Supplement of Atmos. Chem. Phys., 15, 9191–9202, 2015
http://www.atmos-chem-phys.net/15/9191/2015/
doi:10.5194/acp-15-9191-2015-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

A better understanding of hydroxyl radical photochemical sources in cloud waters collected at the puy de Dôme station – experimental versus modelled formation rates

A. Bianco et al.

Correspondence to: L. Deguillaume (l.deguillaume@opgc.univ-bpclermont.fr)
and M. Brigante (marcello.brigante@univ-bpclermont.fr)

Reactions		k_{298} (M^{-n+1} s^{-1})	Ea/R (K)	References	Notes
HO_x chemistry					
$O_3 + h\nu \rightarrow H_2O_2 + O_2 - H_2O$	R(1)	Calculated		(Graedel and Weschler, 1981)	
$H_2O_2 + h\nu \rightarrow 2\ HO^\bullet$	R(2)	Calculated		(Graedel and Weschler, 1981)	
$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$	R(3)	$8.3\ 10^{5}$	2700	(Bielski et al., 1985)	
$HO_2^\bullet + O_2^{\bullet-} \rightarrow H_2O_2 + O_2 + OH^- - H_2O$	R(4)	$9.6\ 10^{7}$	910	(Christensen and Sehested, 1988)	
$O_3 + HO_2^\bullet \rightarrow HO^\bullet + 2\ O_2$	R(5)	$<1.0\ 10^{4}$		(Sehested et al., 1984)	1
$O_3 + O_2^{\bullet-} \rightarrow HO^\bullet + 2\ O_2 + OH^- - H_2O$	R(6)	$1.5\ 10^{9}$	2200	(Sehested et al., 1983)	
Iron chemistry					
$Fe^{3+} + h\nu \rightarrow Fe^{2+} + HO^\bullet + H^+ - H_2O$	R(7)	Calculated		(Benkelberg and Warneck, 1995)	
$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + HO^\bullet$	R(8)	Calculated		(Benkelberg and Warneck, 1995)	
$[Fe(OH)_2]^{+} + h\nu \rightarrow Fe^{2+} + HO^\bullet + OH^-$	R(9)	Calculated		(Benkelberg et al., 1991); (Weschler et al., 1986)	
$[Fe(SO_4)]^{+} + h\nu \rightarrow Fe^{2+} + SO_4^{\bullet-}$	R(10)	Calculated		(Benkelberg and Warneck, 1995)	
$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^\bullet + OH^-$	R(11)	$5.2\ 10^{1}$	5050	(Christensen et al., 1993); (Kremer, 2003)	
$H_2O_2 + FeO^{2+} \rightarrow Fe^{3+} + HO_2^\bullet + OH^-$	R(12)	$9.5\ 10^{3}$	2800	(Jacobsen et al., 1997)	
$O_2^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + H_2O_2 - 2\ H^+$	R(13)	$1.0\ 10^{7}$		(Rush and Bielski, 1985)	
$O_2^{\bullet-} + Fe^{3+} \rightarrow Fe^{2+} + O_2$	R(14)	$1.5\ 10^{8}$			$= k(O_2^{\bullet-} + [Fe(OH)]^{2+})$
$O_2^{\bullet-} + [Fe(OH)]^{2+} \rightarrow Fe^{2+} + O_2 + OH^-$	R(15)	$1.5\ 10^{8}$		(Rush and Bielski, 1985)	
$O_2^{\bullet-} + [Fe(OH)_2]^{+} \rightarrow Fe^{2+} + O_2 + 2\ OH^-$	R(16)	$1.5\ 10^{8}$			$= k(O_2^{\bullet-} + [Fe(OH)]^{2+})$
$HO_2^\bullet + Fe^{2+} \rightarrow Fe^{3+} + H_2O_2 - H^+$	R(17)	$1.2\ 10^{6}$	5050	(Jayson et al., 1973a)	
$HO_2^\bullet + FeO^{2+} \rightarrow Fe^{3+} + O_2 + OH^-$	R(18)	$2.0\ 10^{6}$		(Jacobsen et al., 1997)	
$O_3 + Fe^{2+} \rightarrow FeO^{2+} + O_2$	R(19)	$8.2\ 10^{5}$		(Logager et al., 1992)	
$FeO^{2+} \rightarrow Fe^{3+} + HO^\bullet + OH^- - H_2O$	R(20)	$1.3\ 10^{-2}$	4100	(Jacobsen et al., 1997)	
$FeO^{2+} + Fe^{2+} \rightarrow 2\ Fe^{3+} + 2\ OH^- - H_2O$	R(21)	$7.2\ 10^{4}$	840	(Jacobsen et al., 1997)	
$FeO^{2+} + Fe^{2+} \rightarrow Fe(OH)_2Fe^{4+} - H_2O$	R(22)	$1.8\ 10^{4}$	5050	(Jacobsen et al., 1997)	
$Fe(OH)_2Fe^{4+} \rightarrow 2\ Fe^{3+} + 2\ OH^-$	R(23)	$4.9\ 10^{-1}$	8800	(Jacobsen et al., 1997)	
$Fe(OH)_2Fe^{4+} + H^+ \rightarrow 2\ Fe^{3+} + 2\ H_2O - H^+$	R(24)	2.0	5650	(Jacobsen et al., 1997)	
$Cl_2^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + 2\ Cl^-$	R(25)	$1.0\ 10^{7}$	3060	(Thornton and Laurence, 1973)	
$Cl_2^{\bullet-} + Fe^{2+} \rightarrow [FeCl]^{2+} + Cl^-$	R(26)	$4.0\ 10^{6}$	3700	(Thornton and	

Reactions		k_{298} ($M^{-n+1}\ s^{-1}$)	Ea/R (K)	References	Notes
				Laurence, 1973)	
$Cl^- + Fe(O)^{2+} \rightarrow Fe^{3+} + ClOH^- - H^+$	R(27)	$1.0\ 10^{2}$		(Jacobsen et al., 1998)	
$NO_3^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + NO_3^-$	R(28)	$8.0\ 10^{6}$		(Pikaev et al., 1974)	
$NO_2 + Fe^{2+} \rightarrow Fe^{3+} + NO_2^-$	R(29)	$3.1\ 10^{4}$		(Epstein et al., 1982)	
$HNO_2 + FeO^{2+} \rightarrow Fe^{3+} + NO_2 + OH^-$	R(30)	$1.1\ 10^{4}$	4150	(Jacobsen et al., 1998)	
$NO_2^- + FeO^{2+} \rightarrow Fe^{3+} + NO_2 + OH^- - H^+$	R(31)	$<1.0\ 10^{5}$		(Jacobsen et al., 1998)	
$HSO_3^- + [Fe(OH)]^{2+} \rightarrow Fe^{2+} + SO_3^{\bullet-} - H_2O$	R(32)	$3.0\ 10^{1}$		(Ziajka et al., 1994)	
$SO_5^{\bullet-} + Fe^{2+} \rightarrow [Fe(OH)]^{2+} + HSO_5^- - H_2O$	R(33)	$2.6\ 10^{7}$		(Williams, 1996)	
$HSO_5^- + Fe^{2+} \rightarrow [Fe(OH)]^{2+} + SO_4^{\bullet-}$	R(34)	$3.0\ 10^{4}$		(Gilbert and Stell, 1990)	
$SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$	R(35)	$4.1\ 10^{9}$	-2165	(Buxton et al., 1997)	
$O_2^{\bullet-} + [Fe(SO_4)]^+ \rightarrow Fe^{2+} + SO_4^{2-} + O_2$	R(36)	$1.5\ 10^{8}$		(Rush and Bielski, 1985)	
$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-}$	R(37)	$1.7\ 10^{1}$		(Buxton et al., 1997)	
$HSO_3^- + FeO^{2+} \rightarrow Fe^{3+} + SO_3^{\bullet-} + OH^-$	R(38)	$2.5\ 10^{5}$		(Jacobsen et al., 1998)	
$Fe^{3+} + SO_4^{2-} \rightarrow [Fe(SO_4)]^+$	R(39)	$3.2\ 10^{3}$		(Jayson et al., 1973b)	
$[Fe(SO_4)]^+ \rightarrow Fe^{3+} + SO_4^{2-}$	R(40)	$2.7\ 10^{1}$		(Jayson et al., 1973b)	
$Fe^{3+} + Cl^- \rightarrow [FeCl]^{2+}$	R(41)	4.8		(Xu et al., 1985)	
$[FeCl]^{2+} \rightarrow Fe^{3+} + Cl^-$	R(42)	$9.2\ 10^{-1}$		Estimated following (Nadtochenko and Kiwi, 1998)	[2]
$C_2O_4^{\bullet-} + O_2 \rightarrow 2\ CO_2 + O_2^{\bullet-}$	R(43)	$2.4\ 10^{9}$		(Hislop and Bolton, 1999)	
$CO(O^-)CO(O^-) + Fe^{3+} \rightarrow [Fe(C_2O_4)]^+$	R(44)	$7.5\ 10^{6}$			[3]
$[Fe(C_2O_4)]^+ \rightarrow CO(O^-)CO(O^-) + Fe^{3+}$	R(45)	$3.0\ 10^{-3}$		(Moorhead and Sutin, 1966)	[4]
$CO(O^-)CO(O^-) + [Fe(C_2O_4)]^+ \rightarrow [Fe(C_2O_4)_2]^-$	R(46)	$1.9\ 10^{4}$			[3]
$[Fe(C_2O_4)_2]^- \rightarrow CO(O^-)CO(O^-) + [Fe(C_2O_4)]^+$	R(47)	$3.0\ 10^{-3}$			= k($[Fe(C_2O_4)]^+ \rightarrow CO(O^-)CO(O^-) + Fe^{3+}$)
$CO(O^-)CO(O^-) + [Fe(C_2O_4)_2]^- \rightarrow [Fe(C_2O_4)_3]^{3-}$	R(48)	$4.8\ 10^{1}$			3
$[Fe(C_2O_4)_3]^{3-} \rightarrow CO(O^-)CO(O^-) + [Fe(C_2O_4)_2]^-$	R(49)	$3.0\ 10^{-3}$			= k($[Fe(C_2O_4)]^+ \rightarrow CO(O^-)CO(O^-) + Fe^{3+}$)
$[Fe(C_2O_4)]^+ + h\nu \rightarrow Fe^{2+} + C_2O_4^{\bullet-}$	R(50)	Calculated		(Long et al., 2013)	
$[Fe(C_2O_4)_2]^- + h\nu \rightarrow Fe^{2+} + CO(O^-)CO(O^-) + C_2O_4^{\bullet-}$	R(51)	Calculated		(Faust and Zepp, 1993)	
$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe^{2+} + 2\ CO(O^-)CO(O^-) + C_2O_4^{\bullet-}$	R(52)	Calculated		(Faust and Zepp, 1993)	
Chlorine chemistry					
$Cl^{\bullet} \rightarrow OHCl^- + H^+ - H_2O$	R(53)	$1.7\ 10^{5}$		(Yu, 2004)	

Reactions		k_{298} (M^{-n+1} s^{-1})	Ea/R (K)	References	Notes
$OHCl^{-} + H^{+} \rightarrow Cl^{\bullet} + H_2O$	R(54)	3.3 10^{10}		(Yu and Barker, 2003)	
$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet-}$	R(55)	7.8 10^{9}		(Yu and Barker, 2003)	
$Cl_2^{\bullet-} \rightarrow Cl^{\bullet} + Cl^{-}$	R(56)	5.7 10^{4}		(Yu and Barker, 2003)	
$Cl_2^{\bullet-} \rightarrow OHCl^{-} + Cl^{-} + H^{+} - H_2O$	R(57)	1.3.10^{3}		(Yu, 2004)	
$Cl_2^{\bullet-} + OH^{-} \rightarrow OHCl^{-} + Cl^{-}$	R(58)	2.0 10^{7}		(Grigor'ev et al., 1987)	
$OHCl^{-} + Cl^{-} \rightarrow Cl_2^{\bullet-} + OH^{-}$	R(59)	1.0 10^{4}		(Grigor'ev et al., 1987)	
$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Cl_2 + 2\ Cl^{-}$	R(60)	9.0 10^{8}		(Yu, 2004)	
$Cl_2^{\bullet-} + Cl^{\bullet} \rightarrow Cl_2 + Cl^{-}$	R(61)	2.1 10^{9}		(Yu, 2004)	
$Cl_2 \rightarrow Cl^{-} + HOCl + H^{+} - H_2O$	R(62)	2.2 10^{1}	7600	(Wang and Margerum, 1994)	
$Cl^{-} + HOCl + H^{+} \rightarrow Cl_2 + H_2O$	R(63)	2.1 10^{4}	3500	(Wang and Margerum, 1994)	
$HOCl + HO_2^{\bullet} \rightarrow Cl^{\bullet} + O_2 + H_2O$	R(64)	7.5 10^{6}			= k($HOCl + O_2^{\bullet-}$)
$HOCl + O_2^{\bullet-} \rightarrow Cl^{\bullet} + O_2 + OH^{-}$	R(65)	7.5 10^{6}		(Long and Bielski, 1980)	
$Cl_2 + HO_2^{\bullet} \rightarrow Cl_2^{\bullet-} + O_2 + H^{+}$	R(66)	1.0 10^{9}		(Bjergbakke et al., 1981)	
$Cl_2 + O_2^{\bullet-} \rightarrow Cl_2^{\bullet-} + O_2$	R(67)	1.0 10^{9}			= k($Cl_2 + HO_2^{\bullet}$)
$HO_2^{\bullet} + Cl^{\bullet} \rightarrow Cl^{-} + O_2 + H^{+}$	R(68)	3.1 10^{9}	1500	(Graedel and Goldberg, 1983)	
$H_2O_2 + Cl^{\bullet} \rightarrow Cl^{-} + HO_2^{\bullet} + H^{+}$	R(69)	2.0 10^{9}		(Yu and Barker, 2003)	
$Cl^{-} + NO_3^{\bullet} \rightarrow NO_3^{-} + Cl^{\bullet}$	R(70)	1.0 10^{7}	4300	(Exner et al., 1992)	
$NO_3^{-} + Cl^{\bullet} \rightarrow Cl^{-} + NO_3^{\bullet}$	R(71)	1.0 10^{8}		(Buxton et al., 2000)	
$SO_4^{\bullet-} + Cl^{-} + \rightarrow SO_4^{2-} + Cl^{\bullet}$	R(72)	2.5 10^{8}		(Buxton et al., 1999)	
$SO_4^{2-} + Cl^{\bullet} \rightarrow SO_4^{\bullet-} + Cl^{-}$	R(73)	2.1 10^{8}		(Buxton et al., 1999)	
$HO_2^{\bullet} + Cl_2^{\bullet-} \rightarrow O_2 + 2\ Cl^{-} + H^{+}$	R(74)	1.3 10^{10}		(Jacobi et al., 1996)	
$O_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow O_2 + 2\ Cl^{-}$	R(75)	6.0 10^{9}		(Jacobi et al., 1996)	
$H_2O_2 + Cl_2^{\bullet-} \rightarrow 2\ Cl^{-} + HO_2^{\bullet} + H^{+}$	R(76)	6.2 10^{6}		(Yu, 2004)	
$O_3 + Cl_2^{\bullet-} \rightarrow OHCl + Cl^{\bullet} + O_2 + OH^{-} -H_2O$	R(77)	9.0 10^{7}		(Bielski, 1993)	
$HSO_3^{-} + Cl_2^{\bullet-} \rightarrow SO_3^{\bullet-} + 2\ Cl^{-} + H^{+}$	R(78)	1.7 10^{8}	400	(Jacobi et al., 1996)	
$SO_3^{2-} + Cl_2^{\bullet-} \rightarrow SO_3^{\bullet-} + 2\ Cl^{-}$	R(79)	6.2 10^{7}		(Jacobi et al., 1996)	
Carbonate chemistry					
$HCO_3^{-} + SO_4^{\bullet-} \rightarrow SO_4^{2-} + CO_3^{\bullet-} + H^{+}$	R(80)	2.8 10^{6}	2100	(Huie and Clifton, 1990)	
$CO_3^{2-} + SO_4^{\bullet-} \rightarrow SO_4^{2-} + CO_3^{\bullet-}$	R(81)	4.1 10^{6}	3200	(Padmaja et al., 1993)	
$HCO_3^{-} + Cl^{\bullet} \rightarrow Cl^{-} + CO_3^{\bullet-} + H^{+}$	R(82)	2.4 10^{9}		(Buxton et al., 2000)	
$CO_3^{2-} + Cl^{\bullet} \rightarrow Cl^{-} + CO_3^{\bullet-}$	R(83)	5.0 10^{8}		(Mertens and Von Sonntag, 1995)	
$CO_3^{\bullet-} + CO_3^{\bullet-} \rightarrow 2\ O_2^{\bullet-} + 2\ CO_2 - O_2$	R(84)	2.2 10^{6}		(Huie and Clifton, 1990)	

Reactions		k_{298} (M^{-n+1} s^{-1})	Ea/R (K)	References	Notes
$CO_3^{\bullet-} + HO_2^{\bullet} \rightarrow HCO_3^- + O_2$	R(85)	5.6 10^7		(Behar et al., 1970)	
$CO_3^{\bullet-} + O_2^{\bullet-} \rightarrow CO_3^{2-} + O_2$	R(86)	6.5 10^8		(Eriksen et al., 1985)	
$CO_3^{\bullet-} + H_2O_2 \rightarrow HO_2^{\bullet} + HCO_3^-$	R(87)	4.3 10^5		(Draganic et al., 1991)	
$CO_3^{\bullet-} + SO_3^{2-} \rightarrow CO_3^{2-} + SO_3^{\bullet-}$	R(88)	2.9 10^7	470	(Huie et al., 1991)	
$CO_3^{\bullet-} + O_3 \rightarrow CO_2 + O_2^{\bullet-} + O_2$	R(89)	1.0 10^5		(Sehested et al., 1983)	
$CO_3^{\bullet-} + NO_2 \rightarrow CO_2 + NO_3^-$	R(90)	1.0 10^9		(Lilie et al., 1978)	
N chemistry					
$HNO_2 + h\nu \rightarrow NO + HO^{\bullet}$	R(91)	Calculated		(Graedel and Weschler, 1981)	
$NO_2^- + h\nu + H_2O \rightarrow NO + HO^{\bullet} + OH^-$	R(92)	Calculated		(Graedel and Weschler, 1981) ; (Zellner et al., 1990)	
$HNO_2 + H_2O_2 + H^+ \rightarrow NO_3^- + 2\ H^+ + H_2O$	R(93)	6.3 10^3	6700	(Lee and Lind, 1986)	
$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	R(94)	5.0 10^5	6900	(Damschen and Martin, 1983)	
$HNO_2 + NO_3^{\bullet} \rightarrow NO_2 + NO_3^- + H^+$	R(95)	8.0 10^6		(Katsumura, 1998)	
$NO_2^- + NO_3^{\bullet} \rightarrow NO_2 + NO_3^-$	R(96)	1.4 10^9		(Herrmann and Zellner, 1998)	
$NO_2^- + CO_3^{\bullet-} \rightarrow NO_2 + CO_3^{2-}$	R(97)	6.6 10^5	850	(Huie et al., 1991)	
$NO_2^- + Cl^{\bullet} \rightarrow NO_2 + Cl^-$	R(98)	5.0 10^9		(Buxton et al., 2000)	
$NO_2 + HO_2^{\bullet} \rightarrow HNO_4$	R(99)	1.8 10^9		(Logager and Sehested, 1993)	
$NO_2 + O_2^{\bullet-} \rightarrow NO_4^-$	R(100)	4.5 10^9		(Logager and Sehested, 1993)	
$HNO_4 \rightarrow HO_2^{\bullet} + NO_2$	R(101)	2.6 10^{-2}		(Goldstein and Czapski, 1997)	
$HNO_4 \rightarrow HNO_2 + O_2$	R(102)	7.0 10^{-4}		(Logager and Sehested, 1993)	
$NO_4^- \rightarrow NO_2^- + O_2$	R(103)	1.1		(Goldstein and Czapski, 1997)	
$NO_4^- \rightarrow NO_2 + O_2^{\bullet-}$	R(104)	1.3		(Goldstein and Czapski, 1997)	
$HNO_4 + HSO_3^- \rightarrow SO_4^{2-} + NO_3^- + 2\ H^+$	R(105)	3.3 10^5		(Amels et al., 1996)	
$NO_2 + NO_2 \rightarrow HNO_2 + NO_3^- + H^+ - H_2O$	R(106)	8.4 10^7	-2900	(Park and Lee, 1988)	
$NO_2 + NO \rightarrow 2\ NO_2^- + 2H^+ - H_2O$	R(107)	3.0 10^8		(Hoffmann and Calvert, 1985)	
$NO_3^- + h\nu \rightarrow NO_2 + HO^{\bullet} + OH^- - H_2O$	R(108)	Calculated		(Graedel and Weschler, 1981) ; (Zellner et al., 1990)	
$N_2O_5 \rightarrow 2\ HNO_3 - H_2O$	R(109)	1.0 10^6		Estimated	5
$NO_3^{\bullet} + h\nu \rightarrow NO + O_2$	R(110)	Calculated		(Graedel and	

Reactions		k_{298} (M^{-n+1} s^{-1})	Ea/R (K)	References	Notes
				Weschler, 1981)	
$NO_3^{\bullet} + HO_2^{\bullet} \rightarrow NO_3^- + H^+ + O_2$	R(111)	$3.0\ 10^9$		(Sehested et al., 1994)	
$NO_3^{\bullet} + O_2^{\bullet -} \rightarrow NO_3^- + O_2$	R(112)	$3.0\ 10^9$			= $k(NO_3^{\bullet} + HO_2^{\bullet})$
$NO_3^{\bullet} + OH^- \rightarrow NO_3^- + HO^{\bullet}$	R(113)	$9.4\ 10^7$	2700	(Exner et al., 1992)	
$NO_3^{\bullet} + H_2O_2 \rightarrow NO_3^- + H^+ + HO_2^{\bullet}$	R(114)	$4.9\ 10^6$	2000	(Herrmann et al., 1994)	
$NO_3^{\bullet} + HSO_4^- \rightarrow NO_3^- + H^+ + SO_4^{\bullet -}$	R(115)	$2.6\ 10^5$		(Raabe, 1996)	
$NO_3^{\bullet} + SO_4^{2-} \rightarrow NO_3^- + SO_4^{\bullet -}$	R(116)	$1.0\ 10^5$		(Logager and Sehested, 1993)	
$NO_3^{\bullet} + HSO_3^- \rightarrow SO_3^{\bullet -} + NO_3^- + H^+$	R(117)	$1.3\ 10^9$	2200	(Exner et al., 1992)	
$NO_3^{\bullet} + SO_3^{2-} \rightarrow NO_3^- + SO_3^{\bullet -}$	R(118)	$3.0\ 10^8$		(Exner et al., 1992)	
S chemistry					
$SO_3^{\bullet -} + O_2 \rightarrow SO_5^{\bullet -}$	R(119)	$1.1\ 10^9$		(Das, 2001)	
$SO_3^{\bullet -} + SO_3^{\bullet -} \rightarrow S_2O_6^{2-}$	R(120)	$1.6\ 10^7$	1200	(Buxton et al., 1996b)	
$SO_5^{\bullet -} + HSO_3^- \rightarrow HSO_5^- + SO_3^{\bullet -}$	R(121)	$8.6\ 10^3$		(Buxton et al., 1996b)	
$SO_5^{\bullet -} + HSO_3^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} + H^+$	R(122)	$3.6\ 10^2$		(Buxton et al., 1996b)	
$SO_5^{\bullet -} + SO_3^{2-} \rightarrow HSO_5^- + SO_3^- + OH^- - H_2O$	R(123)	$2.1\ 10^5$		(Buxton et al., 1996b)	
$SO_5^{\bullet -} + SO_3^{2-} \rightarrow SO_4^{\bullet -} + SO_4^{2-}$	R(124)	$5.5\ 10^5$		(Buxton et al., 1996b)	
$SO_5^{\bullet -} + HO_2^{\bullet} \rightarrow HSO_5^- + O_2$	R(125)	$1.7\ 10^9$		(Buxton et al., 1996a)	
$SO_5^{\bullet -} + O_2^{\bullet -} \rightarrow HSO_5^- + O_2 + OH^- - H_2O$	R(126)	$2.3\ 10^8$		(Buxton et al., 1996b)	
$SO_5^{\bullet -} + SO_5^{\bullet -} \rightarrow 2\ SO_4^{\bullet -} + O_2$	R(127)	$2.1\ 10^8$		(Das, 2001)	
$SO_5^{\bullet -} + SO_5^{\bullet -} \rightarrow S_2O_8^{2-} + O_2$	R(128)	$2.2\ 10^8$		(Das, 2001)	
$HSO_5^- + HSO_3^- + H^+ \rightarrow 2\ SO_4^{2-} + 3\ H^+$	R(129)	$1.0\ 10^7$		(Das, 2001)	
$HSO_5^- + SO_3^{2-} + H^+ \rightarrow 2\ SO_4^{2-} + 2\ H^+$	R(130)	$1.0\ 10^7$			= $k(HSO_5^- + HSO_3^-)$
$HSO_5^- + SO_4^{\bullet -} \rightarrow SO_5^{\bullet -} + HSO_4^-$	R(131)	$1.0\ 10^6$		(Das, 2001)	
$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-}$	R(132)	$7.0\ 10^8$		(Das, 2001)	
$SO_4^{\bullet -} + HSO_3^- \rightarrow SO_4^{2-} + H^+ + SO_3^{\bullet -}$	R(133)	$6.8\ 10^8$		(Buxton et al., 1996b)	
$SO_4^{\bullet -} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^{\bullet -}$	R(134)	$3.1\ 10^8$	1200	(Buxton et al., 1996b)	
$SO_4^{\bullet -} + HO_2^{\bullet} \rightarrow SO_4^{2-} + H^+ + O_2$	R(135)	$3.5\ 10^9$		(Jiang et al., 1992)	
$SO_4^{\bullet -} + O_2^{\bullet -} \rightarrow SO_4^{2-} + O_2$	R(136)	$4.0\ 10^9$		(Buxton et al., 1996b)	
$SO_4^{\bullet -} + OH^- \rightarrow SO_4^{2-} + HO^{\bullet}$	R(137)	$2.0\ 10^7$		(Ross et al., 1994)	
$SO_4^{\bullet -} + H_2O_2 \rightarrow SO_4^{2-} + HO_2^{\bullet} + H^+$	R(138)	$1.2\ 10^7$		(Maruthamuthu and Neta, 1978)	
$SO_4^{\bullet -} + NO_3^- \rightarrow SO_4^{2-} + NO_3^{\bullet}$	R(139)	$5.0\ 10^4$		(Exner et al., 1992)	
$SO_4^{\bullet -} \rightarrow HSO_4^- + HO^{\bullet} - H_2O$	R(140)	$3.6\ 10^2$		(Tang et al., 1988)	
$HSO_3^- + O_3 \rightarrow HSO_4^- + O_2$	R(141)	$3.7\ 10^5$	5500	(Hoffmann, 1986)	
$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$	R(142)	$1.5\ 10^9$	5300	(Hoffmann, 1986)	
$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + 2\ H^+ + H_2O - H^+$	R(143)	$9.1\ 10^7$	3600	(Maaß et al., 1999)	

[1] - Sehested et al. (1984) argue that this reaction is very slow with a rate constant lower than 10^4 M^{-1} s^{-1}.
[2] - Xu et al. (1985) calculated k(Fe^{3+} + Cl^-) = 4.8 M^{-1} s^{-1}. The equilibrium constant from Nadtochenko and Kiwi (1998) is equal to 5.3 M^{-1}. Therefore we calculate the backward rate constant by 4.8/5.3 = 9.1 10^{-1} s^{-1}.
[3] - The equilibrium constants are from Martell and Smith (1977). logK(CO(O^-)CO(O^-) + Fe^{3+} $\leftrightarrow$ $[Fe(C_2O_4)]^+$) = 9.4 ; logK(2 CO(O^-)CO(O^-) + Fe^{3+} $\leftrightarrow$ $[Fe(C_2O_4)_2]^-$) = 16.2 ; logK(3 CO(O^-)CO(O^-) + Fe^{3+} $\leftrightarrow$ $[Fe(C_2O_4)_3]^{3-}$) = 20.4). We calculate the equilibrium constants : logK(CO(O^-)CO(O^-) + $[Fe(C_2O_4)]^+$ $\leftrightarrow$ $[Fe(C_2O_4)_2]^-$) = 6.8 ; logK(CO(O^-)CO(O^-) + $[Fe(C_2O_4)_2]^-$ $\leftrightarrow$ $[Fe(C_2O_4)_3]^{3-}$ = 4.2. With these equilibrium constants and the backward rate constant, we calculate the forward rate constants.
[4] - Moorhead and Sutin (1966) measured rate constants for the equilibrium $Fe(OH)^{2+}$ + CO(OH)CO(O^-) $\leftrightarrow$ $Fe(C_2O_4)^+$: $k_{backward}$ = 3.0 10^{-3} s^{-1} and $k_{forward}$ = 2.0 10^4 M^{-1} s^{-1}. The equilibrium constant is similar to Martell and Smith (1977). We suppose that the rate constant of the reaction $[Fe(C_2O_4)]^+$ $\rightarrow$ CO(O^-)CO(O^-) + Fe^{3+} is equal to 3.0 10^{-3} s^{-1}.
[5] - We suppose that the N_2O_5 hydrolysis is fast with a first order rate constant equal to 10^6 s^{-1} (Bertram and Thornton, 2009).

Equilibria

Species		K_a or K_h	-ΔH/R (K)	References	Notes
$H_2O_2 \leftrightarrow HO_2^- + H^+$	T(1)	$2.2\ 10^{-12}$	-3730	(Smith and Martell, 1976)	
$HO_2^\bullet \leftrightarrow O_2^{\bullet-} + H^+$	T(2)	$1.6\ 10^{-5}$		(Bielski et al., 1985)	
$HNO_2 \leftrightarrow NO_2^- + H^+$	T(3)	$1.6\ 10^{-3}$	1760	(Park and Lee, 1988); (Riordan et al., 2005)	
$HNO_3 \leftrightarrow NO_3^- + H^+$	T(4)	$2.2\ 10^{1}$		(N.B.S, 1965)	
$HNO_4 \leftrightarrow NO_4^- + H^+$	T(5)	$1.3\ 10^{-6}$		(Goldstein and Czapski, 1997)	
$HCl \leftrightarrow Cl^- + H^+$	T(6)	$1.7\ 10^{-6}$	-6890	(Marsh and McElroy, 1985)	
$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$	T(7)	$1.3\ 10^{-2}$	-1960	(Maash, 1982)	
$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$	T(8)	$6.4\ 10^{-8}$	-1430	(Maash, 1982)	
$H_2SO_4 \leftrightarrow HSO_4^- + H^+$	T(9)	$1.0\ 10^{3}$		(Cotton and Wilkinson, 1980)	
$HSO_4^- \leftrightarrow SO_4^{2-} + H^+$	T(10)	$1.0\ 10^{-2}$		(Eigen et al., 1964)	
$Fe^{3+} + H_2O \leftrightarrow [Fe(OH)]^{2+} + H^+$	T(11)	$6.0\ 10^{-3}$		(Brandt and van Eldik, 1995)	
$[Fe(OH)]^{2+} + H_2O \leftrightarrow [Fe(OH)_2]^+ + H^+$	T(12)	$7.6\ 10^{-4}$		(Brandt and van Eldik, 1995)	
$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$	T(13)	$4.2\ 10^{-7}$		(Cotton and Wilkinson, 1980)	
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	T(14)	$4.8\ 10^{-11}$		(Cotton and Wilkinson, 1980)	

Table SM1: Chemical mechanism considered in the M2C2 model.

	Date		Origin	Temperature (°C)	pH	Redox potential (mV)	TOC (mg/L)	TC (mg/L)	IC (mg/L)	Anions (μmol/L)						Cations (μmol/L)				
										SO_4^{2-}	Cl^-	Acetate	Formate	Oxalate	Succinate	Na^+	NH_4^+	Mg^{2+}	K^+	Ca^{2+}
1	10/14/2013	4PM-6PM	W	6	6.1	NM	NM	NM	2.7	23.0	45.9	8.7	34.8	4.5	3.3	18.5	66.2	33.7	7.2	2.4
2	10/14/2013	6PM-9PM	W	6.5	5.6	NM	NM	NM	0.9	16.7	82.5	3.3	20.4	2.5	3.7	7.6	33.0	6.4	33.1	0.4
3	10/14/2013	9PM-12PM	W	6.7	5.6	NM	1.6	2.2	0.7	18.5	46.2	2.6	11.7	1.8	4.2	11.9	44.6	5.2	20.9	3.8
4	10/29/2013	5AM-8AM	W	2.2	5.0	261	2.8	3.6	0.8	46.8	246.9	21.1	28.5	2.7	4.2	56.3	38.0	NM	4.8	NM
5	10/29/2013	8AM-12AM	W	3.1	5.6	248	3.2	3.3	0.1	55.8	269.5	19.1	25.3	2.8	5.2	76.3	64.0	NM	11.7	NM
6	11/5/2013	2PM-4PM	W	6	5.8	231	2.0	2.7	0.7	8.5	25.0	13.9	25.5	1.9	3.4	7.8	13.5	NM	34.1	NM
7	11/5/2013	4PM-7PM	W	6	5.5	263	1.1	1.7	0.6	4.5	7.2	17.5	12.4	1.3	3.9	3.7	8.9	NM	25.7	NM
8	11/5/2013	7PM-9PM	W	5.8	5.6	313	0.8	1.4	0.56	7.9	16.6	9.3	24.5	1.7	3.0	4.5	17.7	NM	21.9	NM
9	11/5/2013	9PM-12PM	W	5.5	5.0	290	0.6	1.5	0.8	9.8	16.9	5.7	7.2	1.3	2.3	6.5	26.7	NM	22.7	NM
10	11/6/2013	7AM-10AM	W	7.9	5.4	289	1.1	1.9	0.9	6.1	9.7	7.5	17.2	1.3	5.7	6.0	18.0	NM	24.3	NM
11	11/6/2013	10AM-12AM	W	8	5.7	352	1.9	2.6	0.7	6.7	5.8	7.5	9.5	1.5	2.7	3.3	27.0	NM	25.8	NM
12	3/22/2014	7AM-11AM	W	0	6.7	228	2.9	3.5	0.6	34.8	65.7	13.3	48.3	4.1	0.1	20.9	87.6	12.4	2.3	4.7
13	3/22/2014	11AM-2PM	W	0	6.7	264	5.4	6.1	0.7	37.1	133.8	20.4	43.8	5.4	0.2	36.8	108.8	8.7	4.9	6.6
14	3/25/2014	11AM-1PM	W	-2	6.6	240	3.4	3.9	0.5	49.2	228.5	13.8	30.6	3.2	0.1	56.8	73.2	10.3	9.1	7.1
15	3/25/2014	1PM-3PM	NW	0	6.4	228	6.0	6.6	0.5	32.6	153.8	14.0	65.1	3.3	0.2	38.8	79.6	12.5	6.4	6.9
16	3/25/2014	7PM-9PM	NW	-2	6.1	243	8.7	9.0	0.4	14.8	73.0	12.5	65.0	3.8	0.2	20.8	50.2	13.6	4.0	9.4
17	3/26/2014	8AM-9AM	N	-3	5.5	233	6.5	7.0	0.5	56.4	25.2	26.2	38.3	5.9	0.8	9.6	252.4	7.2	2.9	7.9
18	3/26/2014	9AM-11AM	N	-3	5.4	239	8.6	9.2	0.6	45.4	26.5	15.8	34.9	5.3	0.7	8.3	206.0	9.0	2.4	15.6
19	4/4/2014	8PM-10PM	NW	2	6.2	261	1.5	2.0	0.5	13.5	19.4	9.6	23.6	3.4	0.4	5.0	39.6	5.4	7.8	0.0
20	4/4/2014	10PM-12PM	NW	2	6.5	261	1.7	2.1	0.4	18.2	18.2	7.2	24.2	3.8	0.3	3.9	71.4	4.3	7.1	0.0
21	4/5/2014	1PM-4AM	W	2	6.6	250	2.6	3.1	0.5	26.0	29.4	14.3	32.5	4.4	0.3	6.9	124.1	4.4	7.4	0.0
22	4/5/2014	4AM-7AM	W	2	6.9	237	3.9	4.6	0.7	39.8	48.7	25.4	48.8	6.9	0.4	12.6	192.8	4.3	4.8	0.0
23	4/5/2014	7AM-10AM	W	2	6.8	239	4.5	5.3	0.7	67.5	76.1	30.4	63.4	7.4	0.5	18.0	212.7	5.3	4.3	2.0
24	4/11/2014	11AM-1PM	W	1	5.4	207	1.9	1.9	0.0	7.5	14.0	7.6	3.6	5.4	6.2	27.7	NM	NM	31.9	NM
25	5/11/2014	4AM-6PM	W	0.3	4.7	238	1.8	1.8	0.0	58.1	35.4	11.8	3.8	113.2	13.9	51.4	NM	NM	26.0	NM
26	5/11/2014	7AM-9AM	NW	0	4.1	280	1.8	1.8	0.0	139.3	41.7	5.2	3.3	115.7	9.2	43.8	39.7	NM	20.3	NM

27	5/11/2014	9AM-12AM	NW	-0.1	4.1	298	NM	14.9	0.1	247.4	98.0	3.8	3.4	302.2	18.8	99.9	83.9	NM	17.8	NM
28	5/11/2014	12AM-1PM	NW	0.1	4.2	295	3.6	3.6	0.0	202.8	87.0	10.8	3.1	377.2	27.9	116.7	97.37	NM	21.7	NM
29	12/11/2014	3PM-5PM	W	3	5.4	250	4.0	4.0	0.0	38.3	78.9	11.9	5.4	83.2	21.9	83.5	15.1	NM	19.9	NM
30	12/11/2014	5PM-7PM	W	2	5.5	261	2.3	2.4	0.1	28.7	68.2	12.7	4.8	47.1	21.7	72.2	NM	NM	17.6	NM
31	12/11/2014	7PM-9PM	W	2	5.6	254	2.7	2.8	0.1	24.2	68.9	2.9	2.9	32.5	33.0	77.3	NM	NM	21.3	NM
32	12/11/2014	9PM-12PM	W	2	5.4	254	1.7	1.7	0.1	23.4	64.4	5.2	4.5	20.2	13.5	80.1	NM	NM	17.5	NM
33	14/11/2014	5PM-7PM	S	5	5.5	258	2.2	2.2	0.0	11.3	6.0	4.9	3.6	10.4	5.4	15.7	NM	NM	16.3	NM
34	17/11/2014	4PM-6PM	W	1.1	5.6	249	2.2	2.4	0.1	8.8	4.7	7.6	3.9	11.8	5.6	13.1	NM	NM	21.3	NM
35	17/11/2014	7PM-9PM	W	0.7	5.7	245	1.0	1.1	0.0	8.0	2.0	7.3	3.6	10.0	5.8	10.9	NM	NM	19.9	NM
36	17/11/2014	9PM-12PM	W	0.6	5.3	263	1.2	1.2	0.0	11.0	5.3	6.9	3.8	14.3	6.9	14.2	NM	NM	18.5	NM
37	18/11/2014	6AM-8AM	NW	0.1	5.4	258	1.0	0.9	0.0	28.2	16.5	4.2	3.4	32.6	7.2	23.0	NM	NM	19.1	NM
38	18/11/2014	5PM-7PM	NW	1.8	5.7	243	2.3	2.4	0.1	16.4	11.9	8.8	3.6	22.0	7.0	18.3	2.2	NM	20.2	NM
39	18/11/2014	7PM-9PM	NW	1	5.3	257	1.8	1.8	0.0	14.0	7.3	5.6	3.7	14.1	5.6	18.2	NM	NM	20.2	NM
40	18/11/2014	9PM-12PM	NW	1	4.9	284	1.9	1.9	0.1	20.0	18.0	7.0	3.6	16.0	8.3	17.7	NM	NM	18.7	NM
41	19/11/2014	12PM-2AM	NW	1	4.6	306	2.2	2.2	0.0	26.7	36.7	10.3	3.4	34.7	12.3	28.1	NM	NM	17.1	NM

Table SM2: Physico-chemical parameters of sampled clouds. 23 samples have been analyzed corresponding to 6 cloud events. Acet: acetic acid; Form: formic acid, Oxal: oxalic acid, Succ: succinic acid). NM: not measured.

Cloud sample	Relative contribution (%)					$R^{f}_{HO^\bullet}$ mod ($M\ s^{-1}$)	$R^{f}_{HO^\bullet}$ exp ($M\ s^{-1}$)
	H_2O_2 + hν	Fe (II) + H_2O_2	Fe (III) + hν	NO_3^- + hν	HNO_2 + NO_2^- + hν		
1	86.7	0.0	0.0	2.6	10.6	4.3×10^{-11}	3.3×10^{-11}
2	64.9	0.0	0.0	1.0	34.1	4.2×10^{-11}	NM
3	90.7	0.0	0.0	1.3	7.9	5.0×10^{-11}	NM
4	91.2	0.0	0.0	2.0	6.7	4.6×10^{-11}	1.4×10^{-10}
5	89.1	0.0	0.0	2.2	8.6	4.4×10^{-11}	1.2×10^{-10}
6	99.3	0.0	0.0	0.7	0.0	2.4×10^{-11}	2.8×10^{-11}
7	99.4	0.0	0.0	0.6	0.0	1.9×10^{-11}	5.6×10^{-11}
8	98.4	0.0	0.0	1.6	0.0	3.0×10^{-11}	2.5×10^{-11}
9	97.8	0.0	0.0	2.2	0.0	2.5×10^{-11}	2.2×10^{-11}
10	99.5	0.0	0.0	0.5	0.0	3.1×10^{-11}	2.9×10^{-11}
11	99.3	0.0	0.0	0.7	0.0	5.2×10^{-11}	6.8×10^{-11}
12	22.3	21.6	54.2	0.7	1.2	2.4×10^{-10}	6.1×10^{-11}
13	57.3	10.7	22.4	1.2	8.4	1.3×10^{-10}	4.7×10^{-11}
14	52.4	10.7	35.1	1.8	0.0	6.9×10^{-11}	2.8×10^{-11}
15	92.5	0.0	0.0	2.7	4.9	4.7×10^{-11}	1.1×10^{-11}
16	91.8	0.0	0.0	4.8	3.4	3.0×10^{-11}	NM
17	50.2	12.4	21.7	15.1	0.7	9.8×10^{-11}	6.1×10^{-11}
18	51.8	22.3	10.4	14.6	0.9	9.4×10^{-11}	3.4×10^{-11}
19	94.6	0.0	0.0	2.8	2.6	4.8×10^{-11}	8.1×10^{-11}
20	91.4	0.0	0.0	4.8	3.7	5.2×10^{-11}	8.5×10^{-11}
21	88.0	0.0	0.0	6.4	5.6	7.6×10^{-11}	1.5×10^{-10}
22	90.7	0.0	0.0	5.1	4.2	1.7×10^{-10}	3.4×10^{-10}
23	89.0	0.0	0.0	5.3	5.7	1.7×10^{-10}	4.2×10^{-10}
24	98.0	0.0	0.0	2.0	0.0	2.5×10^{-11}	5.1×10^{-11}
25	60.6	29.2	1.1	4.2	4.9	3.4×10^{-11}	2.4×10^{-11}
26	26.2	70.0	1.1	2.6	0.1	1.0×10^{-10}	1.4×10^{-10}
27	19.3	76.8	0.9	3.0	0.1	1.8×10^{-10}	5.0×10^{-11}
28	17.6	79.0	1.0	2.4	0.0	2.2×10^{-10}	NM

29	39.8	40.3	12.7	2.7	4.5	6.2×10^{-11}	8.5×10^{-11}
30	43.4	27.3	18.6	2.2	8.5	6.2×10^{-11}	8.4×10^{-11}
31	21.7	33.0	39.4	1.1	4.8	1.3×10^{-10}	6.1×10^{-11}
32	92.1	1.6	1.3	3.3	1.7	4.3×10^{-11}	NM
33	31.0	10.2	56.8	2.0	0.0	2.3×10^{-11}	3.3×10^{-12}
34	16.6	27.9	52.0	0.5	3.1	1.5×10^{-10}	2.7×10^{-11}
35	24.0	5.5	48.5	3.7	18.4	2.9×10^{-11}	3.6×10^{-11}
36	60.7	7.3	18.9	13.0	0.2	1.1×10^{-11}	6.0×10^{-11}
37	63.5	8.3	15.6	12.4	0.2	1.0×10^{-11}	2.4×10^{-11}
38	47.7	17.3	6.7	5.9	22.4	1.5×10^{-11}	5.8×10^{-11}
39	67.5	14.7	7.7	10.0	0.1	1.4×10^{-11}	2.7×10^{-11}
40	81.6	4.5	1.3	12.4	0.2	2.1×10^{-11}	1.3×10^{-10}
41	47.0	35.9	2.9	9.0	5.3	3.5×10^{-11}	1.1×10^{-10}

Table SM3: Modelled relative contributions of $HO^{\bullet}$ sources for the 41 cloud samples. Modelled and experimental $R^{f}_{HO^{\bullet}}$ are also indicated. NM: not measured.

Cloud sample	Relative contribution (%)			$R^f_{HO^\bullet}$ mod (M s^{-1})	$R^f_{HO^\bullet}$ exp (M s^{-1})
	H_2O_2 + hν	NO_3^- + hν	HNO_2 + NO_2^- + hν		
1	93.2	3.1	3.7	6.6×10^{-11}	3.3×10^{-11}
2	84.4	1.4	14.2	5.3×10^{-11}	NM
3	95.7	1.6	2.7	7.9×10^{-11}	NM
4	95.3	2.4	2.4	7.3×10^{-11}	1.4×10^{-10}
5	94.4	2.6	3.0	6.9×10^{-11}	1.2×10^{-10}
6	99.2	0.8	0.0	3.9×10^{-11}	2.8×10^{-11}
7	99.3	0.7	0.0	3.1×10^{-11}	5.6×10^{-11}
8	98.3	1.7	0.0	4.9×10^{-11}	2.5×10^{-11}
9	97.6	2.4	0.0	4.2×10^{-11}	2.2×10^{-11}
10	99.4	0.6	0.0	5.1×10^{-11}	2.9×10^{-11}
11	99.2	0.8	0.0	8.6×10^{-11}	6.8×10^{-11}
12	95.2	3.2	1.6	9.4×10^{-11}	6.1×10^{-11}
13	93.4	2.2	4.3	1.3×10^{-10}	4.7×10^{-11}
14	96.2	3.8	0.0	6.2×10^{-11}	2.8×10^{-11}
15	95.3	3.1	1.6	7.6×10^{-11}	1.1×10^{-11}
16	93.5	5.4	1.1	4.8×10^{-11}	NM
17	74.6	25.0	0.4	1.1×10^{-10}	6.1×10^{-11}
18	75.8	23.8	0.5	1.1×10^{-10}	3.4×10^{-11}
19	96.0	3.2	0.8	7.7×10^{-11}	8.1×10^{-11}
20	93.3	5.5	1.2	8.4×10^{-11}	8.5×10^{-11}
21	90.8	7.3	1.8	1.2×10^{-10}	1.5×10^{-10}
22	92.9	5.8	1.4	2.8×10^{-10}	3.4×10^{-10}
23	92.0	6.1	1.9	2.7×10^{-10}	4.2×10^{-10}
24	97.7	2.2	0.0	4.1×10^{-11}	5.1×10^{-11}
25	90.4	7.1	2.6	3.7×10^{-11}	2.4×10^{-11}
26	87.3	12.6	0.1	3.9×10^{-11}	1.4×10^{-10}
27	77.8	22.0	0.2	4.2×10^{-11}	5.0×10^{-11}
28	79.7	20.2	0.2	4.5×10^{-11}	NM
29	89.8	6.8	3.3	4.4×10^{-11}	8.5×10^{-11}
30	89.4	5.0	5.7	4.9×10^{-11}	8.4×10^{-11}
31	88.7	5.0	6.3	5.1×10^{-11}	6.1×10^{-11}
32	95.6	3.8	0.6	6.8×10^{-11}	NM
33	93.3	6.7	0.0	1.1×10^{-11}	3.3×10^{-12}
34	91.8	2.8	5.5	4.6×10^{-11}	2.7×10^{-11}
35	70.6	12.0	17.4	1.6×10^{-11}	3.6×10^{-11}
36	80.7	19.2	0.1	1.3×10^{-11}	6.0×10^{-11}
37	82.0	17.9	0.1	1.3×10^{-11}	2.4×10^{-11}
38	77.6	10.8	11.7	1.5×10^{-11}	5.8×10^{-11}
39	85.7	14.2	0.1	1.8×10^{-11}	2.7×10^{-11}
40	85.4	14.5	0.1	3.3×10^{-11}	1.3×10^{-10}
41	79.5	17.2	3.2	3.3×10^{-11}	1.1×10^{-10}

Table SM4. Modeled relative contributions of $HO^{\bullet}$ sources for the 41 cloud samples considering the new photolysis experimental rates in the model for H_2O_2, nitrite and nitrate and without iron chemistry. Modeled and experimental $R^{f}_{HO^{\bullet}}$ are also indicated. NM: not measured.

References

Amels, T., Elias, H., Götz, U., Steingens, U., and Wannowius, K. J.: Kinetic investigation of the stability of peroxonitric acid and its reaction with sulfur(IV) in aqueous solution, in: Heterogeneous and liquid-phase processes, 1, 1996.

Behar, D., Czapski, G., and Duchovny, I.: Carbonate radical in flash photolysis and pulse radiolysis of aqueous carbonate solutions, J. Phys. Chem., 74, 2206-2210, 10.1021/j100909a029, 1970.

Benkelberg, H. J., Schäfer, A., and Warneck, P.: Product quantum yields for the photodecomposition of H_2O_2 and Fe(III) complexes in aqueous soltion in: Air Pollution research Report 33: Atmospheric Oxidation Processes, edited by: Becker, K. H., CEC, Brussels, 130, 1991.

Benkelberg, H. J., and Warneck, P.: Photodecomposition of iron(III) hydroxo and sulfato complexes in aqueous solution: Wavelength dependence of OH and SO_4^- quantum yields, J. Phys. Chem., 99, 5214-5221, 10.1021/j100014a049, 1995.

Bielski, B. H. J., Cabelli, D. E., Arudi, R. L., and Ross, A. B.: Reactivity of HO_2/O_2^- Radicals in Aqueous Solution, J. Phys.Chem. Ref. Data, 14, 1041-1100, 1985.

Bielski, B. H. J.: A pulse radiolysis study of the reaction of ozone with Cl_2 in aqueous solutions, Rad. Phys. Chem., 41, 527-530, 1993.

Bjergbakke, E., Navaratnam, S., Parsons, B. J., and Swallow, A. J.: Reaction between hydroperoxo radicals and chlorine in aqueous solution, J. Am. Chem. Soc., 103, 5926-5928, 10.1021/ja00409a059, 1981.

Brandt, C., and van Eldik, R.: Transition metal-catalyzed oxidation of sulfur(IV) oxides. Atmospheric-relevant processes and mechanisms, Chem. Rev., 95, 119-190, 10.1021/cr00033a006, 1995.

Buxton, G. V., Malone, T. N., and Salmon, G. A.: Pulse radiolysis study of the reaction of $SO_5^{\cdot-}$ with $HO_2^{\cdot}$, J. Chem. Soc., Faraday Transactions, 92, 1996a.

Buxton, G. V., McGowan, S., Salmon, G. A., Williams, J. E., and Wood, N. D.: A study of the spectra and reactivity of oxysulphur-radical anions involved in the chain oxidation of S(IV): A pulse and γ-radiolysis study, Atmospheric Environment, 30, 2483-2493, http://dx.doi.org/10.1016/1352-2310(95)00473-4, 1996b.

Buxton, G. V., Malone, T. N., and Salmon, G. A.: Reaction of SO_4^- with Fe^{2+}, Mn^{2+} and Cu^{2+} in aqueous solution, J. Chem. Soc., Faraday Transactions, 93, 1997.

Buxton, G. V., Bydder, M., and Salmon, G. A.: The reactivity of chlorine atoms in aqueous solution. Part II. The equilibrium $SO_4^- + Cl^- = Cl + SO_4^{2-}$, Phys. Chem. Chem. Phys., 1, 269-273, 1999.

Buxton, G. V., Bydder, M., Salmon, G. A., and Williams, J.: The reactivity of chlorine atoms in aqueous solution, Part III.The reactions of Cl with solutes, Phys. Chem. Chem. Phys., 2, 237-245, 2000.

Christensen, H., and Sehested, K.: Hydroperoxo and oxygen(1-) radicals at elevated temperatures, J. Phys. Chem., 92, 3007-3011, 10.1021/j100321a060, 1988.

Christensen, H., Sehested, K., and LÃ¸gager, T.: The reaction of hydrogen peroxide with Fe(II) ions at elevated temperatures, Rad. Phys. Chem., 41, 575-578, 1993.

Cotton, F. A., and Wilkinson, G.: Advanced inorganic chemistry: a comprehensive text, 4th ed., John Wiley & Sons, New York, 1455 pp., 1980.

Damschen, D. E., and Martin, L. R.: Aqueous aerosol oxidation of nitrous acid by O_2, O_3, and H_2O_2, Atmos. Environ., 17, 2005-2011, 1983.

Das, T. N.: Reactivity and role of $SO_5^{\cdot-}$ radical in aqueous medium chain oxidation of sulfite to sulfate and atmospheric sulfuric acid generation, J. Phys. Chem., 105, 9145-9155, 2001.

Draganic, Z. D., Negron-Mendoza, A., Sehested, K., Vujosevic, S. I., Navarro-Gonzales, R., Albarran-Sanchez, M. G., and Draganic, I. G.: Radiolysis of aqueous solution of ammonium bicarbonate over a large dose range, Rad. Phys. Chem., 38, 317-321, 1991.

Eigen, M., Krause, W., Maash, H. G., and Demaeyer, L.: Rate constants of photolytic reactions in aqueous solution, in: Progress in reaction kinetics, edited by: Porter, G., Macmillan, N. J., 285-318, 1964.

Epstein, I. R., Kustin, K., and Simoyi, R. H.: Systematic design of chemical oscillators. 6. Nitrous acid decomposition catalyzed by an iron(II) complex: tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II), J. Am. Chem. Soc., 104, 712-717, 10.1021/ja00367a013, 1982.

Eriksen, T. E., Lind, J. A., and Merenyi, G.: On the acid-base equilibrium of the carbonate radical, Rad. Phys. Chem., 26, 197-199, 1985.
Exner, M., Herrmann, H., and Zellner, R.: Laser-based studies of reactions of the nitrate radical in aqueous solution, B. Buns. phys. Chem., 3, 470-477, 1992.
Faust, B. C., and Zepp, R. G.: Photochemistry of aqueous iron(III)-polycarboxylate complexes: roles in the chemistry of atmospheric and surface waters, Environ. Sci. Tech., 27, 2517-2522, 1993.
Gilbert, B. C., and Stell, J. K.: Mechanisms of peroxide decomposition. An ESR study of the reactions of the peroxomonosulphate anion ($HOOSO_3^-$) with Ti(III), Fe(II), and alpha-oxygen-substituted radicals, J. Chem. Soc., Perkin Transactions 2, 1990.
Goldstein, S., and Czapski, G.: Reactivity of peroxynitric acid (O_2NOOH): A pulse radiolysis study, Inorg. Chem., 36, 4156-4162, 1997.
Graedel, T. E., and Weschler, C. J.: Chemistry within aqueous atmospheric aerosols and raindrops, Rev. Geophys., 19, 505-539, 10.1029/RG019i004p00505, 1981.
Graedel, T. E., and Goldberg, K. I.: Kinetic studies of raindrop chemistry 1. Inorganic and organic processes, J. Geophys. Res., 88, 10865-10882, 10.1029/JC088iC15p10865, 1983.
Grigor'ev, A. E., Makarov, I. E., and Pikaev, A. K.: Formation of Cl_2^- in the bulk solution during the radiolysis of concentrated aqueous solutions of chloride, High Ener. Chem, 21, 1987.
Herrmann, H., Exner, M., and Zellner, R.: Reactivity trends in reactions of the nitrate radical (NO_3) with inorganic and organic cloudwater constituents, Geochim.Cosmochim. Acta, 58, 3239-3244, 1994.
Herrmann, H., and Zellner, R.: Reaction of NO_3 radicals in aqueous solution, in: N-Centered Radicals, edited by: Alfassi, Z., Wiley, London, 291-343, 1998.
Hislop, K. A., and Bolton, J. R.: The photochemical generation of hydroxyl radicals in the UV−vis/Ferrioxalate/H_2O_2 system, Environ. Sci.Tech., 33, 3119-3126, 1999.
Hoffmann, M. R., and Calvert, J. G.: Chemical transformation modules for Eulerian acid deposition models, Environmental Protection Agency, 1985.
Hoffmann, M. R.: On the kinetics and mechanism of oxidation of aquated sulfur dioxide by ozone, Atmos. Environ., 20, 1145-1154, 10.1016/0004-6981(86)90147-2, 1986.
Huie, R. E., and Clifton, C. L.: Temperature dependence of the rate constants for reactions of the sulfate radical, SO_4^-, with anions, J. Phys. Chem., 94, 8561-8567, 1990.
Huie, R. E., Shoute, L., and Neta, P.: Temperature dependence of the rate constants for reactions of the carbonate radical with organic and inorganic reductants, Inter. J. Chem. Kin., 23, 541-542, 1991.
Jacobi, H. W., Herrmann, H., and Zellner, R.: Kinetic investigation of the Cl_2^- radical in the aqueous phase, in: Air Pollution research Report 57: Homogenous and heterogenous chemical processes in the troposphere, edited by: Becker, K. H., CEC, Brussels, 1996.
Jacobsen, F., Holcman, J., and Sehested, K.: Activation parameters of ferryl ion reactions in aqueous acid solutions, Inter. J. Chem. Kin., 29, 17-24, 10.1002/(sici)1097-4601(1997)29:1<17::aid-kin3>3.0.co;2-o, 1997.
Jacobsen, F., Holcman, J., and Sehested, K.: Reactions of the ferryl ion with some compounds found in cloud water, Intern. J. Chem. Kin., 30, 215-221, 1998.
Jayson, G. G., Parsons, B. J., and Swallow, A. J.: Oxidation of ferrous ions by perhydroxyl radicals, J. Chem.Soc., Faraday Transactions, 69, 1973a.
Jayson, G. G., Parsons, B. J., and Swallow, A. J.: Appearance of sulphatoferric complexes in the oxidation of ferrous sulphate solutions. A study by pulse radiolysis, J. Chem. Soc., Faraday Transactions, 69, 1973b.
Jiang, P.-Y., Katsumura, Y., Nagaishi, R., Domae, M., Ishikawa, K., Ishigure, K., and Yoshida, Y.: Pulse radiolysis study of concentrated sulfuric acid solutions. Formation mechanism, yield and reactivity of sulfate radicals, J. Chem. Soc., Faraday Transactions, 88, 1653-1658, 1992.
Katsumura, Y.: NO_2 and NO_3 radicals in radiolysis of nitric acid solutions, in: N centered RAdical, edited by: Alfassi, Z. B., Wiley, Chichester, 393, 1998.
Kremer, M. L.: The Fenton reaction. Dependence of the rate on pH, J. Phys. Chem. A, 107, 1734-1741, 10.1021/jp020654p, 2003.
Lee, Y. N., and Lind, J. A.: Kinetics of aqueous oxidation of nitrogen (III) by hydrogen peroxide, J. Geophys. Res., 91, 2793-2800, 1986.
Lilie, R., Hanrahan, J., and Henglein, A.: O^- transfer reactions of the carbonate radical anion, Rad. Phys. Chem., 11, 225-227, 1978.

Logager, T., Holcman, J., Sehested, K., and Pedersen, T.: Oxidation of ferrous ions by ozone in acidic solutions, Inorg. Chem., 31, 3523-3529, 10.1021/ic00043a009, 1992.

Logager, T., and Sehested, K.: Formation and decay of peroxynitric acid : a pulse radiolysis study, 39, American Chemical Society, Washington, DC, 10047-10052 pp., 1993.

Long, C. A., and Bielski, B. H. J.: Rate of reaction of superoxide radical with chloride-containing species, J. Phys. Chem., 84, 555-557, 10.1021/j100442a023, 1980.

Long, Y., Charbouillot, T., Brigante, M., Mailhot, G., Delort, A.-M., Chaumerliac, N., and Deguillaume, L.: Evaluation of modeled cloud chemistry mechanism against laboratory irradiation experiments: The H_xO_y/iron/carboxylic acid chemical system, Atmos. Environ., 77, 686-695, 2013.

Maash, H. G.: Sulfur dioxide/water equilibrium between 0 degrees and 50 degrees Celcius, and examination data at low concentrations, in: Heterogenous Atmospheric Chemistry, Geophys. Monogr. Ser., edited by: Schryer, D. R., AGU, Washington, D. C., 187-1959, 1982.

Maaß, F., Elias, H., and Wannowius, K. J.: Kinetics of oxidation of hydrogen sulfite by hydrogen peroxide in aqueous solution: ionic strength e!ects and temperature dependence, Atmos. Environ., 33, 4413-4419, 1999.

Marsh, A. R. W., and McElroy, W. J.: The dissociation constant and Henry's law constant of HCl in aqueous solution, Atmos. Environ., 19, 1075-1080, 1985.

Maruthamuthu, P., and Neta, P.: Phosphate radicals. Spectra, acid-base equilibriums, and reactions with inorganic compounds, J. Phys. Chem., 82, 710-713, 10.1021/j100495a019, 1978.

Mertens, R., and Von Sonntag, C.: Photolysis (λ= 354 nm) of tetrachloroethene in aqueous solutions, J. Photochem. Photobio: A chem., 85, 1-9, 1995.

Moorhead, E. G., and Sutin, N.: Rate and equilibrium constants for the formation of the monooxalate complex of iron(III), Inorg. Chem., 5, 1866-1871, 1966.

Nadtochenko, V. A., and Kiwi, J.: Photolysis of $FeOH^{2+}$ and $FeCl^{2+}$ in aqueous solution. Photodissociation kinetics and quantum yields, Inorg. Chem., 37, 5233-5238, 10.1021/ic9804723, 1998.

Padmaja, S., Neta, P., and Huie, R. E.: Rate constant for some reactions of inorganic radicals with inorganic ions. Temperature dependence and solvent dependence, J. Phys. Chem., 25, 445-455, 1993.

Park, J. Y., and Lee, Y. N.: Solubility and decomposition kinetics of nitrous acid in aqueous solution, J. Phys. Chem., 92, 6294-6302, 10.1021/j100333a025, 1988.

Pikaev, A. K., Sibirskaya, G. K., Shirshov, E. M., Glazunov, P. Y., and Spitsyn, V. I.: Pulse radiolysis of concentrated aqueous solutions of aqueous acid, Dokl. Phys. Chem. Proc. Acad. Sci., 215, 328-331, 1974.

Raabe, G.: Eine Laserphototyische Studie zur Kinetik der Reaktionen des NO_3 Radicals in Wässriger Lösun, Cuvillier, Göttingen, Germany, 1996.

Riordan, E., Minogue, N., Healy, D., O'Driscol, P., and Sodeau, J. R.: Spectroscopic and optimization modeling study of nitrous acid in aqueous solution, J. Phys. Chem. A, 109, 779-786, 10.1021/jp040269v, 2005.

Ross, A. B., Bielski, B. H. J., Buxton, G. V., Greenstock, C. L., Helman, W. P., Huie, R. E., Grodkowski, J., Neta, P., and Mallard, W. G.: NDLR-NIST Solution kinetics database, version 3: NIST Standard reference database 40. National Institute of Standards and Technology, in, Gaithersburg, MD, 1994.

Rush, J. D., and Bielski, B. H. J.: Pulse radiolytic studies of the reactions of HO_2/O_2^- with Fe(II)/Fe(III) ions. The reactivity of HO_2/O_2^- with ferric ions and its implication on the occurrence of the Haber-Weiss reaction, J. Phys. Chem., 89, 5062-5066 1985.

Sehested, K., Holcman, J., and Hart, E. J.: Rate constants and products of the reactions of e_{aq}^-, O_2^- and H with ozone in aqueous solutions, J. Phys. Chem., 87, 1951-1954, 10.1021/j100234a024, 1983.

Sehested, K., Holcman, J., Bjergbakke, E., and Hart, E. J.: A pulse radiolytic study of the reaction hydroxyl + ozone in aqueous medium, J. Phys. Chem., 88, 4144-4147, 10.1021/j150662a058, 1984.

Sehested, K., Logager, T., Holoman, J., and Nielsen, O. J.: Formation and reactions of the NO_3 radical in aqueous solution, in: Proceedings of EUROTRAC Symposium '94: Transport and Chemical Transformation of Pollutants in the Troposphere, edited by: Borrell, P. M., Cvitas, T., and Seiler, W., SPB Academic Publishing, The Hague, 999-1004, 1994.

Smith, R. M., and Martell, A. E.: Critical Stability Constants, Volume 4: Inorganic Complexes, Plenum, New York, 1976.

Tang, Y., Thorn, R. P., Mauldin Iii, R. L., and Wine, P. H.: Kinetics and spectroscopy of the SO_4^- radical in aqueous solution, J. Photochem. Photobiol. Chem A, 44, 243-258, http://dx.doi.org/10.1016/1010-6030(88)80097-2, 1988.

Thornton, A. T., and Laurence, G. S.: Kinetics of oxidation of transition-metal ions by halogen radical anions. Part I. The oxidation of iron(II) by dibromide and dichloride ions generated by flash photolysis, J. Chem. Soc. Dalton Trans., 1973.

Wang, T. X., and Margerum, D. W.: Kinetics of Reversible Chlorine Hydrolysis: Temperature Dependence and General-Acid/Base-Assisted Mechanisms, Inorg. Chem., 33, 1050-1055, 10.1021/ic00084a014, 1994.

Weschler, C. J., Mandich, M. L., and Graedel, T. E.: Speciation, photosensitivity, and reactions of transition metal Ions in atmospheric droplets, J. Geophys. Res., 91, 5189-5204, 10.1029/JD091iD04p05189, 1986.

Williams, J.: PhD-Thesis, University of Leeds, 1996.

Xu, F. C., Krouse, H. R., and Swaddle, T. W.: Conjugate base pathway for water exchange on aqueous chromium(III): variable-pressure and -temperature kinetic study, Inorg. Chem., 24, 267-270, 10.1021/ic00197a005, 1985.

Yu, X. Y., and Barker, J. R.: Hydrogen peroxide photolysis in acidic aqueous solutions containing chloride ions. I. Chemical Mechanism, J. Phys. Chem. A, 107, 1313-1324, 2003.

Yu, X. Y.: Critical evaluation of rate constants and equilibrium constants of hydrogen peroxide photolysis in acidic aqueous solutions containing chloride ions, J. Phys. Chem. Ref. Data, 33, 2004.

Zellner, R., Exner, M., and Herrmann, H.: Absolute OH quantum yields in the laser photolysis of nitrate, nitrite and dissolved H_2O_2 at 308 and 351 nm in the temperature range 278–353 K, J. Atmos. Chem., 10, 411-425, 10.1007/bf00115783, 1990.

Ziajka, J., Beer, F., and Warneck, P.: Iron-catalysed oxidation of bisulphite aqueous solution: Evidence for a free radical chain mechanism, Atmos. Environ., 28, 2549-2552, 10.1016/1352-2310(94)90405-7, 1994.