluted air masses transported to the sea, *Journal of Geophysical Research-Atmospheres*,  
483 101, 9121-9138, 10.1029/95jd03793, 1996.

484 Sander, R., Vogt, R., Harris, G., and Crutzen, P.: Modeling the chemistry ozone, halogen  
485 compounds, and hydrocarbons in the arctic troposphere during spring, *Tellus Series B-Chemical  
486 and Physical Meteorology*, 49, 522-532, 10.1034/j.1600-0889.49.issue5.8.x, 1997.

487 Sander, S. P., Golden, D., Kurylo, M., Moortgat, G., Wine, P., Ravishankara, A., Kolb, C.,  
488 Molina, M., Finlayson-Pitts, B., and Huie, R.: Chemical kinetics and photochemical data for use  
489 in atmospheric studies evaluation number 15 2006.

490 Scheffler, D., Grothe, H., Willner, H., Frenzel, A., and Zetzsch, C.: Properties of pure nitryl  
491 bromide. Thermal behavior, UV/Vs and FTIR spectra, and photoisomerization to trans-BrONO  
492 in an argon matrix, *Inorganic Chemistry*, 36, 335-338, 10.1021/ic9606946, 1997.

493 Schweitzer, F., Mirabel, P., and George, C.: Multiphase chemistry of N<sub>2</sub>O<sub>5</sub>, ClNO<sub>2</sub>, and  
494 BrNO<sub>2</sub>, *Journal of Physical Chemistry A*, 102, 3942-3952, 10.1021/jp980748s, 1998.

495 Shetter, R. E., and Muller, M.: Photolysis frequency measurements using actinic flux  
496 spectroradiometry during the PEM-Tropics mission: Instrumentation description and some  
497 results, *Journal of Geophysical Research-Atmospheres*, 104, 5647-5661, 10.1029/98jd01381,  
498 1999.

499 Tsalkani, N., Mellouki, A., Poulet, G., Toupance, G., and Lebras, G.: Rate constants  
500 measurements for the reactions of OH and Cl with peroxyacetyl nitrate at 298 K, *Journal of  
501 Atmospheric Chemistry*, 7, 409-419, 10.1007/bf00058713, 1988.

502 Tyndall, G. S., Orlando, J. J., Wallington, T. J., Dill, M., and Kaiser, E. W.: Kinetics and  
503 mechanisms of the reactions of chlorine atoms with ethane, propane, and n-butane, *International  
504 Journal of Chemical Kinetics*, 29, 43-55, 1997.

505 Vakhtin, A. B., Murphy, J. E., and Leone, S. R.: Low-temperature kinetics of reactions of OH  
506 radical with ethene, propene, and 1-butene, *Journal of Physical Chemistry A*, 107, 10055-10062,  
507 10.1021/jp030230a, 2003.

508 Villena, G., Wiesen, P., Cantrell, C., Flocke, F., Fried, A., Hall, S., Hornbrook, R., Knapp, D.,  
509 Kosciuch, E., Mauldin, R., McGrath, J., Montzka, D., Richter, D., Ullmann, K., Walega, J.,  
510 Weibring, P., Weinheimer, A., Staebler, R., Liao, J., Huey, L., and Kleffmann, J.: Nitrous acid

511 (HONO) during polar spring in Barrow, Alaska: A net source of OH radicals?, *Journal of*  
512 *Geophysical Research-Atmospheres*, 116, 10.1029/2011JD016643, 2011.

513 Wallington, T. J., Skewes, L. M., Siegl, W. O., Wu, C. H., and Japar, S. M.: Gas phase reaction  
514 of Cl atoms with a series of oxygenated organic species at 295 K, *International Journal of*  
515 *Chemical Kinetics*, 20, 867-875, 10.1002/kin.550201105, 1988.

516 Wallington, T. J., Skewes, L. M., Siegl, W. O., and Japar, S. M.: A relative rate study of the  
517 reaction of bromine atoms with a variety of organic compounds at 295 K, *International Journal of*  
518 *Chemical Kinetics*, 21, 1069-1076, 10.1002/kin.550211108, 1989.

519 Wang, T. X., Kelley, M. D., Cooper, J. N., Beckwith, R. C., and Margerum, D. W.: Equilibrium,  
520 Kinetic, and UV-Spectral Characteristics of Aqueous Bromine Chloride, Bromine, and Chlorine  
521 Species, *Inorganic Chemistry*, 33, 5872-5878, 10.1021/ic00103a040, 1994.

522 Wang, T. X., and Margerum, D. W.: Kinetics of Reversible Chlorine Hydrolysis: Temperature  
523 Dependence and General-Acid/Base-Assisted Mechanisms, *Inorganic Chemistry*, 33, 1050-1055,  
524 10.1021/ic00084a014, 1994.

525 Weinheimer, A. J., Montzka, D. D., Campos, T. L., Walega, J. G., Ridley, B. A., Donnelly, S.  
526 G., Keim, E. R., Del Negro, L. A., Proffitt, M. H., Margitan, J. J., Boering, K. A., Andrews, A.  
527 E., Daube, B. C., Wofsy, S. C., Anderson, B. E., Collins, J. E., Sachse, G. W., Vay, S. A., Elkins,  
528 J. W., Wamsley, P. R., Atlas, E. L., Flocke, F., Schauffler, S., Webster, C. R., May, R. D.,  
529 Loewenstein, M., Podolske, J. R., Bui, T. P., Chan, K. R., Bowen, S. W., Schoeberl, M. R., Lait,  
530 L. R., and Newman, P. A.: Comparison between DC-8 and ER-2 species measurements in the  
531 tropical middle troposphere: NO, NO<sub>y</sub>, O<sub>3</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, *Journal of Geophysical*  
532 *Research-Atmospheres*, 103, 22087-22096, 10.1029/98jd01421, 1998.

533 Wine, P. H., Wells, J. R., and Nicovich, J. M.: Kinetics of the reaction of F(2P) and Cl(2P) with  
534 HNO<sub>3</sub>, *Journal of Physical Chemistry*, 92, 2223-2228, 10.1021/j100319a028, 1988.

535