A supplement to "A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer" by K. Toyota et al.

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Foreword

This supplement contains additional information describing how we have created a new chemical scheme for the box model SEAMAC, followed by tables listing chemical species, reactions, and relevant parameters included/used in the present work.

S1 C_2H_4 degradation initiated by Cl atoms

The reaction between Cl atoms and C_2H_4 will proceed via Cl atom addition to the double bond of C_2H_4 followed by reaction with O_2 to give $ClCH_2CH_2OO$ radicals:

$$Cl + C_2H_4 \overset{M,O_2}{\rightarrow} ClCH_2CH_2OO \quad (1)$$

whereas a hydrogen abstraction channel is endothermic by 29.7 kJ/mol and of negligible importance at atmospheric temperatures (Kaiser and Wallington, 1996a):

$$Cl + C_2H_4 \rightarrow HCl + C_2H_3. \quad (2)$$

In the present work the rate constant for Reaction (1) is taken from Atkinson et al. (1999).

FTIR product studies for UV-irradiated $Cl_2/C_2H_4/air$ mixtures have identified $ClCH_2CHO$, $ClCH_2CH_2OOH$, and $ClCH_2CH_2OH$ as main degradation products (Wallington et al., 1990; Yarwood et al., 1992). This implies that $ClCH_2CH_2OO$ formed via Reaction (1) will undergo qualitatively similar reactions to those of simple peroxy radicals such as CH_3OO. Thus reactions with either NO, HO_2, or CH_3OO are deemed to be the most likely fate of $ClCH_2CH_2OO$ in the ambient air:

$$ClCH_2CH_2OO + NO \rightarrow ClCH_2CH_2O + NO_2 \quad (3)$$

$$ClCH_2CH_2OO + HO_2 \rightarrow ClCH_2CH_2OOH + O_2 \quad (4)$$

$$ClCH_2CH_2OO + CH_3OO \rightarrow 0.44 \times (ClCH_2CH_2O + CH_3O + O_2) + 0.28 \times (ClCH_2CHO + CH_3OH + O_2) + 0.28 \times (ClCH_2CH_2OH + HCHO + O_2). \quad (5)$$

By fitting to a complex chemical mechanism occurring in the reaction chamber, Wallington et al. (1990) derived the rate constant for Reaction (4) to be $7.5 \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$. This rate is very close to that for an analogous reaction C_2H_5OO + HO_2 ($k_{298} = 7.7 \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$; Atkinson et al., 1999). On the other hand, kinetic data do not exist for Reactions (3) and (5). In addition, the branching ratios of Reaction (5) are unknown as is the case for the majority of cross-reactions of halogenated peroxy radicals with CH_3OO. These unknown parameters are estimated as described in Sect. S9.

$ClCH_2CH_2O$ radicals formed via Reactions (3) and (5) may either decompose or react with O_2:

$$ClCH_2CH_2O \rightarrow ClCH_2 + HCHO \quad (6)$$

$$ClCH_2CH_2O + O_2 \rightarrow ClCH_2CHO + HO_2. \quad (7)$$

Kleindienst et al. (1989) determined the yield of $ClCH_2CHO$ from the reaction Cl + C_2H_4 in NO-rich air at 298 K to be 0.58 ± 0.10 and suggested that 42% of $ClCH_2CH_2O$ radicals formed via Reaction (3) should undergo decomposition. On the other hand, two FTIR product studies performed with UV-irradiated $Cl_2/C_2H_4/air$ mixtures in the absence of NO indicated that Reaction (7) dominates over reaction (6) in 1 atm of air at room temperature (Yarwood et al., 1992; Orlando et al., 1998). This contradiction could have arisen from the fact that alkoxy radicals formed via reactions of peroxy radicals with NO possess internal excitation due to the exothermicity of reactions, whereas those formed via self- or cross-reactions of peroxy radicals do not; excited alkoxy radicals thus produced may decompose before thermalized (Bilde et al., 1998, 1999; Orlando et al., 1998). Actually, Orlando et al.

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(1998) also performed the experiments with added NO. They concluded that very little, if any, decomposition of $ClCH_2CH_2O$ was occurring even in the presence of NO, by fitting to a complex chemical mechanism including secondary reactions. Thus the issue concerning the atmospheric fate of $ClCH_2CH_2O$ appears open to debate. In the present work it is assumed that $ClCH_2CH_2O$ radicals produced via reaction (5) exclusively undergo Reaction (7) and do not decompose via Reaction (6). On the other hand, Reaction (3) is assumed to form internally excited $ClCH_2CH_2O^*$ radicals, which will then undergo either decomposition or reaction with O_2 as follows:

$$ClCH_2CH_2O^* \overset{O_2}{\rightarrow} 0.58 \times (ClCH_2CHO + HO_2) + 0.42 \times (ClCH_2OO + HCHO). \quad (8)$$

As with $ClCH_2CH_2OO$, $ClCH_2OO$ radicals formed via Reaction (8) are most likely lost via reactions with NO, HO_2, and CH_3OO:

$$ClCH_2OO + NO \rightarrow ClCH_2O^* + NO_2 \quad (9)$$

$$ClCH_2OO + HO_2 \rightarrow 0.27 \times (ClCH_2OOH + O_2) + 0.73 \times (HCOCl + O_2 + H_2O) \quad (10)$$

$$ClCH_2OO + CH_3OO \rightarrow 0.65 \times (ClCH_2O + CH_3O + O_2) + 0.35 \times (ClCH_2OH + HCHO + O_2). \quad (11)$$

Their kinetics and mechanisms, except the branching ratios of Reaction (11), have been characterized fairly well by experimental studies (Sehested et al., 1993; Villenave and Lesclaux, 1996; Wallington et al., 1996). The branching ratios of reaction (11) are estimated as described in Sect. S9. $ClCH_2O^*$ radicals formed via Reaction (9) are internally excited due to the exothermicity of the reaction and thus an appreciable fraction of them will decompose to either HCO + HCl or $HCHO$ + Cl before thermalized (Bilde et al., 1999):

$$ClCH_2O^* \rightarrow 0.32 \times (HCO + HCl) + 0.12 \times (HCHO + Cl) + 0.56 \times ClCH_2O. \quad (12)$$

$ClCH_2O$ radicals thus thermalized or formed via reaction (11) will predominantly react with O_2 rather than undergo decomposition via HCl-elimination:

$$ClCH_2O + O_2 \rightarrow HCOCl + HO_2 \quad (13)$$

$$ClCH_2O \rightarrow HCO + HCl \quad (14)$$

where $k_{13}/k_{14} = 4.6 \times 10^{-18}\,\mathrm{cm^3/molecule}$ at 296 K in 700 Torr air (Kaiser and Wallington, 1994).

As is evident from the preceding discussions, relatively stable chlorinated organic oxygenates are formed in the course of Cl-initiated C_2H_4 degradation. They include chlorinated carbonyls ($ClCH_2CHO$ and $HCOCl$), chlorinated hydroperoxides ($ClCH_2CH_2OOH$ and $ClCH_2OOH$), and chlorinated alcohols ($ClCH_2CH_2OH$ and $ClCH_2OH$). Among them the further degradation of $ClCH_2CHO$ will form still other chlorinated organic intermediates including a PAN-type compound, $ClCH_2C(O)OONO_2$ (PClAN), and chloroacetic acid ($ClCH_2COOH$). In the ambient air $ClCH_2CHO$ will either be photolyzed or react with OH radicals:

$$ClCH_2CHO + h\nu \rightarrow ClCH_2 + HCO \overset{O_2}{\rightarrow} ClCH_2OO + CO + HO_2 \quad (15)$$

$$\rightarrow CH_3Cl + CO \quad (16)$$

$$ClCH_2CHO + OH \overset{O_2}{\rightarrow} ClCH_2C(O)OO + H_2O. \quad (17)$$

The rate constant for Reaction (17) and absorption cross sections for $ClCH_2CHO$ have been determined experimentally (Libuda, 1992; Atkinson et al., 1997). The quantum yields of $ClCH_2CHO$ photolysis, i.e. Reactions (15) and (16), are unknown at the present time; they are estimated by red-shifting the wavelength-dependent quantum yields of CH_3CHO photolysis by 10 nm (see Sect. S10). The atmospheric fate of $ClCH_2C(O)OO$ formed via Reaction (17) is expected to be similar to that of $CH_3(O)OO$. Chen et al. (1996) confirmed the formation of PClAN from Cl-initiated $ClCH_2CHO$ degradation in the NO_2-rich air by FTIR product analysis:

$$ClCH_2C(O)OO + NO_2 \overset{M}{\rightleftharpoons} ClCH_2(O)OONO_2. \quad (18)$$

Although the equilibrium constant for Reaction (18) is unknown, it is expected to be close to that for analogous reversible reactions for PAN. In the present work, $ClCH_2C(O)OO$ radicals are assumed to undergo Reactions (19)–(21) along with Reaction (18) at the same rates and yields as analogous reactions for $CH_3C(O)OO$ radicals:

$$ClCH_2C(O)OO + NO \overset{O_2}{\rightarrow} ClCH_2OO + CO_2 + NO_2 \quad (19)$$

$$ClCH_2C(O)OO + HO_2 \rightarrow 0.71 \times (ClCH_2C(O)OOH + O_2) + 0.29 \times (ClCH_2COOH + O_3) \quad (20)$$

$$ClCH_2C(O)OO + CH_3OO \overset{O_2}{\rightarrow} 0.7 \times (ClCH_2OO + CO_2 + HCHO + HO_2 + O_2) + 0.3 \times (ClCH_2COOH + HCHO + O_2). \quad (21)$$

$HCOCl$ is quite stable in the gas phase; using measured rate constants and absorption cross sections, its atmospheric lifetime against OH-attack, Cl-attack, and photolysis has been estimated to be at least 45 days, 14 years, and 50 days, respectively (Libuda et al., 1990). In contrast, HCOCl is highly susceptible to heterogeneous reactions. Previous experimental studies reported the fairly rapid loss of $HCOCl$ via wall reaction on the surface of reaction chambers to give CO + HCl (Libuda et al., 1990; Kaiser and Wallington, 1994; Wallington et al., 1996). Dowideit et al. (1996) found that non-hydrolytic decay of $HCOCl$ to give CO + HCl occurs in water at room temperature at the rate of $k_{\rm dec} = 10^4\,{\rm s}^{-1}$, whereas hydrolysis induced by $\rm OH^-$ to give HCOOH + HCl competes with the non-hydrolytic decay only under strongly basic conditions. Although no experimental data exist for Henry's law constant ($K_{\rm H}$) for HCOCl, it may well be within the range of $K_{\rm H}$ values for alkyl aldehydes, that is, on the order of $10^1\ {\rm M\,atm^{-1}}$ (Zhou and Mopper, 1990). Then, by neglecting mass accommodation term, the upper limit for reactive uptake coefficient ($\Gamma_{\rm rxn}$) of HCOCl on aerosol surface is estimated to be approximately 0.2 at T = 298 K based on the following formula (Finlayson-Pitts and Pitts, 2000):

$$\Gamma_{\rm rxn} = \frac{4K_{\rm H}RT(k_{\rm dec}D_l)^{1/2}}{\bar{c}}$$

where R is universal gas constant (0.082 $\rm L\,atm\,mol^{-1}\,K^{-1}$), D_l is liquid diffusion coefficient ($2\times10^{-5}\ {\rm cm^2\,s^{-1}}$), and $\bar{c}$ is gas molecular velocity. In the present work the reactive uptake coefficient of 0.1 is tentatively assigned for the heterogeneous reaction of HCOCl to give CO + HCl on the surface of sea-salt aerosols, which constrains the lifetime of HCOCl on the order of hours in our model runs. If the value of $K_{\rm H}$ for HCOCl is as small as that for $\rm COCl_2$, i.e. on the order of 0.1 $\rm M\,atm^{-1}$, then the atmospheric lifetime of HCOCl will be constrained by decomposition in cloudwater or deposition to the ocean (De Bruyn et al., 1995; Wild et al., 1996). By taking the revised value of $k_{\rm dec}$ from Dowideit et al. (1996) which is at least two orders of magnitude greater than previously assumed, the atmospheric lifetime of HCOCl against decomposition in cloudwater is estimated to be within 10 days or less. This cloudwater effect is implicitly accounted for by implementing the washout of HCOCl (τ = 8 days) in the present work.

Chlorinated hydroperoxides will be destroyed via either OH-attack or photolysis, although no experimental data exist for these reactions. As for $\rm ClCH_2CH_2OOH$, the following pathways are considered:

$$\rm OH + ClCH_2CH_2OOH \rightarrow H_2O + ClCH_2CH_2OO \quad (22)$$
$$\rm \rightarrow H_2O + ClCH_2CHO + OH \quad (23)$$
$$\rm ClCH_2CH_2OOH + h\nu \rightarrow ClCH_2CH_2O + OH. \quad (24)$$

Similarly, $\rm ClCH_2OOH$ will be destroyed via either of the following pathways:

$$\rm OH + ClCH_2OOH \rightarrow H_2O + ClCH_2OO \quad (25)$$
$$\rm \rightarrow H_2O + HCOCl + OH \quad (26)$$
$$\rm ClCH_2OOH + h\nu \rightarrow ClCH_2O + OH. \quad (27)$$

Rate constants or J values for Reactions (22)–(27) are estimated as described in Sect. S10. The OH-attack on $\rm ClCH_2CH_2OOH$ may have an additional channel to give $\rm ClCHCH_2OOH$ + $\rm H_2O$. It is, however, of minor importance compared with channels (22) and (23), and therefore neglected in the present work. Then the rate constant of Reaction (23) is scaled to maintain the overall rate of the OH-attack (see Sect. S10).

Finally, chlorinated alcohols will be destroyed via reactions with OH radicals:

$$\rm OH + ClCH_2CH_2OH \stackrel{O_2}{\rightarrow} H_2O + ClCH_2CHO + HO_2 \quad (28)$$
$$\rm OH + ClCH_2OH \stackrel{O_2}{\rightarrow} H_2O + HCOCl + HO_2 \quad (29)$$

where channels of minor importance are neglected as in the case of chlorinated hydroperoxides. The rate constant for Reaction (28) was determined by Wallington et al. (1988), whereas that for Reaction (29) needs to be estimated as described in Sect. S10. $\rm ClCH_2OH$ may also undergo unimolecular decomposition to give HCHO + HCl in the gas phase with a decay rate of $1.6\times10^{-3}\ {\rm s^{-1}}$ or less (Tyndall et al., 1993).

S2 Note on Br attack on $\rm C_2H_4$

The reaction Br + $\rm C_2H_4$ will proceed predominantly via the addition channel to give $\rm BrCH_2CH_2OO$ radicals in the ambient air:

$$\rm Br + C_2H_4 \stackrel{M,O_2}{\rightarrow} BrCH_2CH_2OO \quad (30)$$

whereas a hydrogen abstraction channel is too endothermic ($\Delta H_{298} = 97.1 \pm 4.2\,{\rm kJ/mol}$) to possess a noticeable rate at ambient temperature (Bedjanian et al., 1999):

$$\rm Br + C_2H_4 \rightarrow HBr + C_2H_3. \quad (31)$$

S3 Note on the fate of $\rm BrCH_2O/BrCH_2O^*$ radicals

The fate of $\rm BrCH_2O$ (or $\rm BrCH_2O^*$) radicals has been addressed by experimental studies in the context of atmospheric chemistry of $\rm CH_3Br$ initiated by OH- or Cl-attack (Nielsen et al., 1991; Weller et al., 1992; Chen et al., 1995; Orlando et al., 1996). The formation of HCOBr is generally observed in the absence of NO in the reaction systems, which was attributed to a reaction between $\rm BrCH_2O$ and $\rm O_2$ by Nielsen et al. (1991) and Weller et al. (1992):

$$\rm BrCH_2O + O_2 \rightarrow HCOBr + HO_2. \quad (32)$$

The yields of HCOBr were suppressed to levels below instrumental detection limits by adding NO to the reaction systems (Weller et al., 1992; Chen et al., 1995; Orlando et al., 1996), which can be deemed to represent a piece of evidence for internally excited $\rm BrCH_2O^*$ radicals formed via the reaction NO + $\rm BrCH_2OO$ decomposing before reacting with $\rm O_2$:

$$\rm BrCH_2O^* \rightarrow HCHO + Br. \quad (33)$$

However, Chen et al. (1995) and Orlando et al. (1996) observed no dependence of the HCOBr yield on $\rm O_2$ partial pressure even in the absence of NO, and thus concluded that HCOBr observed in the absence of NO was likely to be formed via the reaction $\rm HO_2$ + $\rm BrCH_2OO$ rather than via

Reaction (32). Hence, in the present work, $BrCH_2O$ and $BrCH_2O^*$ radicals are assumed to undergo decomposition virtually exclusively in the ambient air (see Sect. 3.2.2).

S4 C_3H_6 degradation initiated by Cl atoms

The reaction between Cl and C_3H_6 will proceed via the addition of Cl-atoms to the double bond or via H-abstraction from the methyl group:

$$Cl + C_3H_6 \stackrel{M,O_2}{\rightarrow} 0.87 \times CH_3CH(OO)CH_2Cl + 0.13 \times CH_3CHClCH_2OO \quad (34)$$

$$Cl + C_3H_6 \stackrel{O_2}{\rightarrow} HCl + CH_2{=}CHCH_2OO. \quad (35)$$

Their rate constants have been obtained experimentally (Kaiser and Wallington, 1996b; Atkinson et al., 1999). At room temperature and atmospheric pressure, Reaction (34) accounts for approximately 90% of the overall reaction, whereas Reaction (35) accounts for the remainder (Kaiser and Wallington, 1996b). The product branching ratios of Reaction (34), i.e. the ratio between Cl-additions to terminal and central positions, have also been determined experimentally (Lee and Rowland, 1977). Since 70–80% of Cl-initiated degradation of C_3H_6 will proceed via the formation of $CH_3CH(OO)CH_2Cl$ radicals, mechanism descriptions that follow in this section are restricted to topics relevant to this major pathway. Another pathway that follows the $CH_3CHClCH_2OO$ formation is developed in a similar manner, although no experimental basis exists regarding this pathway (see Tables S3–S4). The third pathway following Reaction (35) will result in the formation of acrolein ($CH_2{=}CHCHO$) and peroxyacryloyl nitrate ($CH_2{=}CHC(O)OONO_2$, ACRPAN), whose kinetics and mechanisms have been characterized relatively well by previous experimental studies (see Reactions (G489)–(G514) in Table S3 and Reactions (P60)–(P63) in Table S4).

$CH_3CH(OO)CH_2Cl$ radicals will be lost mainly via reactions with NO, HO_2, or CH_3OO in the ambient air. However, their rate constants need to be estimated as described in Sect. S9:

$$CH_3CH(OO)CH_2Cl + NO \rightarrow CH_3CH(O)CH_2Cl^* + NO_2 \quad (36)$$

$$CH_3CH(OO)CH_2Cl + HO_2 \rightarrow CH_3CH(OOH)CH_2Cl + O_2 \quad (37)$$

$$CH_3CH(OO)CH_2Cl + CH_3OO \rightarrow 0.6 \times (CH_3CH(O)CH_2Cl + CH_3O + O_2) + 0.2 \times (CH_3COCH_2Cl + CH_3OH + O_2) + 0.2 \times (CH_3CH(OH)CH_2Cl + HCHO + O_2). \quad (38)$$

Since no experimental basis is available concerning the branching ratios of Reaction (38), generic values assigned in MCM are adopted here.

To date no experimental study has been performed in an attempt to resolve complete pathways of Cl-initiated C_3H_6 degradation. Kleindienst et al. (1989), however, determined the yield of chloroacetone (CH_3COCH_2Cl) from reaction Cl + C_3H_6 in NO-rich synthetic air at 298 K to be approximately 0.40. Considering the branching ratio of $CH_3CH(OO)CH_2Cl$-formation channel to the overall Cl-attack on C_3H_6, it is estimated that $CH_3CH(O)CH_2Cl^*$ radicals formed via Reaction (36) undergo decomposition and reaction with O_2 with the branching ratios of 0.47 and 0.53, respectively:

$$CH_3CH(O)CH_2Cl^* \rightarrow CH_3CHO + ClCH_2 \stackrel{O_2}{\rightarrow} CH_3CHO + ClCH_2OO \quad (39)$$

$$CH_3CH(O)CH_2Cl^* + O_2 \rightarrow CH_3COCH_2Cl + HO_2. \quad (40)$$

$CH_3CH(O)CH_2Cl$ radicals formed via Reaction (38) are assumed to undergo the same fate as above, since no experimental data exist ruling out this assumption.

CH_3COCH_2Cl will be destroyed via either photolysis or OH-attack in the ambient air. Based on experimentally determined data for the absorption cross sections of CH_3COCH_2Cl and quantum yields for its photolysis (Burkholder et al., 2002), the lifetime of CH_3COCH_2Cl against photolysis is estimated to be less than two days in the mid-latitude MBL:

$$CH_3COCH_2Cl + h\nu \stackrel{O_2}{\rightarrow} CH_3C(O)OO + ClCH_2OO \quad (41)$$

$$\stackrel{O_2}{\rightarrow} CH_3OO + ClCH_2C(O)OO. \quad (42)$$

$ClCH_2OO$ and $ClCH_2C(O)OO$ are also formed from C_2H_4 degradation initiated via Cl-attack and their fate is already described in Sect. S1. Experimental data for OH-attack and/or photolysis of $CH_3CH(OOH)CH_2Cl$ and $CH_3CH(OH)CH_2Cl$ are lacking at the present time and therefore need to be estimated as described in Sect. S10. It should be noted that the photochemical loss of these species gives either CH_3COCH_2Cl or its precursors:

$$CH_3CH(OOH)CH_2Cl + OH \rightarrow CH_3CH(OO)CH_2Cl + H_2O \quad (43)$$

$$CH_3CH(OOH)CH_2Cl + OH \rightarrow CH_3COCH_2Cl + OH + H_2O \quad (44)$$

$$CH_3CH(OOH)CH_2Cl + h\nu \rightarrow CH_3CH(O)CH_2Cl + OH \quad (45)$$

$$CH_3CH(OH)CH_2Cl + OH \stackrel{O_2}{\rightarrow} CH_3COCH_2Cl + HO_2 + H_2O. \quad (46)$$

S5 Additional channel of reaction OH + C_3H_6: H-abstraction from the methyl group

Under the lower tropospheric conditions, e.g. at room temperature and in 1 atm of air, the reaction between OH and

C_3H_6 occurs predominantly via OH-addition to the double bond. By extrapolating the temperature-dependent rate constant recommended over the temperature range 701-896 K, Atkinson (1989) suggested a possibility for a hydrogen abstraction from the methyl group of C_3H_6 accounting for a few percent of the overall reaction between OH and C_3H_6 even at room temperature:

$$OH + C_3H_6 \overset{O_2}{\rightarrow} CH_2{=}CHCH_2OO + H_2O. \quad (47)$$

This channel is commonly neglected in photochemical models of the atmosphere, since experimental studies conducted to date have no more than derived the upper-limit of its rate under the room temperature conditions. It should be noted, however, that the experimentally-derived upper-limit rate constants for Reaction (47) (less than 2–5% of the overall rate including the OH-addition channel; Hoyermann and Sievert, 1979; Biermann et al., 1982) do not contradict the suggestion made by Atkinson (1989).

In order to achieve consistency with the reaction scheme developed for reactions between halogen atoms and C_3H_6 (see Sects. S4 and 3.2.1), it is assumed that Reaction (47) does occur along with the OH-addition channel. The rate constant for Reaction (47) is taken from Atkinson (1989).

S6 Note on C_2H_2 degradation initiated by Cl/Br atoms

In the ambient air the reactions Cl/Br + C_2H_2 are likely to proceed in a similar way to the reaction OH + C_2H_2: the formation of X-C_2H_2 adducts (X = Cl, Br) followed by O_2-addition to give XCH = CHOO radicals, which further undergo isomerization and decomposition to form either HCO + HCOX, HCOCHO + X, or HX + HCO + CO (Barnes et al., 1989; Yarwood et al., 1991; Ramacher et al., 2001):

$$X + C_2H_2 \overset{M,O_2}{\rightarrow} XCH = CHOO \quad (48)$$

$$XCH = CHOO \rightarrow HCOX + HCO$$

$$\overset{O_2}{\rightarrow} HCOX + CO + HO_2 \quad (49)$$

$$\rightarrow HCOCHO + X \quad (50)$$

$$\rightarrow HX + HCO + CO$$

$$\overset{O_2}{\rightarrow} HX + 2\,CO + HO_2. \quad (51)$$

The branching ratios of these pathways are not sensitive to the NO concentration but slightly to temperature (Ramacher et al., 2001). Actually, two geometric isomers exist for XCH = CHOO radicals, i.e. *cis*-XCH = CHOO and *trans*-XCH = CHOO, and the reaction of the former with O_2 to give O_3 (Reaction (52)) may well compete with isomerization/decomposition (49)–(51) in the ambient air (Yarwood et al., 1991; Zhu et al., 1994):

$$cis\text{-}XCH = CHOO + O_2 \rightarrow XCH = CHO + O_3 \quad (52)$$

where the yield of O_3 from C_2H_2 reacted is dependent on O_2 partial pressure and is on the order of 0.1 at 296 K in 700 Torr air for both of Cl- and Br-initiated reactions. XCH = CHO radicals, formed along with O_3, will then react with O_2 to give HCOX + CO + OH:

$$XCH = CHO + O_2 \overset{isom./dec.}{\cdots\rightarrow} HCOX + CO + OH. \quad (53)$$

It appears, however, that the formation of O_3 via reaction (52) is of negligible importance for O_3 budget in the MBL; taking the upper limits for reactant concentrations as $[C_2H_2]$ = 100 pmol/mol (Gregory et al., 1996), [Cl] = 10^5 molecule/cm^3 (Graedel and Keene, 1995), and [Br] = 10^7 molecule/cm^3 (Dickerson et al., 1999), and assuming the yields of O_3 from both of the reactions Cl/Br + C_2H_2 to be 0.1, the rate of O_3 production is estimated to be not more than 5 pmol/mol/day at 298 K in 1 atm of air. Considering further the rapid exchange between OH- and HO_2-radicals occurring in the ambient air, the reaction products of O_3-forming pathway via Reactions (52)–(53) are virtually equivalent to those of Reaction (49).

Hence, in the present work, the branching ratios of reactions Br/Cl + C_2H_2 are taken from the values as derived in the FTIR product study performed by Yarwood et al. (1991) while disregarding the contributions from O_3-forming pathways (see Reactions (52)–(53) in Sect. 3.3).

S7 Cl/ClO/BrO + alkyl peroxy radicals

In the present work, products and their yields for the gas-phase reactions of CH_3OO with halogen radicals (Cl/ClO/BrO) are reassigned to accord with available experimental data.

The reaction between Cl atoms and CH_3OO will proceed via two channels of comparable branching ratios (DeMore et al., 1997):

$$Cl + CH_3OO \rightarrow HCl + CH_2OO^* \quad (54)$$

$$\overset{O_2}{\rightarrow} ClO + HCHO + HO_2. \quad (55)$$

Here the first channel is assumed to give energy-rich Criegee biradicals (CH_2OO^*) that undergo the same reaction pathways as those produced via O_3 + C_2H_4:

$$O_3 + C_2H_4 \rightarrow HCHO + CH_2OO^* \quad (56)$$

$$CH_2OO^* \rightarrow CO_2 + H_2 \quad (57)$$

$$\rightarrow CO + H_2O \quad (58)$$

$$\rightarrow OH + HCO \overset{O_2}{\rightarrow} OH + HO_2 + CO \quad (59)$$

$$CH_2OO^* \overset{M}{\rightarrow} CH_2OO \overset{H_2O}{\rightarrow} HCOOH. \quad (60)$$

Branching ratios of pathways (57)–(60) are taken from Atkinson et al. (1997): ϕ_{57} = 0.13, ϕ_{58} = 0.38, ϕ_{59} = 0.12, and ϕ_{60} = 0.37. It is interesting to note that the formation of Criegee biradicals via Reaction (54) has been verified experimentally by measuring CO (Maricq et al., 1994).

The reaction between ClO and CH_3OO proceeds via the following two channels with a branching ratio of the latter being greater at lower temperatures (Atkinson et al., 1997):

$$ClO + CH_3OO \overset{M,O_2}{\rightarrow} Cl + O_2 + HCHO + HO_2 \quad (61)$$
$$\rightarrow CH_3OCl + O_2. \quad (62)$$

CH_3OCl thus produced will be lost via photolysis, or alternatively, reactions with OH radicals or Cl atoms in the ambient air. Its reactive uptake onto aerosols can also take place (see Sect. S8).

Aranda et al. (1997) performed laboratory experiments to determine the rate constant and product yields for reaction BrO + CH_3OO at 298 K:

$$BrO + CH_3OO \rightarrow Br + O_2 + CH_3O \quad (63)$$
$$\rightarrow HOBr + CH_2OO. \quad (64)$$

Based on the LIF measurement of CH_3O and the mass spectrometry of HOBr, branching ratios for Reactions (63) and (64) were determined to be 0.3 ± 0.1 and 0.8 ± 0.2, respectively. Here reaction stoichiometry suggests the production of Criegee biradical via Reaction (64). Aranda et al. (1997) estimated Reaction (64) to be thermodynamically neutral or slightly exothermic ($\Delta H_{298} = -6.7 \pm 22.6\,\mathrm{kJ/mol}$), suggesting the feasibility of the reaction. It should be noted, however, that this reaction is much less exothermic than ozone-alkene reactions. For instance, the enthalpy of Reaction (56') is $\Delta H_{298} = -224.2\,\mathrm{kJ/mol}$:

$$O_3 + C_2H_4 \rightarrow HCHO + CH_2OO \quad (56')$$

where the heat of formation data for each species is taken from DeMore et al. (1997) except for stabilized Criegee biradical (CH_2OO): $\Delta H_f = 188.4\,\mathrm{kJ/mol}$ (Aranda et al., 1997). Hence we assume that Reaction (64) directly gives stabilized Criegee biradical rather than energy-rich biradical.

In the present work, mechanism extrapolation to organic peroxy radicals other than CH_3OO is not performed except for Reactions (65) and (66) for which experimental data are available (Maricq et al., 1994):

$$Cl + C_2H_5OO \rightarrow HCl + C_2H_5OO^* \quad (65)$$
$$\overset{O_2}{\rightarrow} ClO + CH_3CHO + HO_2. \quad (66)$$

Here energy-rich Criegee biradicals ($C_2H_5OO^*$) are produced in the first channel as in the case of reaction Cl + CH_3OO. The fate of $C_2H_5OO^*$ is assumed identical to that produced via reaction O_3 + C_3H_6.

S8 Aqueous-phase reactions of CH_3OCl

CH_3OCl is formed via Reaction (62) in the gas phase. Unfortunately little is known about heterogeneous reactions of CH_3OCl; to our knowledge there exists no published data on this issue. However, t-butyl hypochlorite ($(CH_3)_3COCl$), a homologue of CH_3OCl, is known to exhibit strong halogenating activities towards organic compounds in the aqueous phase, as is also the case for Cl_2 and HOCl (March, 1992). This would imply that aqueous-phase chemistry of CH_3OCl is analogous to that of HOCl. Indeed, laboratory experiments performed by Thorsten Benter (University of Wuppertal) and his colleagues imply that the reactive uptake of CH_3OCl on HCl-doped ice surface and on H_2SO_4-doped dry NaCl surface both occurs analogously to that of HOCl (Th. Benter, private communication, 2003). In their experiments for the heterogeneous reaction of CH_3OCl + HCl on ice surface, the production of Cl_2 and CH_3OH was confirmed and its reaction probability was approximately 10 times smaller than that of HOCl + HCl. Hence it is assumed in the present work that mass accommodation coefficient for CH_3OCl is identical to that for HOCl and that CH_3OCl is 10 times less soluble to water than HOCl is. Then the following reactions are assumed to take place in deliquesced sea-salt aerosols at the same rates as those of HOCl reactions:

$$CH_3OCl + Cl^- + H^+ \rightarrow CH_3OH + Cl_2 \quad (67)$$
$$CH_3OCl + Br^- + H^+ \rightarrow CH_3OH + BrCl. \quad (68)$$

Although no experimental verification currently exists, it is also assumed that CH_3OCl oxidizes S(IV) at the same rate as HOCl + SO_3^{2-} (Fogelman et al., 1989):

$$CH_3OCl + SO_3^{2-} \overset{H_2O}{\rightarrow} CH_3OH + Cl^- + SO_4^{2-} + H^+ \quad (69)$$
$$CH_3OCl + HSO_3^- \overset{H_2O}{\rightarrow} CH_3OH + Cl^- + SO_4^{2-} + 2\,H^+. \quad (70)$$

S9 A protocol for the reactions of halogen-containing organic peroxy radicals

As mentioned in Sects. 3.2.2, S1 and S4, the most likely fate of halogen-containing organic peroxy radicals in the ambient air is reactions with either NO, HO_2, or CH_3OO radicals, although relevant kinetic and mechanistic data are lacking in the majority of cases.

In the present work, the rate constants for the reactions of chlorinated organic peroxy radicals with NO and HO_2 are estimated based on the MCM protocol (Saunders et al., 2003), where no experimental data exist. Besides, the same protocol is assumed to apply to the reactions of brominated organic peroxy radicals with NO and HO_2. There are two justifications for this assumption. Firstly, Yarwood et al. (1992) found that the yields of $ClCH_2CHO$, $ClCH_2CH_2OOH$, and $ClCH_2CH_2OH$ formed from UV-irradiated Cl_2/C_2H_4/air mixtures were virtually identical to those of $BrCH_2CHO$, $BrCH_2CH_2OOH$, and $BrCH_2CH_2OH$, respectively, formed from UV-irradiated Br_2/C_2H_4/air mixtures by FTIR product analysis. Secondly, rate constants for the self-reactions of $BrCH_2CH_2OO$ ($k = 4.0 \times 10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$) and of $ClCH_2CH_2OO$ ($k = 3.3 \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$) are fairly close to each other and more than an order of magnitude greater than that for the self-reaction of C_2H_5OO (Crowley and Moortgat, 1992; Villenave et al., 2003).

A possibility of forming halogen-substituted alkyl nitrates ($RONO_2$) via termolecular reactions involving NO and halogenated organic peroxy radicals is disregarded in the present work, since their formation has not been confirmed by experimental studies to date. By analogy with non-halogenated counterparts (Atkinson, 1990; Lightfoot et al., 1992), the branching ratios of $RONO_2$-forming channel in the reactions RO_2 + NO are likely to be negligibly small, if any, as far as the reactions of up to C_3-hydrocarbons are concerned.

Kinetic and mechanistic data for the reactions of halogenated organic peroxy radicals with CH_3OO are lacking except for the reaction $ClCH_2OO$ + CH_3OO (Villenave and Lesclaux, 1996). Madronich and Calvert (1990) proposed an empirical approach to estimate rate constants and product branching ratios for cross-reactions between organic peroxy radicals (so-called permutation reactions) where their experimental data exist for each of self-reactions. This approach has been proved to work fairly well at least for the reaction $ClCH_2OO$ + CH_3OO (Villenave and Lesclaux, 1996), and is therefore adopted for estimating kinetics and mechanisms for this class of reactions in the present work. Here kinetic and mechanistic data for the self-reactions of $ClCH_2CH_2OO$, $BrCH_2CH_2OO$, $CH_3CHClOO$, and $BrCH_2OO$ are taken from experimentally determined values (Lightfoot et al., 1992; Yarwood et al., 1992; Villenave and Lesclaux, 1995; Atkinson et al., 1997; Villenave et al., 2003). Rate constants for the self-reactions of $CH_3CH(OO)CH_2X$ and CH_3CHXCH_2OO (X = Cl or Br) are estimated following a protocol proposed by Villenave et al. (2003). As to the other halogenated organic peroxy radicals, no experimental basis currently exists to predict kinetics and mechanisms even for their self-reactions. For such species, the rate constants and product branching ratios of cross-reactions with CH_3OO are taken from generic values assigned in the work of MCM (Saunders et al., 2003).

Actually, Kirchner and Stockwell (1996) (hereafter KS96) proposed an empirical formula to predict the rate constants for the self-reactions of alkyl peroxy radicals including those which contain electron-withdrawing halogen atoms in their alkyl groups. Although the rate constant predicted by the KS96 formula shows fair agreement (well within a factor of 3) with those derived experimentally in the cases of XCH_2CH_2OO radicals (where X = Cl or Br), agreement is very poor in the cases of XCH_2OO radicals (the KS96-based rate constant is 5- to 17-fold greater than those derived experimentally) and $CH_3C(OO)CH_2X$ radicals (the KS96-based rate constant is 6-fold smaller than that recommended by Villenave et al. (2003)). This suggests that the KS96 formula does not necessarily work well for halogenated organic peroxy radicals formed from up to C_3-hydrocarbons, and justifies simply using the generic value taken from MCM for the rate constants of cross-reactions where the rate constants of self-reactions are unknown.

Finally, the self-reactions of halogenated organic peroxy radicals are included in the present reaction scheme only where experimental data exist, since these reactions are of negligible importance in the ambient air compared with the cross-reactions with CH_3OO.

S10 A protocol for the degradation of organic intermediates: hydroperoxides, aldehydes, ketones, alcohols, etc.

By analogy with non-halogenated counterparts, halogenated organic hydroperoxides, percarboxylic acids, aldehydes, ketones, and alcohols are most likely destroyed via either reactions with OH radicals or photolysis in the ambient air. However, kinetic and mechanistic data for such reactions are again lacking in many cases and thus need to be estimated.

Where no experimental data exist, rate constants for the reactions of halogenated organic intermediates with OH radicals are estimated by structure-activity relationships (SAR) (Atkinson, 1987; Kwok and Atkinson, 1995) with supplemented parameters taken from the work of MCM. In particular, the neighboring group activation parameter for '-OOH' for the purpose of reaction rate estimation is assigned to be 13 for C_1-species and 8.4 for C_2- and C_3-species following the MCM protocol (Jenkin et al., 1997; Saunders et al., 2003). The rate constant of H-abstraction from '-OOH' group is also taken from Jenkin et al. (1997). Actually, there often exist more than two distinct product channels for H-abstraction from the C–H bonds of C_2- and C_3-species. Although the SAR method is capable of predicting the rate constant of each channel, channels of minor importance are disregarded and the rate constant of primary channel is scaled proportionally to maintain the overall rate. This should be a reasonable compromise to avoid making the reaction scheme too complicated, considering the dearth of experimental data.

Photochemical loss of halogenated and non-halogenated organic intermediates via reactions with Cl, Br, or NO_3 is taken into account only where experimental data exist. Since these reactions are generally of minor importance for the budget of organic intermediates considered, mechanism extrapolation is not basically performed for reactions for which no experimental data exist.

Photolysis reactions are considered for halogenated carbonyls (RC(O)R' and RCHO), hydroperoxides (ROOH), and percarboxylic acids (RC(O)OOH), as with non-halogenated counterparts. Again, experimental data for their absorption cross sections in the actinic range are lacking in many cases. Thus, where no experimental data exist, J values for halogenated organic compounds need to be estimated.

As shown in Figs. S1a-b, the longer-wavelength tails of UV absorption bands for carbonyl compounds are shifted in a fairly consistent manner by the presence of substituents at α-position: blue-shifted by about 10 nm via OH-

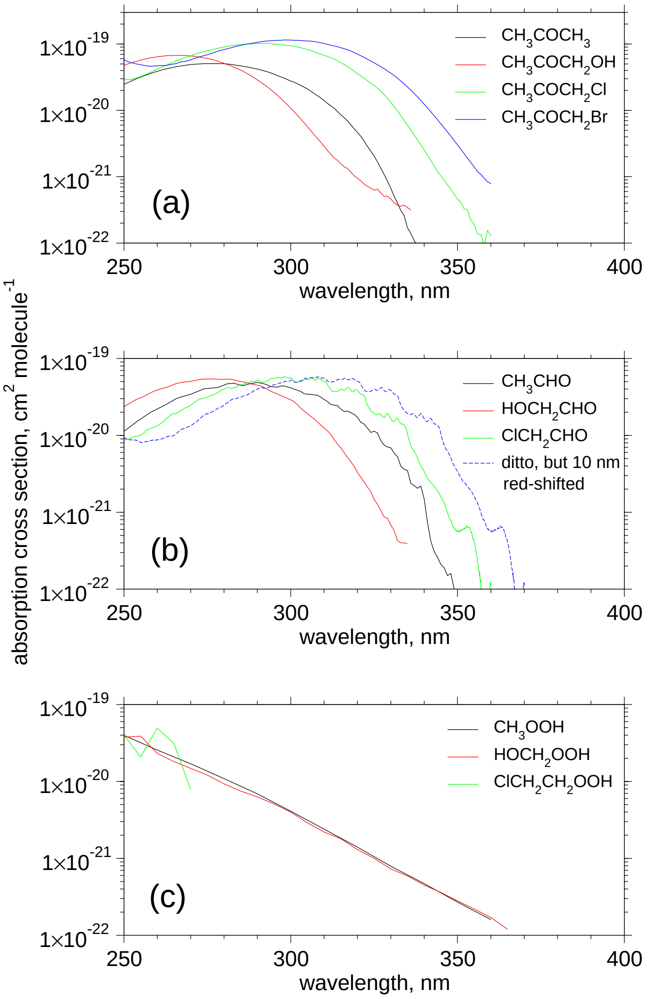

Fig. S1. **(a)** Experimentally determined absorption cross sections for acetone and its substituted analogues: CH_3COCH_3 (black line; Atkinson et al., 1999), CH_3COCH_2OH (red line; Orlando et al., 1999), CH_3COCH_2Cl and CH_3COCH_2Br (green and blue lines, respectively; Burkholder et al., 2002); **(b)** absorption cross sections for acetaldehyde and its substituted analogues: CH_3CHO (black line; Atkinson et al., 1999), $HOCH_2CHO$ (red line; Bacher et al., 2001), and $ClCH_2CHO$ (green line; Libuda, 1992); absorption cross sections for $BrCH_2CHO$ have not been reported in the literature and are therefore assumed red-shifted by 10 nm relative to those for $ClCH_2CHO$ (blue dashed line); and **(c)** absorption cross sections for methyl hydroperoxide and its analogues: CH_3OOH (black line; Atkinson et al., 1999), $HOCH_2OOH$ (red line; Bauerle and Moortgat, 1999), and $ClCH_2CH_2OOH$ (green line; Chakir et al., 2003).

substitution and red-shifted by about 10–30 nm via Cl- or Br-substitution. Absorption cross sections for $ClCH_2CHO$ were determined experimentally (Libuda, 1992), whereas those for $BrCH_2CHO$ are unknown at the present time. The quantum yields of $ClCH_2CHO/BrCH_2CHO$ photolysis are also unknown. In the present work, absorption cross sections for $BrCH_2CHO$ are estimated to be red-shifted by 10 nm relative to those for $ClCH_2CHO$. Then, wavelength-dependent quantum yields for two channels of CH_3CHO photolysis to give CH_4 + CO and CH_3 + HCO, respectively, recommended by Atkinson et al. (1997) are used as a reference for estimating quantum yields of haloacetaldehyde photolysis; wavelength-dependent quantum yields of the photolysis of $ClCH_2CHO$ and $BrCH_2CHO$ are estimated to be red-shifted by 10 nm and 20 nm, respectively, relative to those of CH_3CHO photolysis. Similarly, J values for other halogen-substituted alkyl aldehydes are estimated by taking absorption cross sections of non-halogenated counterparts from the literature and then red-shifted by 10 nm for chlorinated aldehydes and by 20 nm for brominated aldehydes. Wavelength-dependent quantum yields are red-shifted accordingly. J values for halogenated ketones of interest in the present work, i.e. CH_3COCH_2Cl and CH_3COCH_2Br, are calculated based on experimentally determined absorption cross sections and quantum yields (Burkholder et al., 2002).

To our knowledge, experimental data for absorption cross sections in the actinic range do not exist for hydroperoxides other than CH_3OOH, $HOCH_2OOH$, and $ClCH_2CH_2OOH$ (Atkinson et al., 1999; Bauerle and Moortgat, 1999; Chakir et al., 2003). A comparison between their absorption cross sections reveals that the longer-wavelength tails of UV absorption bands for hydroperoxides do not exhibit significant changes by the presence of substituents or by a change in the carbon number of alkyl group (see Fig. S1c). It is therefore assumed that absorption cross sections for halogenated hydroperoxides are generally identical to those for CH_3OOH. Then the quantum yields of unity are assumed as with CH_3OOH photolysis. Following the MCM protocol for estimating J values for non-halogenated compounds (Jenkin et al., 1997), halogenated percarboxylic acids ($RC(O)OOH$) are also assumed to have the same J value as CH_3OOH.

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Table S1. Gas-Phase Species Considered in SEAMAC, and Their Dry Deposition Velocities (v_0)[a], Wet Deposition Lifetimes (τ_{wet}), Initial Mixing Ratios (χ_{ini}), and Fixed Mixing Ratios (χ_{const}) Where Fixed Constant[b]

No.	Species	v_0, cm/s	τ_{wet}, day	χ_{ini}	χ_{const}
1	O_2	–	–	–	0.2095 mol/mol
2	O_3	–	–	–	20 nmol/mol [c]
3	$O(^3P)$	–	–	–	–
4	$O(^1D)$	–	–	–	–
5	N_2	–	–	–	0.7808 mol/mol
6	NO	–	–	–	–
7	NO_3	–	–	–	–
8	N_2O_5	1.0	–	–	–
9	HO_2NO_2	–	–	–	–
10	HONO	–	–	–	–
11	NO_2	0.1	–	20 pmol/mol	–
12	HNO_3	2.0	8.0	6 pmol/mol	–
13	NH_3	–	–	–	100 pmol/mol
14	H_2	–	–	–	550 nmol/mol [d]
15	H_2O	–	–	–	$\sim$ 0.017 mol/mol [e]
16	OH	1.0	–	–	–
17	HO_2	1.0	–	–	–
18	H_2O_2	1.0	8.0	1 nmol/mol	–
19	CH_4	–	–	–	1.7 μmol/mol [f]
20	C_2H_6	–	–	–	400 pmol/mol [f]
21	C_3H_8	–	–	–	18 pmol/mol [f]
22	C_2H_4	–	–	–	–
23	C_3H_6	–	–	–	–
24	C_2H_2	–	–	–	35 pmol/mol (baseline)[f] or 200 pmol/mol [g]
25	CO	–	–	–	80 nmol/mol [f]
26	CO_2	–	–	–	350 μmol/mol
27	CH_3OO	0.5	–	–	–
28	CH_3OH	0.1	–	–	–
29	HCHO	0.5	8.0	300 pmol/mol	–
30	CH_3OOH	0.5	–	800 pmol/mol	–
31	$HOCH_2OO$	0.5	–	–	–
32	$CH_2(OH)_2$	0.5	8.0	–	–
33	$HOCH_2OOH$	0.5	8.0	–	–
34	HCOOH	1.0	8.0	50 pmol/mol	–
35	HCl	2.0	8.0	60 pmol/mol	–
36	Cl_2	–	–	–	–
37	Cl	–	–	–	–
38	ClO	–	–	–	–
39	OClO	–	–	–	–
40	HOCl	0.2	–	–	–
41	CH_3OCl	0.2	–	–	–
42	Cl_2O_2	–	–	–	–
43	$ClNO_2$	–	–	–	–
44	$ClONO_2$	–	–	–	–
45	HBr	2.0	8.0	–	–
46	Br_2	–	–	–	–
47	BrCl	–	–	–	–
48	Br	–	–	–	–
49	BrO	–	–	–	–

Table S1. (continued)

No.	Species	v_0, cm/s	τ_{wet}, day	χ_{ini}	χ_{const}
50	$HOBr$	0.2	–	–	–
51	$BrNO_2$	–	–	–	–
52	$BrONO_2$	–	–	–	–
53	C_2H_5OO	0.5	–	–	–
54	C_2H_5OH	0.1	–	–	–
55	C_2H_5OOH	0.5	–	–	–
56	CH_3CHO	–	8.0	90 pmol/mol	–
57	$CH_3C(O)OO$	0.5	–	–	–
58	$CH_3C(O)OONO_2$ (PAN)	0.1	–	0.1 pmol/mol	–
59	CH_3COOH	1.0	8.0	50 pmol/mol	–
60	$CH_3C(O)OOH$	0.5	–	80 pmol/mol	–
61	n-C_3H_7OO	0.5	–	–	–
62	n-C_3H_7OH	0.1	–	–	–
63	n-C_3H_7OOH	0.5	–	–	–
64	C_2H_5CHO	0.5	8.0	–	–
65	$C_2H_5C(O)OO$	0.5	–	–	–
66	$C_2H_5C(O)OONO_2$ (PPN)	0.1	–	–	–
67	C_2H_5COOH	1.0	8.0	–	–
68	$C_2H_5C(O)OOH$	0.5	–	–	–
69	i-C_3H_7OO	0.5	–	–	–
70	i-C_3H_7OH	0.1	–	–	–
71	i-C_3H_7OOH	0.5	–	–	–
72	CH_3COCH_3	–	–	–	400 pmol/mol ^{h}
73	CH_3COCH_2OO	0.5	–	–	–
74	CH_3COCH_2OH	0.1	–	–	–
75	CH_3COCH_2OOH	0.5	–	–	–
76	CH_3COCHO	0.5	8.0	–	–
77	$HOCH_2CH_2OO$	0.5	–	–	–
78	$HOCH_2CH_2O$	–	–	–	–
79	$HOCH_2CH_2OH$	0.1	–	–	–
80	$HOCH_2CH_2OOH$	0.5	–	–	–
81	$HOCH_2CHO$	0.5	8.0	–	–
82	$HOCH_2C(O)OO$	0.5	–	–	–
83	$HOCH_2C(O)OONO_2$ (PHAN)	0.1	–	–	–
84	$HOCH_2COOH$	1.0	8.0	–	–
85	$HOCH_2C(O)OOH$	0.5	–	–	–
86	$HCOCHO$	0.5	8.0	–	–
87	$HCOC(O)OO$	0.5	–	–	–
88	$HCOC(O)OONO_2$ (GLYPAN)	0.5	–	–	–
89	$HCOCOOH$	1.0	8.0	–	–
90	$HCOC(O)OOH$	0.5	8.0	–	–
91	$ClCH_2CH_2OO$	0.5	–	–	–
92	$ClCH_2CH_2O^*$	–	–	–	–
93	$ClCH_2CH_2OH$	0.1	–	–	–
94	$ClCH_2CH_2OOH$	0.5	–	–	–
95	$ClCH_2CHO$	0.5	8.0	–	–
96	$ClCH_2C(O)OO$	0.5	–	–	–
97	$ClCH_2C(O)OONO_2$ (PClAN)	0.1	–	–	–
98	$ClCH_2COOH$	1.0	8.0	–	–
99	$ClCH_2C(O)OOH$	0.5	–	–	–
100	$ClCH_2OO$	0.5	–	–	–
101	$ClCH_2O^*$	–	–	–	–

Table S1. (continued)

No.	Species	v_0, cm/s	τ_{wet}, day	χ_{ini}	χ_{const}
102	$ClCH_2O$	–	–	–	–
103	$ClCH_2OH$	0.1	–	–	–
104	$ClCH_2OOH$	0.5	–	–	–
105	$HCOCl$	0.5	8.0	–	–
106	$BrCH_2CH_2OO$	0.5	–	–	–
107	$BrCH_2CH_2O^*$	–	–	–	–
108	$BrCH_2CH_2OH$	0.1	–	–	–
109	$BrCH_2CH_2OOH$	0.5	–	–	–
110	$BrCH_2CHO$	0.5	8.0	–	–
111	$BrCH_2CO$	–	–	–	–
112	$BrCH_2C(O)OO$	0.5	–	–	–
113	$BrCH_2C(O)OONO_2$ (PBrAN)	0.1	–	–	–
114	$BrCH_2COOH$	1.0	8.0	–	–
115	$BrCH_2C(O)OOH$	0.5	–	–	–
116	$BrCH_2OO$	0.5	–	–	–
117	$BrCH_2O$	–	–	–	–
118	$BrCH_2OH$	0.1	–	–	–
119	$BrCH_2OOH$	0.5	–	–	–
120	$CH_3CH(OO)CH_2OH$	0.5	–	–	–
121	$CH_3CH(OH)CH_2OH$	0.1	–	–	–
122	$CH_3CH(OH)CHO$	0.5	8.0	–	–
123	$CH_3CH(OH)C(O)OO$	0.5	–	–	–
124	$CH_3CH(OH)C(O)OONO_2$ (i-PROPOLPAN)	0.1	–	–	–
125	$CH_3CH(OH)C(O)OOH$	0.5	–	–	–
126	$CH_3CH(OH)CH_2OO$	0.5	–	–	–
127	$CH_3CH(OOH)CH_2OH$	0.5	–	–	–
128	$CH_3CH(OH)CH_2OOH$	0.5	–	–	–
129	$CH_3CH(OO)CH_2Cl$	0.5	–	–	–
130	CH_3CHOCH_2Cl	–	–	–	–
131	$CH_3CH(OH)CH_2Cl$	0.1	–	–	–
132	$CH_3CH(OOH)CH_2Cl$	0.5	–	–	–
133	CH_3COCH_2Cl	0.1	–	–	–
134	$CH_3COCHClOO$	0.5	–	–	–
135	$CH_3COCHClOH$	0.1	–	–	–
136	$CH_3COCHClOOH$	0.5	–	–	–
137	$CH_3COCOCl$	0.5	8.0	–	–
138	$CH_3COCOOH$	1.0	8.0	–	–
139	$CH_3CHClCH_2OO$	0.5	–	–	–
140	$CH_3CHClCH_2OH$	0.1	–	–	–
141	$CH_3CHClCH_2OOH$	0.5	–	–	–
142	$CH_3CHClCHO$	0.5	8.0	–	–
143	$CH_3CHClC(O)OO$	0.5	–	–	–
144	$CH_3CHClC(O)OONO_2$ (i-ClACETPAN)	0.1	–	–	–
145	$CH_3CHClCOOH$	1.0	8.0	–	–
146	$CH_3CHClC(O)OOH$	0.5	–	–	–
147	$CH_3CHClOO$	0.5	–	–	–
148	$CH_3CHClOOH$	0.5	–	–	–
149	CH_3COCl	0.5	8.0	–	–
150	CH_3Cl	–	–	–	–
151	$CH_2{=}CHCH_2OO$	0.5	–	–	–
152	$CH_2{=}CHCH_2OH$	0.1	–	–	–
153	$CH_2{=}CHCH_2OOH$	0.5	–	–	–

Table S1. (continued)

No.	Species	v_0, cm/s	τ_{wet}, day	χ_{ini}	χ_{const}
154	$CH_2=CHCHO$	0.5	8.0	–	–
155	$CH_2=CHC(O)OO$	0.5	–	–	–
156	$CH_2=CHC(O)OONO_2$ (ACRPAN)	0.1	–	–	–
157	$CH_2=CHCOOH$	1.0	8.0	–	–
158	$CH_2=CHC(O)OOH$	0.5	–	–	–
159	$CH_3CH(OO)CH_2Br$	0.5	–	–	–
160	CH_3CHOCH_2Br	–	–	–	–
161	$CH_3CH(OH)CH_2Br$	0.1	–	–	–
162	$CH_3CH(OOH)CH_2Br$	0.5	–	–	–
163	CH_3COCH_2Br	0.1	–	–	–
164	$CH_3COCHBrOO$	0.5	–	–	–
165	$CH_3COCHBrO$	–	–	–	–
166	$CH_3COCHBrOH$	0.1	–	–	–
167	$CH_3COCHBrOOH$	0.5	–	–	–
168	$CH_3COCOBr$	0.5	8.0	–	–
169	$CH_3CHBrCH_2OO$	0.5	–	–	–
170	$CH_3CHBrCH_2OH$	0.1	–	–	–
171	$CH_3CHBrCH_2OOH$	0.5	–	–	–
172	$CH_3CHBrCHO$	0.5	8.0	–	–
173	$CH_3CHBrC(O)OO$	0.5	–	–	–
174	$CH_3CHBrC(O)OONO_2$ (i-BrACETPAN)	0.1	–	–	–
175	$CH_3CHBrCOOH$	1.0	8.0	–	–
176	$CH_3CHBrC(O)OOH$	0.5	–	–	–
177	$CH_3CHBrOO$	0.5	–	–	–
178	CH_3CHBrO	–	–	–	–
179	$CH_3CHBrOOH$	0.5	–	–	–
180	CH_3COBr	0.5	8.0	–	–
181	CH_3Br	–	–	–	–
182	$CHBr_3$	–	–	–	1 pmol/mol [i]
183	$CHBr_2OO$	0.5	–	–	–
184	$HCOBr$	0.5	8.0	–	–
185	CBr_2O	0.1	8.0	–	–
186	$CH_2=CO$ (ketene)	0.1	8.0	–	–
187	CH_2OO^*	0.5	–	–	–
188	CH_2OO	0.5	–	–	–
189	CH_3CHOO^*	0.5	–	–	–
190	CH_3CHOO	0.5	–	–	–
191	CH_3SCH_3 (DMS)	–	–	75 pmol/mol	–
192	$CH_3S(O)CH_3$ (DMSO)	1.0	8.0	–	–
193	CH_3SO_2	–	–	–	–
194	CH_3SO_3	–	–	–	–
195	CH_3SO_2H	1.0	8.0	–	–
196	CH_3SO_3H	2.0	8.0	–	–
197	SO_2	1.0	8.0	60 pmol/mol	–
198	SO_3	–	–	–	–
199	H_2SO_4	2.0	8.0	–	–

Notes: [a] Dry deposition velocities are either taken from the literature (Sander and Crutzen, 1996; Moldanová and Ljungström, 2001) or estimated in the present work (see Section 4); [b] The initial mixing ratios are set to zero for species whose initial (χ_{ini}) or fixed (χ_{const}) mixing ratios are not specified in the table; [c] Johnson et al. (1990), Oltmans and Levy (1994); [d] Warneck (1998); [e] At the relative humidity of 76.2% and the temperature of 293 K; [f] Gregory et al. (1996); [g] Koppmann et al. (1992); [h] Singh et al. (2001); [i] Penkett et al. (1985), Yokouchi et al. (1997).

Table S2. Aqueous-Phase Species Considered in SEAMAC and Their Activity Coefficients (γ_{a})^a

No.	Species	γ_{a}	No.	Species	γ_{a}	No.	Species	γ_{a}
1	O_2	1.0	35	CH_3COO^-	0.44	68	$ClNO_2$	1.0
2	O_3	1.0	36	C_2H_5COOH	1.0	69	HBr	1.0
3	$O(^3P)$	1.0	37	$C_2H_5COO^-$	0.44	70	Br^-	1.6
4	H_2O	0.762	38	$HOCH_2COOH$	1.0	71	Br	1.0
5	H^+	4.3	39	$HOCH_2COO^-$	0.44	72	Br_2^-	0.44
6	OH^-	1.6	40	$HCOCOOH$	1.0	73	Br_3^-	0.44
7	OH	1.0	41	$HCOCOO^-$	0.44	74	Br_2	1.0
8	HO_2	1.0	42	$CH_3COCOOH$	1.0	75	$BrCl$	1.0
9	O_2^-	0.44	43	CH_2COCOO^-	0.44	76	Br_2Cl^-	0.44
10	H_2O_2	1.0	44	$CH_2CHCOOH$	1.0	77	$BrCl_2^-$	0.44
11	HO_2^-	0.44	45	CH_2CHCOO^-	0.44	78	$BrNO_2$	1.0
12	NH_3	1.0	46	ClCH2COOH	1.0	79	$HOBr$	1.0
13	NH_4^+	0.74	47	ClCH2COO$^-$	0.44	80	BrO^-	0.44
14	NO	1.0	48	BrCH2COOH	1.0	81	$HBrO_2$	1.0
15	NO_2	1.0	49	BrCH2COO$^-$	0.44	82	BrO_2^-	0.44
16	$HONO$	1.0	50	$CH_3CHClCOOH$	1.0	83	BrO_3^-	0.44
17	NO_2^-	0.44	51	$CH_3CHClCOO^-$	0.44	84	$BrOH^-$	0.44
18	HNO_3	1.0	52	$CH_3CHBrCOOH$	1.0	85	BrO	1.0
19	NO_3^-	0.46	53	$CH_3CHBrCOO^-$	0.44	86	BrO_2	1.0
20	HO_2NO_2	1.0	54	CO_2	1.0	87	Br_2O_4	1.0
21	NO_4^-	0.44	55	HCO_3^-	0.53	88	SO_2	1.0
22	NO_3	1.0	56	CO_3^-	0.44	89	HSO_3^-	0.92
23	CH_3OH	1.0	57	Na^+	1.0	90	SO_3^{2-}	0.049
24	CH_3OO	1.0	58	HCl	1.0	91	$HOCH_2SO_3^-$ (HMS^-)	0.92
25	CH_3OOH	1.0	59	Cl^-	1.9	92	HSO_4^-	0.92
26	CH_3CO_3H	1.0	60	Cl	1.0	93	SO_4^{2-}	0.049
27	$CH_3CO_3^-$	0.44	61	Cl_2^-	0.44	94	HSO_5^-	0.92
28	$HCHO$	1.0	62	Cl_3^-	0.44	95	SO_5^{2-}	0.049
29	$CH_2(OH)_2$	1.0	63	$HOCl$	1.0	96	SO_3^-	0.44
30	$HCOOH$	1.0	64	ClO^-	0.44	97	SO_4^-	0.44
31	$HCOO^-$	1.1	65	CH_3OCl	1.0	98	SO_5^-	0.44
32	CH_3CHO	1.0	66	$ClOH^-$	0.44	99	CH_3SO_3H	1.0
33	$CH_3CH(OH)_2$	1.0	67	Cl_2	1.0	100	$CH_3SO_3^-$	0.44
34	CH_3COOH	1.0						

Note: ^{a} Taken from Sander and Crutzen (1996) for species included in their model and calculated by the Debye-Hückel equation (Atkins, 1990) for the remainders.

Table S3. Gas-Phase Reactions [a, b, c]

No.	Reaction	Rate Constant	Reference
G1	$O(^3P) + O_2 \xrightarrow{M} O_3$	$k_0 = 6.00 \times 10^{-34} (T/300)^{-2.4}$	1
G2	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	$1.80 \times 10^{-11} \exp(110/T)$	2
G3	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	$3.20 \times 10^{-11} \exp(70/T)$	2
G4	$O(^3P) + O_3 \rightarrow 2\,O_2$	$8.00 \times 10^{-12} \exp(-2060/T)$	2
G5	$O(^1D) + O_3 \rightarrow 2\,O(^3P) + O_2$	1.20×10^{-10}	2
G6	$O(^1D) + O_3 \rightarrow 2\,O_2$	1.20×10^{-10}	2
G7	$O(^1D) + H_2O \rightarrow 2\,OH$	2.20×10^{-10}	1
G8	$O(^1D) + H_2 \xrightarrow{O_2} OH + HO_2$	1.10×10^{-10}	2
G9	$O(^3P) + OH \xrightarrow{O_2} HO_2 + O_2$	$2.20 \times 10^{-11} \exp(120/T)$	2
G10	$O(^3P) + HO_2 \rightarrow OH + O_2$	$3.00 \times 10^{-11} \exp(200/T)$	1
G11	$O(^3P) + H_2O_2 \rightarrow OH + HO_2$	$1.40 \times 10^{-12} \exp(-2000/T)$	2
G12	$OH + O_3 \rightarrow HO_2 + O_2$	$1.50 \times 10^{-12} \exp(-880/T)$	1
G13	$HO_2 + O_3 \rightarrow OH + 2\,O_2$	$2.00 \times 10^{-14} \exp(-680/T)$	1
G14	$OH + HO_2 \rightarrow H_2O + O_2$	$4.80 \times 10^{-11} \exp(250/T)$	1
G15	$OH + H_2O_2 \rightarrow H_2O + HO_2$	$2.90 \times 10^{-12} \exp(-160/T)$	2
G16	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.3 \times 10^{-13} \exp(600/T) \times f(H_2O)$	2
G17	$HO_2 + HO_2 \xrightarrow{M} H_2O_2 + O_2$	$k_0 = 1.9 \times 10^{-33} \exp(980/T) \times f(H_2O)$	3
		$f(H_2O) = 1 + 1.4 \times 10^{-21}\,[H_2O]\,\exp(2200/T)$	
G18	$OH + H_2 \xrightarrow{O_2} H_2O + HO_2$	$5.50 \times 10^{-12} \exp(-2000/T)$	2
G19	$OH + OH \rightarrow H_2O + O(^3P)$	$4.20 \times 10^{-12} \exp(-240/T)$	2
G20	$OH + OH \xrightarrow{M} H_2O_2$		
		$F_c = 0.5,\ k_0 = 6.90 \times 10^{-31}(T/300)^{-0.8},\ k_\infty = 2.6 \times 10^{-11}$	3
G21	$O(^3P) + NO_2 \rightarrow NO + O_2$	$5.60 \times 10^{-12} \exp(180/T)$	1
G22	$O(^3P) + NO_3 \rightarrow NO_2 + O_2$	1.00×10^{-11}	2
G23	$O(^3P) + NO \xrightarrow{M} NO_2$		
		$F_c = 0.6,\ k_0 = 9.0 \times 10^{-32}(T/300)^{-1.5},\ k_\infty = 3.0 \times 10^{-11}$	1
G24	$O(^3P) + NO_2 \xrightarrow{M} NO_3$		
		$F_c = \exp(-T/1300),\ k_0 = 9.0 \times 10^{-32}(T/300)^{-2.0},\ k_\infty = 2.2 \times 10^{-11}$	3
G25	$NO + O_3 \rightarrow NO_2 + O_2$	$3.00 \times 10^{-12} \exp(-1500/T)$	1
G26	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.20 \times 10^{-13} \exp(-2450/T)$	2
G27	$HO_2 + NO \rightarrow OH + NO_2$	$3.50 \times 10^{-12} \exp(250/T)$	2
G28	$NO + NO_3 \rightarrow 2\,NO_2$	$1.50 \times 10^{-11} \exp(170/T)$	2
G29	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	$4.50 \times 10^{-14} \exp(-1260/T)$	2
G30	$NO_2 + NO_3 \xrightarrow{M} N_2O_5$		
		$F_c = 0.33,\ k_0 = 2.7 \times 10^{-30}(T/300)^{-3.4},\ k_\infty = 2.0 \times 10^{-12}(T/300)^{0.2}$	3
G31	$N_2O_5 \xrightarrow{M} NO_2 + NO_3$		
		$F_c = 0.33,\ k_0 = 1.0 \times 10^{-3}(T/300)^{-3.5} \exp(-11000/T),\ k_\infty = 9.7 \times 10^{14}(T/300)^{0.1} \exp(-11080/T)$	3
G32	$OH + NO_3 \rightarrow HO_2 + NO_2$	2.20×10^{-11}	2
G33	$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2$	3.50×10^{-12}	2
G34	$OH + NO_2 \xrightarrow{M} HNO_3$		
		$F_c = 0.6,\ k_0 = 2.4 \times 10^{-30}(T/300)^{-3.1},\ k_\infty = 1.7 \times 10^{-11}(T/300)^{-2.1}$	1
G35	$OH + HNO_3 \rightarrow H_2O + NO_3$	$k = k_0 + k_3[M]/(1 + k_3[M]/k_2)$	1
		$k_0 = 2.4 \times 10^{-14} \exp(460/T),\ k_2 = 2.7 \times 10^{-17} \exp(2199/T),\ k_3 = 6.5 \times 10^{-34} \exp(1335/T)$	
G36	$OH + NO \xrightarrow{M} HONO$		
		$F_c = 0.9,\ k_0 = 7.4 \times 10^{-31}(T/300)^{-2.4},\ k_\infty = 4.50 \times 10^{-11}$	2
G37	$OH + HONO \rightarrow H_2O + NO_2$	$1.80 \times 10^{-11} \exp(-390/T)$	2
G38	$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$		
		$F_c = 0.6,\ k_0 = 1.8 \times 10^{-31}(T/300)^{-3.2},\ k_\infty = 4.7 \times 10^{-12}$	3

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G39	$HO_2NO_2 \xrightarrow{M} HO_2 + NO_2$		
		$F_c = 0.6,\ k_0 = 5.0 \times 10^{-6} \exp(-10000/T),\ k_\infty = 2.6 \times 10^{15} \exp(-10900/T)$	3
G40	$OH + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2$	$1.30 \times 10^{-12} \exp(380/T)$	2
G41	$OH + CO \xrightarrow{O_2} HO_2 + CO_2$	$1.50 \times 10^{-13}(1 + P_{\mathrm{atm}})$	2
G42	$O(^1D) + CH_4 \xrightarrow{O_2} OH + CH_3OO$	1.50×10^{-10}	2
G43	$OH + CH_4 \xrightarrow{O_2} H_2O + CH_3OO$	$2.45 \times 10^{-12} \exp(-1775/T)$	2
G44	$Cl + CH_4 \xrightarrow{O_2} HCl + CH_3OO$	$9.60 \times 10^{-12} \exp(-1360/T)$	1
G45	$HO_2 + CH_3OO \rightarrow CH_3OOH + O_2$	$3.80 \times 10^{-13} \exp(800/T)$	2
G46	$CH_3OO + CH_3OO \rightarrow CH_3OH + HCHO + O_2$	$1.50 \times 10^{-13} \exp(190/T)$	2
G47	$CH_3OO + CH_3OO \xrightarrow{O_2} 2\,HCHO + 2\,HO_2 + O_2$	$1.00 \times 10^{-13} \exp(190/T)$	2
G48	$CH_3OO + NO \xrightarrow{O_2} NO_2 + HCHO + HO_2$	$3.00 \times 10^{-12} \exp(280/T)$	2
G49	$CH_3OO + NO_3 \xrightarrow{O_2} HCHO + HO_2 + NO_2 + O_2$	1.30×10^{-12}	4
G50	$O(^3P) + HCHO \xrightarrow{O_2} OH + CO + HO_2$	$3.40 \times 10^{-11} \exp(-1600/T)$	2
G51	$NO_3 + HCHO \xrightarrow{O_2} HNO_3 + CO + HO_2$	5.80×10^{-16}	2
G52	$OH + HCHO \xrightarrow{O_2} H_2O + CO + HO_2$	1.00×10^{-11}	2
G53	$Br + HCHO \xrightarrow{O_2} HBr + CO + HO_2$	$1.70 \times 10^{-11} \exp(-800/T)$	4
G54	$Cl + HCHO \xrightarrow{O_2} HCl + CO + HO_2$	$8.20 \times 10^{-11} \exp(-34/T)$	4
G55	$OH + CH_3OH \xrightarrow{O_2} H_2O + HCHO + HO_2$	$3.10 \times 10^{-12} \exp(-360/T)$	4
G56	$Cl + CH_3OH \xrightarrow{O_2} HCl + HCHO + HO_2$	5.50×10^{-11}	4
G57	$OH + CH_3OOH \rightarrow H_2O + CH_3OO$	$1.90 \times 10^{-12} \exp(190/T)$	4
G58	$OH + CH_3OOH \rightarrow H_2O + HCHO + OH$	$1.00 \times 10^{-12} \exp(190/T)$	4
G59	$Br + CH_3OOH \rightarrow HBr + CH_3OO$	$2.63 \times 10^{-12} \exp(-1610/T)$	5
G60	$Cl + CH_3OOH \rightarrow HCl + HCHO + OH$	5.90×10^{-11}	4
G61	$HO_2 + HCHO \rightarrow HOCH_2OO$	$9.70 \times 10^{-15} \exp(625/T)$	4
G62	$HOCH_2OO \xrightarrow{M} HO_2 + HCHO$	$k_{\mathrm{uni}} = 2.4 \times 10^{12} \exp(-7000/T)$	4
G63	$HOCH_2OO + NO \xrightarrow{O_2} HCOOH + HO_2 + NO_2$	5.60×10^{-12}	6
G64	$HOCH_2OO + NO_3 \xrightarrow{O_2} HCOOH + HO_2 + NO_2 + O_2$	2.50×10^{-12}	7
G65	$HOCH_2OO + HO_2 \rightarrow HOCH_2OOH + O_2$	$3.36 \times 10^{-15} \exp(2300/T)$	4
G66	$HOCH_2OO + HO_2 \rightarrow HCOOH + H_2O + O_2$	$2.24 \times 10^{-15} \exp(2300/T)$	4
G67	$HOCH_2OO + CH_3OO \xrightarrow{O_2} HCOOH + HCHO + 2\,HO_2 + O_2$	1.20×10^{-12}	8
G68	$HOCH_2OO + CH_3OO \rightarrow HCOOH + CH_3OH + O_2$	4.00×10^{-13}	8
G69	$HOCH_2OO + CH_3OO \rightarrow CH_2(OH)_2 + HCHO + O_2$	4.00×10^{-13}	8
G70	$HOCH_2OO + HOCH_2OO \rightarrow HCOOH + CH_2(OH)_2 + O_2$	$5.70 \times 10^{-14} \exp(750/T)$	4
G71	$HOCH_2OO + HOCH_2OO \xrightarrow{O_2} 2\,HCOOH + 2\,HO_2 + O_2$	5.50×10^{-12}	4
G72	$OH + CH_2(OH)_2 \xrightarrow{O_2} H_2O + HCOOH + HO_2$	1.17×10^{-11}	This work
G73	$OH + HOCH_2OOH \rightarrow HOCH_2OO$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G74	$OH + HOCH_2OOH \rightarrow H_2O + HCOOH + OH$	4.26×10^{-11}	This work
G75	$OH + HCOOH \xrightarrow{O_2} H_2O + HO_2 + CO_2$	4.00×10^{-13}	2
G76	$Br + O_3 \rightarrow BrO + O_2$	$1.70 \times 10^{-11} \exp(-800/T)$	2
G77	$Br + HO_2 \rightarrow HBr + O_2$	$1.40 \times 10^{-11} \exp(-590/T)$	9
G78	$Br + NO_3 \rightarrow BrO + NO_2$	1.60×10^{-11}	2
G79	$BrO + O(^3P) \rightarrow Br + O_2$	$1.90 \times 10^{-11} \exp(230/T)$	2
G80	$BrO + HO_2 \rightarrow HOBr + O_2$	$3.70 \times 10^{-12} \exp(-545/T)$	9
G81	$BrO + NO \rightarrow Br + NO_2$	$8.70 \times 10^{-12} \exp(260/T)$	9
G82	$BrO + NO_2 \xrightarrow{M} BrONO_2$		
		$F_c = \exp(-T/327),\ k_0 = 4.7 \times 10^{-31}(T/300)^{-3.1},\ k_\infty = 1.4 \times 10^{-11}(T/300)^{-1.2}$	9
G83	$BrONO_2 \xrightarrow{M} BrO + NO_2$	$k_{\mathrm{uni}} = 2.79 \times 10^{13} \exp(-12360/T)$	10

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G84	$BrO + CH_3OO \rightarrow HOBr + CH_2OO$	4.10×10^{-12}	11
G85	$BrO + CH_3OO \xrightarrow{O_2} Br + HCHO + HO_2 + O_2$	1.60×10^{-12}	11
G86	$BrO + BrO \rightarrow 2\,Br + O_2$	2.70×10^{-12}	9
G87	$BrO + BrO \rightarrow Br_2 + O_2$	$2.90 \times 10^{-14}\exp(840/T)$	9
G88	$BrO + ClO \rightarrow Br + OClO$	$9.50 \times 10^{-13}\exp(550/T)$	1
G89	$BrO + ClO \rightarrow Br + Cl + O_2$	$2.30 \times 10^{-12}\exp(260/T)$	1
G90	$BrO + ClO \rightarrow BrCl + O_2$	$4.10 \times 10^{-13}\exp(290/T)$	1
G91	$Br_2 + Cl \rightarrow BrCl + Br$	1.66×10^{-10}	12
G92	$BrCl + Br \rightarrow Br_2 + Cl$	3.32×10^{-15}	12
G93	$Br + Cl_2 \rightarrow BrCl + Cl$	1.10×10^{-15}	13
G94	$BrCl + Cl \rightarrow Br + Cl_2$	1.45×10^{-11}	14
G95	$O(^3P) + HBr \rightarrow OH + Br$	$5.80 \times 10^{-12}\exp(-1500/T)$	2
G96	$O(^1D) + HBr \rightarrow OH + Br$	1.50×10^{-10}	2
G97	$OH + HBr \rightarrow H_2O + Br$	1.10×10^{-11}	2
G98	$Cl + CH_3OO \rightarrow HCl + CH_2OO^*$	8.00×10^{-11}	2
G99	$Cl + CH_3OO \xrightarrow{O_2} ClO + HCHO + HO_2$	8.00×10^{-11}	2
G100	$Cl + CH_3OCl \xrightarrow{O_2} Cl_2 + HCHO + HO_2$	4.87×10^{-11}	15
G101	$Cl + CH_3OCl \xrightarrow{O_2} HCl + HCOCl + HO_2$	1.22×10^{-11}	15
G102	$Cl + O_3 \rightarrow ClO + O_2$	$2.30 \times 10^{-11}\exp(-200/T)$	1
G103	$ClO + ClO \rightarrow Cl_2 + O_2$	$1.00 \times 10^{-12}\exp(-1590/T)$	2
G104	$ClO + ClO \rightarrow 2\,Cl + O_2$	$3.00 \times 10^{-11}\exp(-2450/T)$	2
G105	$ClO + ClO \rightarrow OClO + Cl$	$3.50 \times 10^{-13}\exp(-1370/T)$	2
G106	$ClO + ClO \xrightarrow{M} Cl_2O_2$		
		$F_c = 0.6,\ k_0 = 1.7 \times 10^{-32}(T/300)^{-4},\ k_\infty = 5.4 \times 10^{-12}$	9
G107	$Cl_2O_2 \xrightarrow{M} ClO + ClO$		
		$F_c = 0.6,\ k_0 = 1.0 \times 10^{-6}\exp(-8000/T),\ k_\infty = 4.8 \times 10^{15}\exp(-8820/T)$	9
G108	$ClO + OH \rightarrow Cl + HO_2$	$7.40 \times 10^{-12}\exp(270/T)$	1
G109	$ClO + OH \rightarrow HCl + O_2$	$3.20 \times 10^{-13}\exp(320/T)$	1
G110	$ClO + HO_2 \rightarrow HOCl + O_2$	$4.80 \times 10^{-13}\exp(700/T)$	2
G111	$ClO + CH_3OO \xrightarrow{O_2} Cl + HCHO + HO_2$	$4.90 \times 10^{-12}\exp(-330/T)$	3
G112	$ClO + CH_3OO \rightarrow CH_3OCl + O_2$	$2.60 \times 10^{-13}\exp(260/T)$	3
G113	$ClO + NO \rightarrow Cl + NO_2$	$6.40 \times 10^{-12}\exp(290/T)$	2
G114	$ClO + NO_2 \xrightarrow{M} ClONO_2$		9
		$F_c = \exp(-T/430),\ k_0 = 1.6 \times 10^{-31}(T/300)^{-3.4},\ k_\infty = 1.5 \times 10^{-11}$	9
G115	$ClONO_2 \xrightarrow{M} ClO + NO_2$	$k_{\mathrm{uni}} = 6.92 \times 10^{-7}\,[\mathrm{M}]\exp(-10908/T)$	16
G116	$NO + OClO \rightarrow NO_2 + ClO$	$2.50 \times 10^{-12}\exp(-600/T)$	2
G117	$OH + OClO \rightarrow HOCl + O_2$	$4.50 \times 10^{-13}\exp(800/T)$	2
G118	$OH + HCl \rightarrow H_2O + Cl$	$2.60 \times 10^{-12}\exp(-350/T)$	1
G119	$OH + HOCl \rightarrow H_2O + ClO$	$3.00 \times 10^{-12}\exp(-500/T)$	2
G120	$OH + CH_3OCl \xrightarrow{O_2} HCOCl + HO_2 + H_2O$	$2.40 \times 10^{-12}\exp(-360/T)$	2
G121	$OH + C_2H_6 \xrightarrow{O_2} H_2O + C_2H_5OO$	$8.70 \times 10^{-12}\exp(-1070/T)$	2
G122	$Cl + C_2H_6 \xrightarrow{O_2} HCl + C_2H_5OO$	$7.70 \times 10^{-11}\exp(-90/T)$	2
G123	$C_2H_5OO + NO \xrightarrow{O_2} CH_3CHO + HO_2 + NO_2$	$2.50 \times 10^{-12}\exp(380/T)$	4
G124	$C_2H_5OO + HO_2 \rightarrow C_2H_5OOH + O_2$	$3.80 \times 10^{-13}\exp(900/T)$	4
G125	$C_2H_5OO + NO_3 \xrightarrow{O_2} CH_3CHO + HO_2 + NO_2 + O_2$	2.30×10^{-12}	4
G126	$C_2H_5OO + CH_3OO \xrightarrow{O_2} CH_3CHO + HCHO + 2\,HO_2 + O_2$	1.21×10^{-13}	17
G127	$C_2H_5OO + CH_3OO \rightarrow CH_3CHO + CH_3OH + O_2$	4.00×10^{-14}	17
G128	$C_2H_5OO + CH_3OO \rightarrow C_2H_5OH + HCHO + O_2$	4.00×10^{-14}	17

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G129	$C_2H_5OO + C_2H_5OO \xrightarrow{O_2}$ $1.24 \times (CH_3CHO + HO_2) + 0.38 \times (CH_3CHO + C_2H_5OH) + O_2$	6.40×10^{-14}	3
G130	$C_2H_5OO + Cl \xrightarrow{O_2} CH_3CHO + HO_2 + ClO$	7.40×10^{-11}	2
G131	$C_2H_5OO + Cl \rightarrow CH_3CHOO^* + HCl$	7.70×10^{-11}	2
G132	$CH_3CHO + OH \xrightarrow{O_2} CH_3C(O)OO + H_2O$	$5.60 \times 10^{-12} \exp(310/T)$	4
G133	$CH_3CHO + NO_3 \xrightarrow{O_2} CH_3C(O)OO + HNO_3$	$1.40 \times 10^{-12} \exp(-1860/T)$	4
G134	$CH_3CHO + Cl \xrightarrow{O_2} CH_3C(O)OO + HCl$	7.20×10^{-11}	4
G135	$CH_3CHO + Br \xrightarrow{O_2} CH_3C(O)OO + HBr$	$1.30 \times 10^{-11} \exp(-360/T)$	4
G136	$C_2H_5OH + OH \xrightarrow{O_2} CH_3CHO + HO_2 + H_2O$	$4.10 \times 10^{-12} \exp(-70/T)$	4
G137	$C_2H_5OH + Cl \xrightarrow{O_2} CH_3CHO + HO_2 + HCl$	9.00×10^{-11}	4
G138	$C_2H_5OOH + OH \rightarrow H_2O + C_2H_5OO$	$1.90 \times 10^{-12} \exp(190/T)$	7
G139	$C_2H_5OOH + OH \rightarrow H_2O + CH_3CHO + OH$	8.01×10^{-12}	7
G140	$C_2H_5OOH + Cl \rightarrow HCl + CH_3CHO + OH$	1.07×10^{-10}	18
G141	$CH_3C(O)OO + HO_2 \rightarrow CH_3C(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	4, 7
G142	$CH_3C(O)OO + HO_2 \rightarrow CH_3COOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	4, 7
G143	$CH_3C(O)OO + CH_3OO \xrightarrow{O_2} CH_3OO + CO_2 + HCHO + HO_2 + O_2$	$1.26 \times 10^{-12} \exp(500/T)$	4, 8
G144	$CH_3C(O)OO + CH_3OO \rightarrow CH_3COOH + HCHO + O_2$	$5.40 \times 10^{-13} \exp(500/T)$	4, 8
G145	$CH_3C(O)OO + CH_3C(O)OO \rightarrow 2\,CH_3OO + 2\,CO_2 + O_2$	$2.90 \times 10^{-12} \exp(500/T)$	4
G146	$CH_3C(O)OO + C_2H_5OO \xrightarrow{O_2} CH_3OO + CO_2 + CH_3CHO + HO_2 + O_2$	7.00×10^{-12}	4, 8
G147	$CH_3C(O)OO + C_2H_5OO \rightarrow CH_3COOH + CH_3CHO + O_2$	3.00×10^{-12}	4, 8
G148	$CH_3C(O)OO + NO \xrightarrow{O_2} CH_3OO + CO_2 + NO_2$	$7.80 \times 10^{-12} \exp(300/T)$	4
G149	$CH_3C(O)OO + NO_3 \xrightarrow{O_2} CH_3OO + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G150	$CH_3COOH + OH \xrightarrow{O_2} CH_3OO + CO_2 + H_2O$	8.00×10^{-13}	4
G151	$CH_3C(O)OOH + OH \rightarrow CH_3C(O)OO + H_2O$	3.70×10^{-12}	7
G152	$CH_3C(O)OO + NO_2 \xrightarrow{M} PAN$	$F_c = 0.3,\ k_0 = 2.7 \times 10^{-28}(T/300)^{-7.1},\ k_\infty = 1.2 \times 10^{-11}(T/300)^{0.9}$	4
G153	$PAN \xrightarrow{M} CH_3C(O)OO + NO_2$	$F_c = 0.3,\ k_0 = 4.9 \times 10^{-3} \exp(-12100/T),\ k_\infty = 5.4 \times 10^{16} \exp(-13830/T)$	4
G154	$OH + C_3H_8 \xrightarrow{O_2} 0.264 \times n\text{-}C_3H_7OO + 0.736 \times i\text{-}C_3H_7OO + H_2O$	$8.00 \times 10^{-12} \exp(-590/T)$	4, 7
G155	$Cl + C_3H_8 \xrightarrow{O_2} 0.43 \times n\text{-}C_3H_7OO + 0.57 \times i\text{-}C_3H_7OO + HCl$	1.40×10^{-10}	4, 19
G156	$n\text{-}C_3H_7OO + NO \xrightarrow{O_2} C_2H_5CHO + HO_2 + NO_2$	$2.90 \times 10^{-12} \exp(350/T)$	4
G157	$n\text{-}C_3H_7OO + HO_2 \rightarrow n\text{-}C_3H_7OOH + O_2$	$1.51 \times 10^{-13} \exp(1300/T)$	7
G158	$n\text{-}C_3H_7OO + NO_3 \xrightarrow{O_2} C_2H_5CHO + HO_2 + NO_2 + O_2$	2.50×10^{-12}	7
G159	$n\text{-}C_3H_7OO + CH_3OO \xrightarrow{O_2} C_2H_5CHO + HCHO + 2\,HO_2 + O_2$	3.60×10^{-13}	8
G160	$n\text{-}C_3H_7OO + CH_3OO \rightarrow C_2H_5CHO + CH_3OH + O_2$	1.20×10^{-13}	8
G161	$n\text{-}C_3H_7OO + CH_3OO \rightarrow n\text{-}C_3H_7OH + HCHO + O_2$	1.20×10^{-13}	8
G162	$n\text{-}C_3H_7OO + CH_3C(O)OO \xrightarrow{O_2}$ $C_2H_5CHO + HO_2 + CH_3OO + CO_2 + O_2$	7.00×10^{-12}	7
G163	$n\text{-}C_3H_7OO + CH_3C(O)OO \rightarrow C_2H_5CHO + CH_3COOH + O_2$	3.00×10^{-12}	7
G164	$n\text{-}C_3H_7OO + n\text{-}C_3H_7OO \xrightarrow{O_2}$ $1.2 \times (C_2H_5CHO + HO_2) + 0.4 \times (C_2H_5CHO + n\text{-}C_3H_7OH) + O_2$	3.00×10^{-13}	4, 8
G165	$C_2H_5CHO + OH \xrightarrow{O_2} C_2H_5C(O)OO + H_2O$	$5.60 \times 10^{-12} \exp(310/T)$	4
G166	$C_2H_5CHO + NO_3 \xrightarrow{O_2} C_2H_5C(O)OO + HNO_3$	$1.40 \times 10^{-12} \exp(-1860/T)$	20
G167	$C_2H_5CHO + Cl \xrightarrow{O_2} C_2H_5C(O)OO + HCl$	7.20×10^{-11}	4
G168	$C_2H_5CHO + Br \xrightarrow{O_2} C_2H_5C(O)OO + HBr$	$5.75 \times 10^{-11} \exp(-610/T)$	21
G169	$n\text{-}C_3H_7OH + OH \xrightarrow{O_2} C_2H_5CHO + HO_2 + H_2O$	5.50×10^{-12}	4

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G170	$n\text{-}C_3H_7OH + Cl \xrightarrow{O_2} C_2H_5CHO + HO_2 + HCl$	1.50×10^{-10}	4
G171	$n\text{-}C_3H_7OOH + OH \rightarrow H_2O + n\text{-}C_3H_7OO$	$1.90 \times 10^{-12}\, \exp(190/T)$	7
G172	$n\text{-}C_3H_7OOH + OH \rightarrow H_2O + C_2H_5CHO + OH$	1.10×10^{-11}	7
G173	$C_2H_5C(O)OO + NO \xrightarrow{O_2} C_2H_5OO + NO_2 + CO_2$	$1.20 \times 10^{-11}\, \exp(240/T)$	4
G174	$C_2H_5C(O)OO + NO_3 \xrightarrow{O_2} C_2H_5OO + NO_2 + O_2 + CO_2$	4.00×10^{-12}	7
G175	$C_2H_5C(O)OO + HO_2 \rightarrow C_2H_5C(O)OOH + O_2$	$3.05 \times 10^{-13}\, \exp(1040/T)$	8
G176	$C_2H_5C(O)OO + HO_2 \rightarrow C_2H_5COOH + O_3$	$1.25 \times 10^{-13}\, \exp(1040/T)$	8
G177	$C_2H_5C(O)OO + CH_3OO \xrightarrow{O_2} C_2H_5OO + CO_2 + HCHO + HO_2 + O_2$	7.00×10^{-12}	7
G178	$C_2H_5C(O)OO + CH_3OO \rightarrow C_2H_5COOH + HCHO + O_2$	3.00×10^{-12}	7
G179	$C_2H_5COOH + OH \xrightarrow{O_2} H_2O + C_2H_5OO + CO_2$	1.20×10^{-12}	4
G180	$C_2H_5C(O)OOH + OH \rightarrow H_2O + C_2H_5C(O)OO$	4.42×10^{-12}	7
G181	$C_2H_5C(O)OO + NO_2 \xrightarrow{M} PPN$		$= k_{G152}$
G182	$PPN \xrightarrow{M} C_2H_5C(O)OO + NO_2$		$= k_{G153}$
G183	$i\text{-}C_3H_7OO + NO \xrightarrow{O_2} CH_3COCH_3 + HO_2 + NO_2$	$2.70 \times 10^{-12}\, \exp(360/T)$	4
G184	$i\text{-}C_3H_7OO + HO_2 \rightarrow i\text{-}C_3H_7OOH + O_2$	$1.51 \times 10^{-13}\, \exp(1300/T)$	7
G185	$i\text{-}C_3H_7OO + NO_3 \xrightarrow{O_2} CH_3COCH_3 + HO_2 + NO_2 + O_2$	2.50×10^{-12}	7
G186	$i\text{-}C_3H_7OO + CH_3OO \xrightarrow{O_2} CH_3COCH_3 + HCHO + 2\,HO_2 + O_2$	2.40×10^{-14}	8
G187	$i\text{-}C_3H_7OO + CH_3OO \rightarrow CH_3COCH_3 + CH_3OH + O_2$	8.00×10^{-15}	8
G188	$i\text{-}C_3H_7OO + CH_3OO \rightarrow i\text{-PrOH} + HCHO + O_2$	8.00×10^{-15}	8
G189	$i\text{-}C_3H_7OO + CH_3C(O)OO \xrightarrow{O_2}$ $CH_3COCH_3 + HO_2 + CH_3OO + CO_2 + O_2$	7.00×10^{-12}	7
G190	$i\text{-}C_3H_7OO + CH_3C(O)OO \rightarrow CH_3COCH_3 + CH_3COOH + O_2$	3.00×10^{-12}	7
G191	$CH_3COCH_3 + OH \xrightarrow{O_2} CH_3COCH_2OO + H_2O$	$1.10 \times 10^{-12}\, \exp(-520/T)$	4
G192	$CH_3COCH_3 + Cl \xrightarrow{O_2} CH_3COCH_2OO + HCl$	3.50×10^{-12}	4
G193	$CH_3COCH_2OO + NO \xrightarrow{O_2} CH_3C(O)OO + HCHO + NO_2$	8.00×10^{-12}	22
G194	$CH_3COCH_2OO + HO_2 \rightarrow CH_3COCH_2OOH + O_2$	9.00×10^{-12}	4
G195	$CH_3COCH_2OO + NO_3 \xrightarrow{O_2} CH_3C(O)OO + HCHO + NO_2 + O_2$	2.50×10^{-12}	7
G196	$CH_3COCH_2OO + CH_3OO \rightarrow CH_3COCHO + CH_3OH + O_2$	1.90×10^{-12}	4
G197	$CH_3COCH_2OO + CH_3OO \rightarrow CH_3COCH_2OH + HCHO + O_2$	7.60×10^{-13}	4
G198	$CH_3COCH_2OO + CH_3OO \xrightarrow{O_2}$ $CH_3C(O)OO + 2\,HCHO + HO_2 + CO_2 + O_2$	1.14×10^{-12}	4
G199	$CH_3COCH_2OO + CH_3C(O)OO \rightarrow$ $CH_3COCHO + CH_3COOH + O_2$	2.50×10^{-12}	4
G200	$CH_3COCH_2OO + CH_3C(O)OO \xrightarrow{O_2}$ $CH_3C(O)OO + HCHO + CH_3OO + CO_2 + O_2$	2.50×10^{-12}	4
G201	$CH_3COCH_2OO + CH_3COCH_2OO \xrightarrow{O_2}$ $2\,CH_3C(O)OO + 2\,HCHO + O_2$	1.40×10^{-12}	4
G202	$CH_3COCH_2OO + CH_3COCH_2OO \rightarrow$ $CH_3COCHO + CH_3COCH_2OH + O_2$	7.00×10^{-13}	4
G203	$CH_3COCHO + OH \xrightarrow{O_2} CH_3C(O)OO + CO + H_2O$	1.50×10^{-11}	4
G204	$CH_3COCHO + Cl \xrightarrow{O_2} CH_3C(O)OO + CO + HCl$	4.80×10^{-11}	23
G205	$CH_3COCH_2OH + OH \xrightarrow{O_2} CH_3COCHO + HO_2 + H_2O$	3.01×10^{-12}	24
G206	$CH_3COCH_2OH + Cl \xrightarrow{O_2} CH_3COCHO + HO_2 + HCl$	5.60×10^{-11}	24
G207	$CH_3COCH_2OOH + OH \rightarrow CH_3COCH_2OO + H_2O$	$1.90 \times 10^{-12}\, \exp(190/T)$	7
G208	$CH_3COCH_2OOH + OH \rightarrow CH_3COCHO + OH + H_2O$	8.39×10^{-12}	7
G209	$i\text{-PrOH} + OH \xrightarrow{O_2}$ $H_2O + 0.861 \times (CH_3COCH_3 + HO_2) + 0.139 \times CH_3CH(OH)CH_2OO$	$2.70 \times 10^{-12}\, \exp(190/T)$	4, 7

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G210	i-PrOH + Cl $\overset{O_2}{\rightarrow}$ $HCl + 0.861 \times (CH_3COCH_3 + HO_2) + 0.139 \times CH_3CH(OH)CH_2OO$	8.40×10^{-11}	4[d]
G211	$i\text{-}C_3H_7OOH + OH \rightarrow i\text{-}C_3H_7OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	7
G212	$i\text{-}C_3H_7OOH + OH \rightarrow CH_3COCH_3 + OH + H_2O$	1.66×10^{-11}	7
G213	$OH + C_2H_4 \rightarrow HOCH_2CH_2OO$	$F_c = 0.48,\ k_0 = 7.0 \times 10^{-29}(T/300)^{-3.1},\ k_\infty = 9.0 \times 10^{-12}$	4
G214	$Cl + C_2H_4 \rightarrow ClCH_2CH_2OO$	$F_c = 0.6,\ k_0 = 1.7 \times 10^{-29}(T/300)^{-3.3},\ k_\infty = 3.0 \times 10^{-10}$	4
G215	$Br + C_2H_4 \overset{M,O_2}{\rightarrow} BrCH_2CH_2OO$	$k = k_1 \times k_2[O_2]/k_3$; $k_1 = 2.85 \times 10^{-13} \exp(224/T),\ k_2 = 7.5 \times 10^{-12},\ k_3 = 8.5 \times 10^{12} \exp(-3200/T)$	25
G216	$O_3 + C_2H_4 \rightarrow HCHO + CH_2OO^*$	$9.10 \times 10^{-15} \exp(-2580/T)$	4
G217	$HOCH_2CH_2OO + NO \rightarrow HOCH_2CH_2O + NO_2$	9.00×10^{-12}	4
G218	$HOCH_2CH_2OO + HO_2 \rightarrow HOCH_2CH_2OOH + O_2$	$2.00 \times 10^{-13} \exp(1250/T)$	7
G219	$HOCH_2CH_2OO + NO_3 \rightarrow HOCH_2CH_2O + NO_2 + O_2$	2.50×10^{-12}	7
G220	$HOCH_2CH_2OO + CH_3OO \overset{O_2}{\rightarrow} HOCH_2CH_2O + HCHO + HO_2 + O_2$	1.20×10^{-12}	8
G221	$HOCH_2CH_2OO + CH_3OO \rightarrow HOCH_2CHO + CH_3OH + O_2$	4.00×10^{-13}	8
G222	$HOCH_2CH_2OO + CH_3OO \rightarrow HOCH_2CH_2OH + HCHO + O_2$	4.00×10^{-13}	8
G223	$HOCH_2CH_2OO + HOCH_2CH_2OO \rightarrow HOCH_2CH_2O + HOCH_2CH_2O + O_2$	$3.90 \times 10^{-14} \exp(1000/T)$	4
G224	$HOCH_2CH_2OO + HOCH_2CH_2OO \rightarrow HOCH_2CHO + HOCH_2CH_2OH + O_2$	$3.90 \times 10^{-14} \exp(1000/T)$	4
G225	$HOCH_2CH_2O \overset{M}{\rightarrow} 2\,HCHO + HO_2$	$k_{uni} = 9.50 \times 10^{13} \exp(-5988/T)$	8
G226	$HOCH_2CH_2O + O_2 \rightarrow HOCH_2CHO + HO_2$	$3.70 \times 10^{-14} \exp(-460/T)$	8
G227	$HOCH_2CH_2OH + OH \overset{O_2}{\rightarrow} HOCH_2CHO + HO_2 + H_2O$	1.49×10^{-11}	26
G228	$HOCH_2CHO + OH \overset{O_2}{\rightarrow} HOCH_2C(O)OO + H_2O$	8.00×10^{-12}	4
G229	$HOCH_2CHO + OH \overset{O_2}{\rightarrow} HCOCHO + HO_2 + H_2O$	2.00×10^{-12}	4
G230	$HOCH_2CHO + Cl \overset{O_2}{\rightarrow} HOCH_2C(O)OO + HCl$	5.15×10^{-11}	27[e]
G231	$HOCH_2CHO + Cl \overset{O_2}{\rightarrow} HCOCHO + HO_2 + HCl$	2.78×10^{-11}	27[e]
G232	$HCOCHO + OH \overset{O_2}{\rightarrow} 2\,CO + HO_2 + H_2O$	6.60×10^{-12}	4, 7
G233	$HCOCHO + OH \overset{O_2}{\rightarrow} HCOC(O)OO + H_2O$	4.40×10^{-12}	4, 7
G234	$HCOCHO + Cl \overset{O_2}{\rightarrow} 2\,CO + HO_2 + HCl$	2.28×10^{-11}	28
G235	$HCOCHO + Cl \overset{O_2}{\rightarrow} HCOC(O)OO + HCl$	1.52×10^{-11}	28
G236	$HCOCHO + Br \overset{O_2}{\rightarrow} 2\,CO + HO_2 + HBr$	8.40×10^{-14}	25
G237	$HCOCHO + Br \overset{O_2}{\rightarrow} HCOC(O)OO + HBr$	5.60×10^{-14}	25
G238	$HOCH_2CH_2OOH + OH \rightarrow HOCH_2CH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	7
G239	$HOCH_2CH_2OOH + OH \rightarrow HOCH_2CHO + OH + H_2O$	1.38×10^{-11}	7
G240	$HOCH_2C(O)OO + NO \overset{O_2}{\rightarrow} HCHO + HO_2 + CO_2 + NO_2$	$8.10 \times 10^{-12} \exp(270/T)$	7
G241	$HOCH_2C(O)OO + NO_3 \overset{O_2}{\rightarrow} HCHO + HO_2 + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G242	$HOCH_2C(O)OO + HO_2 \rightarrow HOCH_2C(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	8
G243	$HOCH_2C(O)OO + HO_2 \rightarrow HOCH_2COOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	8
G244	$HOCH_2C(O)OO + CH_3OO \overset{O_2}{\rightarrow} 2\,HCHO + 2\,HO_2 + CO_2 + O_2$	7.00×10^{-12}	7
G245	$HOCH_2C(O)OO + CH_3OO \rightarrow HOCH_2COOH + HCHO + O_2$	3.00×10^{-12}	7
G246	$HOCH_2COOH + OH \overset{O_2}{\rightarrow} HCHO + HO_2 + CO_2 + H_2O$	2.73×10^{-12}	7
G247	$HOCH_2C(O)OOH + OH \rightarrow HOCH_2C(O)OO + H_2O$	6.19×10^{-12}	7
G248	$HOCH_2C(O)OO + NO_2 \overset{M}{\rightarrow} PHAN$		$= k_{G152}$
G249	$PHAN \overset{M}{\rightarrow} HOCH_2C(O)OO + NO_2$		$= k_{G153}$
G250	$HCOC(O)OO + NO \overset{O_2}{\rightarrow} CO + HO_2 + NO_2 + CO_2$	$8.10 \times 10^{-12} \exp(270/T)$	7

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G251	$HCOC(O)OO + NO_3 \overset{O_2}{\rightarrow} CO + HO_2 + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G252	$HCOC(O)OO + HO_2 \rightarrow HCOC(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	8
G253	$HCOC(O)OO + HO_2 \rightarrow HCOCOOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	8
G254	$HCOC(O)OO + CH_3OO \overset{O_2}{\rightarrow} CO + HCHO + 2\,HO_2 + CO_2 + O_2$	7.00×10^{-12}	7
G255	$HCOC(O)OO + CH_3OO \rightarrow HCOCOOH + HCHO + O_2$	3.00×10^{-12}	7
G256	$HCOCOOH + OH \overset{O_2}{\rightarrow} CO + HO_2 + CO_2 + H_2O$	1.23×10^{-11}	7
G257	$HCOC(O)OOH + OH \rightarrow HCOC(O)OO + H_2O$	1.58×10^{-11}	7
G258	$HCOC(O)OO + NO_2 \overset{M}{\rightarrow} GLYPAN$		$= k_{G152}$
G259	$GLYPAN \overset{M}{\rightarrow} HCOC(O)OO + NO_2$		$= k_{G153}$
G260	$ClCH_2CH_2OO + NO \rightarrow ClCH_2CH_2O^* + NO_2$	$4.06 \times 10^{-12} \exp(360/T)$	7
G261	$ClCH_2CH_2OO + HO_2 \rightarrow ClCH_2CH_2OOH + O_2$	7.50×10^{-12}	29
G262	$ClCH_2CH_2OO + NO_3 \rightarrow ClCH_2CH_2O^* + NO_2 + O_2$	2.50×10^{-12}	7
G263	$ClCH_2CH_2OO + CH_3OO \overset{O_2}{\rightarrow} ClCH_2CHO + HCHO + 2\,HO_2 + O_2$	7.74×10^{-13}	This work
G264	$ClCH_2CH_2OO + CH_3OO \rightarrow ClCH_2CHO + CH_3OH + O_2$	4.93×10^{-13}	This work
G265	$ClCH_2CH_2OO + CH_3OO \rightarrow ClCH_2CH_2OH + HCHO + O_2$	4.93×10^{-13}	This work
G266	$ClCH_2CH_2OO + ClCH_2CH_2OO \overset{O_2}{\rightarrow} 2\,ClCH_2CHO + 2\,HO_2 + O_2$	$6.27 \times 10^{-14} \exp(1020/T)$	30, 31
G267	$ClCH_2CH_2OO + ClCH_2CH_2OO \rightarrow$ $ClCH_2CHO + ClCH_2CH_2OH + O_2$	$4.73 \times 10^{-14} \exp(1020/T)$	30, 31
G268	$ClCH_2CH_2O^* \overset{O_2}{\rightarrow} ClCH_2CHO + HO_2$	$k_{uni} = 5.8 \times 10^5$	This work
G269	$ClCH_2CH_2O^* \overset{O_2}{\rightarrow} ClCH_2OO + HCHO$	$k_{uni} = 4.2 \times 10^5$	This work
G270	$ClCH_2CH_2OH + OH \overset{O_2}{\rightarrow} ClCH_2CHO + HO_2 + H_2O$	1.28×10^{-12}	32
G271	$ClCH_2CH_2OH + Cl \overset{O_2}{\rightarrow} ClCH_2CHO + HO_2 + HCl$	3.01×10^{-11}	29
G272	$ClCH_2CHO + OH \overset{O_2}{\rightarrow} ClCH_2C(O)OO + H_2O$	3.10×10^{-12}	3
G273	$ClCH_2CHO + Cl \overset{O_2}{\rightarrow} ClCH_2C(O)OO + HCl$	4.30×10^{-11}	31
G274	$ClCH_2CH_2OOH + OH \rightarrow ClCH_2CH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G275	$ClCH_2CH_2OOH + OH \rightarrow ClCH_2CHO + OH + H_2O$	3.26×10^{-12}	This work
G276	$ClCH_2C(O)OO + NO \overset{O_2}{\rightarrow} ClCH_2OO + CO_2 + NO_2$	$8.10 \times 10^{-12} \exp(270/T)$	7
G277	$ClCH_2C(O)OO + NO_3 \overset{O_2}{\rightarrow} ClCH_2OO + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G278	$ClCH_2C(O)OO + HO_2 \rightarrow ClCH_2C(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	8
G279	$ClCH_2C(O)OO + HO_2 \rightarrow ClCH_2COOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	8
G280	$ClCH_2C(O)OO + CH_3OO \overset{O_2}{\rightarrow}$ $ClCH_2OO + CO_2 + HCHO + HO_2 + O_2$	7.00×10^{-12}	7
G281	$ClCH_2C(O)OO + CH_3OO \rightarrow ClCH_2COOH + HCHO + O_2$	3.00×10^{-12}	7
G282	$ClCH_2COOH + OH \overset{O_2}{\rightarrow} ClCH_2OO + CO_2 + H_2O$	7.83×10^{-13}	This work
G283	$ClCH_2C(O)OOH + OH \rightarrow ClCH_2C(O)OO + H_2O$	3.86×10^{-12}	This work
G284	$ClCH_2C(O)OO + NO_2 \overset{M}{\rightarrow} PClAN$		$= k_{G152}$
G285	$PClAN \overset{M}{\rightarrow} ClCH_2C(O)OO + NO_2$		$= k_{G153}$
G286	$CH_3Cl + OH \overset{O_2}{\rightarrow} ClCH_2OO + H_2O$	$4.00 \times 10^{-12} \exp(-1400/T)$	2
G287	$CH_3Cl + Cl \overset{O_2}{\rightarrow} ClCH_2OO + HCl$	$3.20 \times 10^{-11} \exp(-1250/T)$	2
G288	$ClCH_2OO + NO \rightarrow ClCH_2O^* + NO_2$	1.90×10^{-11}	3
G289	$ClCH_2OO + HO_2 \rightarrow$ $0.73 \times (HCOCl + H_2O + O_2) + 0.27 \times (ClCH_2OOH + O_2)$	$3.20 \times 10^{-13} \exp(820/T)$	3, 33
G290	$ClCH_2OO + NO_3 \rightarrow ClCH_2O^* + NO_2 + O_2$	2.50×10^{-12}	7
G291	$ClCH_2OO + CH_3OO \overset{O_2}{\rightarrow} ClCH_2O + HCHO + HO_2 + O_2$	1.63×10^{-12}	17
G292	$ClCH_2OO + CH_3OO \rightarrow ClCH_2OH + HCHO + O_2$	8.70×10^{-13}	17
G293	$ClCH_2OO + ClCH_2OO \rightarrow ClCH_2O + ClCH_2O + O_2$	$3.90 \times 10^{-13} \exp(735/T)$	30
G294	$ClCH_2O^* \overset{O_2}{\rightarrow} CO + HO_2 + HCl$	$k_{uni} = 3.2 \times 10^5$	34

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G295	$ClCH_2O^* \rightarrow Cl + HCHO$	$k_{uni} = 1.2 \times 10^5$	34
G296	$ClCH_2O^* \rightarrow ClCH_2O$	$k_{uni} = 5.6 \times 10^5$	34
G297	$ClCH_2O \xrightarrow{O_2} CO + HO_2 + HCl$	$k_{uni} = 1.0 \times 10^6$	3
G298	$ClCH_2O + O_2 \rightarrow HCOCl + HO_2$	4.60×10^{-12}	3
G299	$ClCH_2OOH + OH \rightarrow ClCH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G300	$ClCH_2OOH + OH \rightarrow HCOCl + OH + H_2O$	4.61×10^{-12}	This work
G301	$ClCH_2OOH + Cl \rightarrow HCOCl + OH + HCl$	5.91×10^{-13}	33
G302	$ClCH_2OH + OH \rightarrow HCOCl + HO_2 + H_2O$	1.38×10^{-12}	This work
G303	$ClCH_2OH + Cl \xrightarrow{O_2} HCOCl + HO_2 + HCl$	4.00×10^{-12}	35
G304	$ClCH_2OH \rightarrow HCHO + HCl$	$k_{uni} = 1.6 \times 10^{-3}$	35
G305	$BrCH_2CH_2OO + NO \rightarrow BrCH_2CH_2O^* + NO_2$	$4.06 \times 10^{-12} \exp(360/T)$	$= k_{G260}$
G306	$BrCH_2CH_2OO + HO_2 \rightarrow BrCH_2CH_2OOH + O_2$	7.50×10^{-12}	$= k_{G261}$
G307	$BrCH_2CH_2OO + NO_3 \rightarrow BrCH_2CH_2O^* + NO_2 + O_2$	2.50×10^{-12}	$= k_{G262}$
G308	$BrCH_2CH_2OO + CH_3OO \xrightarrow{O_2} BrCH_2CHO + HCHO + 2\,HO_2 + O_2$	1.08×10^{-12}	This work
G309	$BrCH_2CH_2OO + CH_3OO \rightarrow BrCH_2CHO + CH_3OH + O_2$	6.86×10^{-13}	This work
G310	$BrCH_2CH_2OO + CH_3OO \rightarrow BrCH_2CH_2OH + HCHO + O_2$	6.86×10^{-13}	This work
G311	$BrCH_2CH_2OO + BrCH_2CH_2OO \xrightarrow{O_2} 2\,BrCH_2CHO + 2\,HO_2 + O_2$	$3.51 \times 10^{-14} \exp(1247/T)$	36, 31
G312	$BrCH_2CH_2OO + BrCH_2CH_2OO \rightarrow$ $BrCH_2CHO + BrCH_2CH_2OH + O_2$	$2.64 \times 10^{-14} \exp(1247/T)$	36, 31
G313	$BrCH_2CH_2O^* \xrightarrow{O_2} BrCH_2CHO + HO_2$	$k_{uni} = 5.8 \times 10^5$	$= k_{G268}$
G314	$BrCH_2CH_2O^* \xrightarrow{O_2} BrCH_2OO + HCHO$	$k_{uni} = 4.2 \times 10^5$	$= k_{G269}$
G315	$BrCH_2CH_2OH + OH \xrightarrow{O_2} BrCH_2CHO + HO_2 + H_2O$	1.97×10^{-12}	This work
G316	$BrCH_2CHO + OH \rightarrow BrCH_2CO + H_2O$	3.89×10^{-12}	This work[f]
G317	$BrCH_2CHO + Br \rightarrow BrCH_2CO + HBr$	1.83×10^{-13}	31
G318	$BrCH_2CO \xrightarrow{O_2} BrCH_2C(O)OO$	$k_{uni} = 5.0 \times 10^5$	37
G319	$BrCH_2CO \xrightarrow{O_2} BrCH_2OO + CO$	$k_{uni} = 2.5 \times 10^5$	37
G320	$BrCH_2CO \rightarrow Br + CH_2{=}CO$	$k_{uni} = 2.5 \times 10^5$	37
G321	$OH + CH_2{=}CO \xrightarrow{O_2} HCHO + HO_2 + CO$	1.69×10^{-11}	38
G322	$Cl + CH_2{=}CO \xrightarrow{O_2} ClCH_2OO + CO$	2.51×10^{-10}	39
G323	$BrCH_2CH_2OOH + OH \rightarrow BrCH_2CH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G324	$BrCH_2CH_2OOH + OH \rightarrow BrCH_2CHO + OH + H_2O$	3.93×10^{-12}	This work
G325	$BrCH_2C(O)OO + NO \xrightarrow{O_2} BrCH_2OO + CO_2 + NO_2$	$8.10 \times 10^{-12} \exp(270/T)$	$= k_{G276}$
G326	$BrCH_2C(O)OO + NO_3 \xrightarrow{O_2} BrCH_2OO + CO_2 + NO_2 + O_2$	4.00×10^{-12}	$= k_{G277}$
G327	$BrCH_2C(O)OO + HO_2 \rightarrow BrCH_2C(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	$= k_{G278}$
G328	$BrCH_2C(O)OO + HO_2 \rightarrow BrCH_2COOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	$= k_{G279}$
G329	$BrCH_2C(O)OO + CH_3OO \xrightarrow{O_2}$ $BrCH_2OO + CO_2 + HCHO + HO_2 + O_2$	7.00×10^{-12}	$= k_{G280}$
G330	$BrCH_2C(O)OO + CH_3OO \rightarrow BrCH_2COOH + HCHO + O_2$	3.00×10^{-12}	$= k_{G281}$
G331	$BrCH_2COOH + OH \xrightarrow{O_2} BrCH_2OO + CO_2 + H_2O$	7.14×10^{-13}	This work
G332	$BrCH_2C(O)OOH + OH \rightarrow BrCH_2C(O)OO + H_2O$	3.79×10^{-12}	This work
G333	$BrCH_2C(O)OO + NO_2 \xrightarrow{M}$ PBrAN		$= k_{G152}$
G334	PBrAN $\xrightarrow{M} BrCH_2C(O)OO + NO_2$		$= k_{G153}$
G335	$CH_3Br + OH \xrightarrow{O_2} BrCH_2OO + H_2O$	$4.00 \times 10^{-12} \exp(-1470/T)$	2
G336	$CH_3Br + Cl \xrightarrow{O_2} BrCH_2OO + HCl$	$1.50 \times 10^{-11} \exp(-1060/T)$	2
G337	$BrCH_2OO + NO \rightarrow Br + HCHO + NO_2$	$4.00 \times 10^{-12} \exp(300/T)$	2
G338	$BrCH_2OO + NO_3 \rightarrow Br + HCHO + NO_2 + O_2$	2.50×10^{-12}	$= k_{G290}$
G339	$BrCH_2OO + HO_2 \rightarrow$ $0.9 \times (BrCH_2OOH + O_2) + 0.1 \times (HCOBr + H_2O + O_2)$	6.71×10^{-12}	40, 41

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G340	$BrCH_2OO + CH_3OO \xrightarrow{O_2} BrCH_2O + HCHO + HO_2 + O_2$	8.13×10^{-13}	This work
G341	$BrCH_2OO + CH_3OO \rightarrow BrCH_2OH + HCHO + O_2$	4.37×10^{-13}	This work
G342	$BrCH_2OO + BrCH_2OO \rightarrow BrCH_2O + BrCH_2O + O_2$	1.05×10^{-12}	40
G343	$BrCH_2O \rightarrow Br + HCHO$	$k_{uni} = 3.0 \times 10^{7}$	42
G344	$BrCH_2O + O_2 \rightarrow HCOBr + HO_2$	5.99×10^{-14}	43
G345	$BrCH_2OOH + OH \rightarrow BrCH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G346	$BrCH_2OOH + OH \rightarrow HCOBr + OH + H_2O$	3.40×10^{-12}	This work
G347	$BrCH_2OH + OH \xrightarrow{O_2} HCOBr + HO_2 + H_2O$	1.06×10^{-12}	This work
G348	$BrCH_2OH \rightarrow HCHO + HBr$	$k_{uni} = 1.6 \times 10^{-3}$	$= k_{G304}$
G349	$CH_2OO^* \xrightarrow{M} CH_2OO$	$k_{uni} = 3.7 \times 10^{5}$	4
G350	$CH_2OO^* \rightarrow CO_2 + H_2$	$k_{uni} = 1.3 \times 10^{5}$	4
G351	$CH_2OO^* \rightarrow CO + H_2O$	$k_{uni} = 3.8 \times 10^{5}$	4
G352	$CH_2OO^* \xrightarrow{O_2} OH + CO + HO_2$	$k_{uni} = 1.2 \times 10^{5}$	4
G353	$CH_2OO + H_2O \rightarrow HCOOH + H_2O$	4.00×10^{-18}	44
G354	$OH + C_3H_6 \xrightarrow{O_2} CH_2{=}CHCH_2OO + H_2O$	$7.20 \times 10^{-18}\, T^2 \exp(31/T)$	45
G355	$OH + C_3H_6 \xrightarrow{M,O_2} 0.87 \times CH_3CH(OO)CH_2OH + 0.13 \times CH_3CH(OH)CH_2OO$		
	$F_c = 0.5,\ k_0 = 8.0 \times 10^{-27} (T/300)^{-3.5},\ k_\infty = 3.0 \times 10^{-11}$		4, 7
G356	$Cl + C_3H_6 \xrightarrow{O_2} CH_2{=}CHCH_2OO + HCl$	2.31×10^{-11}	46
G357	$Cl + C_3H_6 \xrightarrow{M,O_2} 0.87 \times CH_3CH(OO)CH_2Cl + 0.13 \times CH_3CHClCH_2OO$		
	$F_c = 0.6,\ k_0 = 4.0 \times 10^{-28},\ k_\infty = 2.8 \times 10^{-10}$		4, 47
G358	$Br + C_3H_6 \xrightarrow{O_2} CH_2{=}CHCH_2OO + HBr$	$8.15 \times 10^{-13} \exp(-1250/T)$	48
G359	$Br + C_3H_6 \xrightarrow{M,O_2} 0.87 \times CH_3CH(OO)CH_2Br + 0.13 \times CH_3CHBrCH_2OO$		
		3.28×10^{-12}	49, 50
G360	$O_3 + C_3H_6 \rightarrow CH_3CHO + CH_2OO^*$	$2.75 \times 10^{-15} \exp(-1880/T)$	4
G361	$O_3 + C_3H_6 \rightarrow HCHO + CH_3CHOO^*$	$2.75 \times 10^{-15} \exp(-1880/T)$	4
G362	$CH_3CH(OO)CH_2OH + NO \xrightarrow{O_2} CH_3CHO + HCHO + HO_2 + NO_2$	$2.54 \times 10^{-12} \exp(360/T)$	7
G363	$CH_3CH(OO)CH_2OH + NO_3 \xrightarrow{O_2}$ $CH_3CHO + HCHO + HO_2 + NO_2 + O_2$	2.50×10^{-12}	7
G364	$CH_3CH(OO)CH_2OH + HO_2 \rightarrow CH_3CH(OOH)CH_2OH + O_2$	$1.51 \times 10^{-13} \exp(1300/T)$	7
G365	$CH_3CH(OO)CH_2OH + CH_3OO \xrightarrow{O_2}$ $CH_3CHO + 2\,HCHO + 2\,HO_2 + O_2$	5.28×10^{-13}	8
G366	$CH_3CH(OO)CH_2OH + CH_3OO \rightarrow CH_3COCH_2OH + CH_3OH + O_2$	1.76×10^{-13}	8
G367	$CH_3CH(OO)CH_2OH + CH_3OO \rightarrow$ $CH_3CH(OH)CH_2OH + HCHO + O_2$	1.76×10^{-13}	8
G368	$CH_3CH(OH)CH_2OH + OH \rightarrow$ $0.613 \times CH_3COCH_2OH + 0.387 \times CH_3CH(OH)CHO + HO_2 + H_2O$	1.20×10^{-11}	7
G369	$CH_3CH(OH)CHO + OH \xrightarrow{O_2} CH_3CH(OH)C(O)OO + H_2O$	2.65×10^{-11}	7
G370	$CH_3CH(OH)C(O)OO + NO \xrightarrow{O_2} CH_3CHO + HO_2 + CO_2 + NO_2$	$8.10 \times 10^{-12} \exp(270/T)$	7
G371	$CH_3CH(OH)C(O)OO + NO_3 \xrightarrow{O_2}$ $CH_3CHO + HO_2 + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G372	$CH_3CH(OH)C(O)OO + HO_2 \rightarrow CH_3CH(OH)C(O)OOH + O_2$	$4.30 \times 10^{-13} \exp(1040/T)$	8
G373	$CH_3CH(OH)C(O)OO + CH_3OO \xrightarrow{O_2}$ $CH_3CHO + HCHO + 2\,HO_2 + CO_2 + O_2$	1.00×10^{-11}	7
G374	$CH_3CH(OH)C(O)OOH + OH \rightarrow CH_3CH(OH)C(O)OO + H_2O$	9.34×10^{-12}	8
G375	$CH_3CH(OH)C(O)OO + NO_2 \xrightarrow{M}$ i-PROPOLPAN		$= k_{G152}$
G376	i-PROPOLPAN $\xrightarrow{M} CH_3CH(OH)C(O)OO + NO_2$		$= k_{G153}$
G377	$CH_3CH(OOH)CH_2OH + OH \rightarrow CH_3CH(OO)CH_2OH + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	7
G378	$CH_3CH(OOH)CH_2OH + OH \rightarrow CH_3COCH_2OH + OH + H_2O$	2.44×10^{-11}	7

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G379	$CH_3CH(OH)CH_2OO + NO \xrightarrow{O_2} CH_3CHO + HCHO + HO_2 + NO_2$	$2.54 \times 10^{-12} \exp(360/T)$	7
G380	$CH_3CH(OH)CH_2OO + NO_3 \xrightarrow{O_2} CH_3CHO + HCHO + HO_2 + NO_2 + O_2$	2.50×10^{-12}	7
G381	$CH_3CH(OH)CH_2OO + HO_2 \rightarrow CH_3CH(OH)CH_2OOH + O_2$	$1.51 \times 10^{-13} \exp(1300/T)$	7
G382	$CH_3CH(OH)CH_2OO + CH_3OO \xrightarrow{O_2} CH_3CHO + 2\,HCHO + 2\,HO_2 + O_2$	1.20×10^{-12}	8
G383	$CH_3CH(OH)CH_2OO + CH_3OO \rightarrow CH_3CH(OH)CHO + CH_3OH + O_2$	4.00×10^{-13}	8
G384	$CH_3CH(OH)CH_2OO + CH_3OO \rightarrow CH_3CH(OH)CH_2OH + HCHO + O_2$	4.00×10^{-13}	8
G385	$CH_3CH(OH)CH_2OOH + OH \rightarrow CH_3CH(OH)CH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	7
G386	$CH_3CH(OH)CH_2OOH + OH \rightarrow CH_3CH(OH)CHO + OH + H_2O$	1.83×10^{-11}	7
G387	$CH_3CH(OO)CH_2Cl + NO \rightarrow CH_3CHOCH_2Cl + NO_2$	$4.06 \times 10^{-12} \exp(360/T)$	7
G388	$CH_3CH(OO)CH_2Cl + NO_3 \rightarrow CH_3CHOCH_2Cl + NO_2 + O_2$	2.50×10^{-12}	7
G389	$CH_3CH(OO)CH_2Cl + HO_2 \rightarrow CH_3CH(OOH)CH_2Cl + O_2$	$1.51 \times 10^{-13} \exp(1300/T)$	7
G390	$CH_3CH(OO)CH_2Cl + CH_3OO \xrightarrow{O_2} CH_3CHOCH_2Cl + HCHO + HO_2 + O_2$	5.16×10^{-13}	This work
G391	$CH_3CH(OO)CH_2Cl + CH_3OO \rightarrow CH_3COCH_2Cl + CH_3OH + O_2$	1.72×10^{-13}	This work
G392	$CH_3CH(OO)CH_2Cl + CH_3OO \rightarrow CH_3CH(OH)CH_2Cl + HCHO + O_2$	1.72×10^{-13}	This work
G393	$CH_3CHOCH_2Cl \xrightarrow{O_2} CH_3COCH_2Cl + HO_2$	$k_{\rm uni} = 5.3 \times 10^5$	This work
G394	$CH_3CHOCH_2Cl \xrightarrow{O_2} CH_3CHO + ClCH_2OO$	$k_{\rm uni} = 4.7 \times 10^5$	This work
G395	$CH_3CH(OH)CH_2Cl + OH \xrightarrow{O_2} CH_3COCH_2Cl + HO_2 + H_2O$	3.20×10^{-12}	This work
G396	$CH_3CH(OOH)CH_2Cl + OH \rightarrow CH_3CH(OO)CH_2Cl + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G397	$CH_3CH(OOH)CH_2Cl + OH \rightarrow CH_3COCH_2Cl + OH + H_2O$	6.49×10^{-12}	This work
G398	$CH_3COCH_2Cl + OH \xrightarrow{O_2} CH_3COCHClOO + H_2O$	3.68×10^{-13}	This work
G399	$CH_3COCH_2Cl + Cl \xrightarrow{O_2} CH_3COCHClOO + HCl$	4.00×10^{-12}	51[g]
G400	$CH_3COCHClOO + NO \xrightarrow{O_2} CH_3C(O)OO + CO + HCl + NO_2$	$5.59 \times 10^{-12} \exp(360/T)$	7, 52
G401	$CH_3COCHClOO + NO_3 \rightarrow CH_3C(O)OO + CO + HCl + NO_2 + O_2$	2.50×10^{-12}	7
G402	$CH_3COCHClOO + HO_2 \rightarrow CH_3COCHClOOH + O_2$	$3.20 \times 10^{-13} \exp(820/T)$	7
G403	$CH_3COCHClOO + CH_3OO \xrightarrow{O_2} CH_3C(O)OO + CO + HCl + HCHO + HO_2 + O_2$	1.20×10^{-12}	8
G404	$CH_3COCHClOO + CH_3OO \rightarrow CH_3COCOCl + CH_3OH + O_2$	4.00×10^{-13}	8
G405	$CH_3COCHClOO + CH_3OO \rightarrow CH_3COCHClOH + HCHO + O_2$	4.00×10^{-13}	8
G406	$CH_3COCOOH + OH \xrightarrow{O_2} CH_3C(O)OO + CO_2 + H_2O$	6.22×10^{-13}	This work
G407	$CH_3COCHClOH + OH \xrightarrow{O_2} CH_3COCOCl + HO_2 + H_2O$	2.18×10^{-12}	This work
G408	$CH_3COCHClOOH + OH \rightarrow CH_3COCHClOO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G409	$CH_3COCHClOOH + OH \rightarrow CH_3COCOCl + OH + H_2O$	4.76×10^{-12}	This work
G410	$CH_3CHClCH_2OO + NO \xrightarrow{O_2} CH_3CHClCHO + HO_2 + NO_2$	$4.06 \times 10^{-12} \exp(360/T)$	7
G411	$CH_3CHClCH_2OO + NO_3 \xrightarrow{O_2} CH_3CHClCHO + HO_2 + NO_2 + O_2$	2.50×10^{-12}	7
G412	$CH_3CHClCH_2OO + HO_2 \rightarrow CH_3CHClCH_2OOH + O_2$	$1.51 \times 10^{-13} \exp(1300/T)$	7
G413	$CH_3CHClCH_2OO + CH_3OO \xrightarrow{O_2} CH_3CHClCHO + HCHO + 2\,HO_2 + O_2$	1.45×10^{-12}	This work
G414	$CH_3CHClCH_2OO + CH_3OO \rightarrow CH_3CHClCHO + CH_3OH + O_2$	4.90×10^{-13}	This work
G415	$CH_3CHClCH_2OO + CH_3OO \rightarrow CH_3CHClCH_2OH + HCHO + O_2$	4.90×10^{-13}	This work
G416	$CH_3CHClCH_2OH + OH \xrightarrow{O_2} CH_3CHClCHO + HO_2 + H_2O$	2.28×10^{-12}	This work
G417	$CH_3CHClCH_2OOH + OH \rightarrow CH_3CHClCH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G418	$CH_3CHClCH_2OOH + OH \rightarrow CH_3CHClCHO + OH + H_2O$	3.78×10^{-12}	This work

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G419	$CH_3CHClCHO + OH \xrightarrow{O_2} CH_3CHClC(O)OO + H_2O$	6.70×10^{-12}	This work
G420	$CH_3CHClC(O)OO + NO \xrightarrow{O_2} CH_3CHClOO + CO_2 + NO_2$	$8.10\times10^{-12}\exp(270/T)$	7
G421	$CH_3CHClC(O)OO + NO_3 \xrightarrow{O_2} CH_3CHClOO + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G422	$CH_3CHClC(O)OO + HO_2 \rightarrow CH_3CHClC(O)OOH + O_2$	$3.05\times10^{-13}\exp(1040/T)$	8
G423	$CH_3CHClC(O)OO + HO_2 \rightarrow CH_3CHClCOOH + O_3$	$1.25\times10^{-13}\exp(1040/T)$	8
G424	$CH_3CHClC(O)OO + CH_3OO \xrightarrow{O_2}$ $CH_3CHClOO + CO_2 + HCHO + HO_2 + O_2$	7.00×10^{-12}	7
G425	$CH_3CHClC(O)OO + CH_3OO \rightarrow CH_3CHClCOOH + HCHO + O_2$	3.00×10^{-12}	7
G426	$CH_3CHClCOOH + OH \rightarrow CH_3CHClOO + CO_2 + H_2O$	1.12×10^{-12}	This work
G427	$CH_3CHClC(O)OOH + OH \rightarrow CH_3CHClC(O)OO + H_2O$	4.20×10^{-12}	This work
G428	$CH_3CHClC(O)OO + NO_2 \xrightarrow{M}$ i-ClACETPAN		$= k_{G152}$
G429	i-ClACETPAN $\xrightarrow{M} CH_3CHClC(O)OO + NO_2$		$= k_{G153}$
G430	$CH_3CHClOO + NO \xrightarrow{O_2} CH_3C(O)OO + HCl + NO_2$	$5.59\times10^{-12}\exp(360/T)$	7, 52
G431	$CH_3CHClOO + NO_3 \xrightarrow{O_2} CH_3C(O)OO + HCl + NO_2 + O_2$	2.50×10^{-12}	7
G432	$CH_3CHClOO + HO_2 \rightarrow CH_3CHClOOH + O_2$	$3.20\times10^{-13}\exp(820/T)$	7
G433	$CH_3CHClOO + CH_3OO \xrightarrow{O_2}$ $CH_3C(O)OO + HCl + HCHO + HO_2 + O_2$	2.72×10^{-12}	This work
G434	$CH_3CHClOO + CH_3CHClOO \xrightarrow{O_2} 2\,CH_3C(O)OO + 2\,HCl + O_2$	5.00×10^{-12}	3
G435	$CH_3CHClOOH + OH \rightarrow CH_3CHClOO + H_2O$	$1.90\times10^{-12}\exp(190/T)$	This work
G436	$CH_3CHClOOH + OH \rightarrow CH_3COCl + OH + H_2O$	6.26×10^{-12}	This work
G437	$CH_3CH(OO)CH_2Br + NO \rightarrow CH_3CHOCH_2Br + NO_2$	$4.06\times10^{-12}\exp(360/T)$	$= k_{G387}$
G438	$CH_3CH(OO)CH_2Br + NO_3 \rightarrow CH_3CHOCH_2Br + NO_2 + O_2$	2.50×10^{-12}	$= k_{G388}$
G439	$CH_3CH(OO)CH_2Br + HO_2 \rightarrow CH_3CH(OOH)CH_2Br + O_2$	$1.51\times10^{-13}\exp(1300/T)$	$= k_{G389}$
G440	$CH_3CH(OO)CH_2Br + CH_3OO \xrightarrow{O_2}$ $CH_3CHOCH_2Br + HCHO + HO_2$	5.16×10^{-13}	This work
G441	$CH_3CH(OO)CH_2Br + CH_3OO \rightarrow CH_3COCH_2Br + CH_3OH + O_2$	1.72×10^{-13}	This work
G442	$CH_3CH(OO)CH_2Br + CH_3OO \rightarrow$ $CH_3CH(OH)CH_2Br + HCHO + O_2$	1.72×10^{-13}	This work
G443	$CH_3CHOCH_2Br \xrightarrow{O_2} CH_3COCH_2Br + HO_2$	$k_{uni} = 8.6\times10^{5}$	This work
G444	$CH_3CHOCH_2Br \xrightarrow{O_2} CH_3CHO + BrCH_2OO$	$k_{uni} = 1.4\times10^{5}$	This work
G445	$CH_3CH(OH)CH_2Br + OH \xrightarrow{O_2} CH_3COCH_2Br + HO_2 + H_2O$	3.76×10^{-12}	This work
G446	$CH_3CH(OOH)CH_2Br + OH \rightarrow CH_3CH(OO)CH_2Br + H_2O$	$1.90\times10^{-12}\exp(190/T)$	This work
G447	$CH_3CH(OOH)CH_2Br + OH \rightarrow CH_3COCH_2Br + OH + H_2O$	8.01×10^{-12}	This work
G448	$CH_3COCH_2Br + OH \xrightarrow{O_2} CH_3COCHBrOO + H_2O$	2.98×10^{-13}	This work
G449	$CH_3COCH_2Br + Cl \xrightarrow{O_2} CH_3COCHBrOO + HCl$	4.00×10^{-12}	$= k_{G399}$
G450	$CH_3COCHBrOO + NO \rightarrow CH_3COCHO + Br + NO_2$	$5.59\times10^{-12}\exp(360/T)$	$= k_{G400}{}^{h}$
G451	$CH_3COCHBrOO + NO_3 \rightarrow CH_3COCHO + Br + NO_2 + O_2$	2.50×10^{-12}	$= k_{G401}{}^{h}$
G452	$CH_3COCHBrOO + HO_2 \rightarrow CH_3COCHBrOOH + O_2$	6.71×10^{-12}	$= k_{G339}$
G453	$CH_3COCHBrOO + CH_3OO \xrightarrow{O_2}$ $CH_3COCHBrO + HCHO + HO_2 + O_2$	1.20×10^{-12}	$= k_{G403}$
G454	$CH_3COCHBrOO + CH_3OO \rightarrow CH_3COCOBr + CH_3OH + O_2$	4.00×10^{-13}	$= k_{G404}$
G455	$CH_3COCHBrOO + CH_3OO \rightarrow CH_3COCHBrOH + HCHO + O_2$	4.00×10^{-13}	$= k_{G405}$
G456	$CH_3COCHBrO \rightarrow CH_3COCHO + Br$	$k_{uni} = 7.3\times10^{5}$	$= k_{G485}$
G457	$CH_3COCHBrO \xrightarrow{O_2} CH_3COCOBr + HO_2$	$k_{uni} = 2.7\times10^{5}$	$= k_{G486}$
G458	$CH_3COCHBrOH + OH \xrightarrow{O_2} CH_3COCOBr + HO_2 + H_2O$	1.67×10^{-12}	This work
G459	$CH_3COCHBrOOH + OH \rightarrow CH_3COCHBrOO + H_2O$	$1.90\times10^{-12}\exp(190/T)$	This work
G460	$CH_3COCHBrOOH + OH \rightarrow CH_3COCOBr + OH + H_2O$	3.53×10^{-12}	This work

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G461	$CH_3CHBrCH_2OO + NO \xrightarrow{O_2} CH_3CHBrCHO + HO_2 + NO_2$	$4.06 \times 10^{-12} \exp(360/T)$	$= k_{G410}$
G462	$CH_3CHBrCH_2OO + NO_3 \xrightarrow{O_2} CH_3CHBrCHO + HO_2 + NO_2 + O_2$	2.50×10^{-12}	$= k_{G411}$
G463	$CH_3CHBrCH_2OO + HO_2 \rightarrow CH_3CHBrCH_2OOH + O_2$	$1.51 \times 10^{-13} \exp(1300/T)$	$= k_{G412}$
G464	$CH_3CHBrCH_2OO + CH_3OO \xrightarrow{O_2}$ $CH_3CHBrCHO + HCHO + 2\,HO_2 + O_2$	1.45×10^{-12}	This work
G465	$CH_3CHBrCH_2OO + CH_3OO \rightarrow CH_3CHBrCHO + CH_3OH + O_2$	4.90×10^{-13}	This work
G466	$CH_3CHBrCH_2OO + CH_3OO \rightarrow CH_3CHBrCH_2OH + HCHO + O_2$	4.90×10^{-13}	This work
G467	$CH_3CHBrCH_2OH + OH \xrightarrow{O_2} CH_3CHBrCHO + HO_2 + H_2O$	2.38×10^{-12}	This work
G468	$CH_3CHBrCH_2OOH + OH \rightarrow CH_3CHBrCH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G469	$CH_3CHBrCH_2OOH + OH \rightarrow CH_3CHBrCHO + OH + H_2O$	4.34×10^{-12}	This work
G470	$CH_3CHBrCHO + OH \xrightarrow{O_2} CH_3CHBrC(O)OO + H_2O$	8.26×10^{-12}	This work
G471	$CH_3CHBrC(O)OO + NO \xrightarrow{O_2} CH_3CHBrOO + CO_2 + NO_2$	$8.10 \times 10^{-12} \exp(270/T)$	$= k_{G420}$
G472	$CH_3CHBrC(O)OO + NO_3 \xrightarrow{O_2} CH_3CHBrOO + CO_2 + NO_2 + O_2$	4.00×10^{-12}	$= k_{G421}$
G473	$CH_3CHBrC(O)OO + HO_2 \rightarrow CH_3CHBrC(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	$= k_{G422}$
G474	$CH_3CHBrC(O)OO + HO_2 \rightarrow CH_3CHBrCOOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	$= k_{G423}$
G475	$CH_3CHBrC(O)OO + CH_3OO \xrightarrow{O_2}$ $CH_3CHBrOO + CO_2 + HCHO + HO_2 + O_2$	7.00×10^{-12}	$= k_{G424}$
G476	$CH_3CHBrC(O)OO + CH_3OO \rightarrow CH_3CHBrCOOH + HCHO + O_2$	3.00×10^{-12}	$= k_{G425}$
G477	$CH_3CHBrCOOH + OH \xrightarrow{O_2} CH_3CHBrOO + CO_2 + H_2O$	9.86×10^{-13}	This work
G478	$CH_3CHBrC(O)OOH + OH \rightarrow CH_3CHBrC(O)OO + H_2O$	4.07×10^{-12}	This work
G479	$CH_3CHBrC(O)OO + NO_2 \xrightarrow{M}$ i-BrACETPAN		$= k_{G152}$
G480	i-BrACETPAN $\xrightarrow{M} CH_3CHBrC(O)OO + NO_2$		$= k_{G153}$
G481	$CH_3CHBrOO + NO \rightarrow CH_3CHO + Br + NO_2$	$5.59 \times 10^{-12} \exp(360/T)$	$= k_{G430}$ [h]
G482	$CH_3CHBrOO + NO_3 \rightarrow CH_3CHO + Br + NO_2 + O_2$	2.50×10^{-12}	$= k_{G431}$ [h]
G483	$CH_3CHBrOO + HO_2 \rightarrow CH_3CHBrOOH + O_2$	6.71×10^{-12}	$= k_{G339}$
G484	$CH_3CHBrOO + CH_3OO \xrightarrow{O_2} CH_3CHBrO + HCHO + HO_2 + O_2$	2.72×10^{-12}	$= k_{G433}$
G485	$CH_3CHBrO \rightarrow CH_3CHO + Br$	$k_{uni} = 7.3 \times 10^5$	53
G486	$CH_3CHBrO \xrightarrow{O_2} CH_3COBr + HO_2$	$k_{uni} = 2.7 \times 10^5$	53
G487	$CH_3CHBrOOH + OH \rightarrow CH_3CHBrOO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G488	$CH_3CHBrOOH + OH \rightarrow CH_3COBr + OH + H_2O$	4.64×10^{-12}	This work
G489	$CH_2{=}CHCH_2OO + NO \xrightarrow{O_2} CH_2{=}CHCHO + HO_2 + NO_2$	1.05×10^{-11}	54
G490	$CH_2{=}CHCH_2OO + NO_3 \xrightarrow{O_2} CH_2{=}CHCHO + HO_2 + NO_2 + O_2$	2.50×10^{-12}	7
G491	$CH_2{=}CHCH_2OO + HO_2 \rightarrow CH_2{=}CHCH_2OOH + O_2$	5.60×10^{-12}	55
G492	$CH_2{=}CHCH_2OO + CH_3OO \xrightarrow{O_2}$ $CH_2{=}CHCHO + HCHO + 2\,HO_2 + O_2$	$1.32 \times 10^{-13} \exp(515/T)$	17
G493	$CH_2{=}CHCH_2OO + CH_3OO \rightarrow CH_2{=}CHCHO + CH_3OH + O_2$	$7.40 \times 10^{-14} \exp(515/T)$	17
G494	$CH_2{=}CHCH_2OO + CH_3OO \rightarrow CH_2{=}CHCH_2OH + HCHO + O_2$	$7.40 \times 10^{-14} \exp(515/T)$	17
G495	$CH_2{=}CHCH_2OO + C_2H_5OO \xrightarrow{O_2}$ $CH_2{=}CHCHO + CH_3CHO + 2\,HO_2 + O_2$	6.20×10^{-13}	17
G496	$CH_2{=}CHCH_2OO + C_2H_5OO \rightarrow CH_2{=}CHCHO + C_2H_5OH + O_2$	1.90×10^{-13}	17
G497	$CH_2{=}CHCH_2OO + C_2H_5OO \rightarrow$ $CH_2{=}CHCH_2OH + CH_3CHO + O_2$	1.90×10^{-13}	17
G498	$CH_2{=}CHCH_2OO + CH_2{=}CHCH_2OO \rightarrow$ $1.22 \times (CH_2{=}CHCHO + HO_2)$ $+ 0.39 \times (CH_2{=}CHCHO + CH_2{=}CHCH_2OH) + O_2$	6.81×10^{-13}	56
G499	$CH_2{=}CHCH_2OH + OH \xrightarrow{O_2} CH_2{=}CHCHO + HO_2 + H_2O$	3.41×10^{-12}	This work
G500	$CH_2{=}CHCH_2OOH + OH \rightarrow CH_2{=}CHCH_2OO + H_2O$	$1.90 \times 10^{-12} \exp(190/T)$	This work
G501	$CH_2{=}CHCH_2OOH + OH \rightarrow CH_2{=}CHCHO + OH$	7.85×10^{-12}	This work

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G502	$CH_2{=}CHCHO + OH \xrightarrow{O_2} \cdots \rightarrow 0.32 \times (HOCH_2CHO + \text{products}) + 0.68 \times (CH_2{=}CHC(O)OO + H_2O)$	2.00×10^{-11}	57
G503	$CH_2{=}CHCHO + Cl \xrightarrow{O_2} \cdots \rightarrow 0.78 \times (ClCH_2CHO + \text{products}) + 0.22 \times (CH_2{=}CHC(O)OO + HCl)$	2.20×10^{-10}	58
G504	$CH_2{=}CHCHO + Br \xrightarrow{O_2} \cdots \rightarrow 0.8 \times (BrCH_2CHO + \text{products}) + 0.2 \times (CH_2{=}CHC(O)OO + HBr)$	3.21×10^{-12}	59
G505	$CH_2{=}CHC(O)OO + NO \xrightarrow{O_2} HCHO + CO + HO_2 + CO_2 + NO_2$	$8.10 \times 10^{-12} \exp(270/T)$	7
G506	$CH_2{=}CHC(O)OO + NO_3 \xrightarrow{O_2} HCHO + CO + HO_2 + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G507	$CH_2{=}CHC(O)OO + HO_2 \rightarrow CH_2{=}CHC(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	8
G508	$CH_2{=}CHC(O)OO + HO_2 \rightarrow CH_2{=}CHCOOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	8
G509	$CH_2{=}CHC(O)OO + CH_3OO \xrightarrow{O_2} HCHO + CO + CO_2 + HCHO + 2\,HO_2 + O_2$	7.00×10^{-12}	7
G510	$CH_2{=}CHC(O)OO + CH_3OO \rightarrow CH_2{=}CHCOOH + HCHO + O_2$	3.00×10^{-12}	7
G511	$CH_2{=}CHC(O)OOH + OH \rightarrow CH_2{=}CHC(O)OO + H_2O$	1.22×10^{-11}	7
G512	$CH_2{=}CHCOOH + OH \xrightarrow{O_2} HCHO + CO + HO_2 + CO_2 + H_2O$	8.66×10^{-12}	7
G513	$CH_2{=}CHC(O)OO + NO_2 \xrightarrow{M}$ ACRPAN		$= k_{G152}$
G514	ACRPAN $\xrightarrow{M} CH_2{=}CHC(O)OO + NO_2$		$= k_{G153}$
G515	$CH_3CHOO^* \xrightarrow{M} CH_3CHOO$	$k_{uni} = 1.5 \times 10^5$	4
G516	$CH_3CHOO^* \xrightarrow{O_2} CH_3OO + CO + OH$	$k_{uni} = 5.4 \times 10^5$	4
G517	$CH_3CHOO^* \xrightarrow{O_2} CO + HO_2 + HCHO + HO_2$	$k_{uni} = 1.7 \times 10^5$	4
G518	$CH_3CHOO^* \rightarrow CH_4 + CO_2$	$k_{uni} = 1.4 \times 10^5$	4
G519	$CH_3CHOO + H_2O \rightarrow CH_3COOH + H_2O$	4.00×10^{-18}	44
G520	$OH + C_2H_2 \xrightarrow{M,O_2} 0.364 \times (HCOOH + CO + HO_2) + 0.636 \times (HCOCHO + OH)$	$F_c = 0.62,\ k_0 = 5.0 \times 10^{-30}(T/300)^{-1.5},\ k_\infty = 9.0 \times 10^{-13}(T/300)^{2.0}$	3
G521	$Cl + C_2H_2 \xrightarrow{M,O_2} 0.26 \times (HCOCl + CO + HO_2) + 0.21 \times (HCOCHO + Cl) + 0.53 \times (HCl + 2\,CO + HO_2)$	$F_c = 0.6,\ k_0 = 6.1 \times 10^{-30}(T/300)^{-3.0},\ k_\infty = 2.0 \times 10^{-10}$	4, 59
G522	$Br + C_2H_2 \xrightarrow{M,O_2} 0.17 \times (HCOBr + CO + HO_2) + 0.09 \times (HCOCHO + Br) + 0.74 \times (HBr + 2\,CO + HO_2)$	$9.39 \times 10^{-15} \exp(341/T)$	25, 60
G523	$HCOCl + OH \rightarrow CO + Cl + H_2O$	$3.67 \times 10^{-11} \exp(-1419/T)$	61
G524	$HCOCl + Cl \rightarrow CO + Cl + HCl$	$1.20 \times 10^{-11} \exp(-815/T)$	3
G525	$HCOCl + Br \rightarrow CO + Cl + HBr$	4.00×10^{-14}	$= k_{G528}$
G526	$HCOBr + OH \rightarrow CO + Br + H_2O$	$3.67 \times 10^{-11} \exp(-1419/T)$	$= k_{G523}$
G527	$HCOBr + Cl \rightarrow CO + Br + HCl$	$1.20 \times 10^{-11} \exp(-815/T)$	$= k_{G524}$
G528	$HCOBr + Br \rightarrow CO + Br + HBr$	4.00×10^{-14}	60
G529	$CHBr_3 + OH \xrightarrow{O_2} \cdots \rightarrow Br + CBr_2O + H_2O$	$1.60 \times 10^{-12} \exp(-710/T)$	2, 62
G530	$CHBr_3 + Cl \xrightarrow{O_2} \cdots \rightarrow Br + CBr_2O + HCl$	$4.00 \times 10^{-12} \exp(-809/T)$	63, 62
G531	OH + DMS (abs.) $\xrightarrow{O_2} \cdots \rightarrow CH_3SO_2 + HCHO + H_2O$	$1.13 \times 10^{-11} \exp(-254/T)$	3
G532	OH + DMS (add.) $\xrightarrow{O_2} \cdots \rightarrow 0.5 \times (DMSO + HO_2) + 0.5 \times (CH_3SO_2 + CH_3OO)$	$1.7 \times 10^{-43}[O_2] \exp(7810/T)/(1 + 5.5 \times 10^{-31}[O_2] \exp(7460/T))$	3
G533	NO_3 + DMS $\xrightarrow{O_2} \cdots \rightarrow CH_3SO_2 + HCHO + HNO_3$	$1.90 \times 10^{-13} \exp(500/T)$	2
G534	BrO + DMS $\rightarrow$ DMSO + Br	$1.30 \times 10^{-14} \exp(1033/T)$	64
G535	Cl + DMS $\xrightarrow{O_2} \cdots \rightarrow CH_3SO_2 + HCHO + HCl$	3.30×10^{-10}	3
G536	OH + DMSO $\xrightarrow{O_2} CH_3SO_2H + CH_3OO$	8.70×10^{-11}	65

Table S3. (continued)

No.	Reaction	Rate Constant	Reference
G537	$OH + CH_3SO_2H \rightarrow CH_3SO_2 + H_2O$	1.00×10^{-10}	66
G538	$CH_3SO_2 \overset{M,O_2}{\rightarrow} SO_2 + CH_3OO$	$k_{uni} = 2.6 \times 10^{11} \exp(-9056/T)$	67
G539	$CH_3SO_2 + O_3 \rightarrow CH_3SO_3 + O_2$	1.00×10^{-14}	68
G540	$CH_3SO_2 + HO_2 \rightarrow CH_3SO_3 + OH$	2.50×10^{-13}	69
G541	$CH_3SO_2 + CH_3OO \overset{O_2}{\rightarrow} CH_3SO_3 + HCHO + HO_2$	2.50×10^{-13}	69
G542	$CH_3SO_3 \overset{M,O_2}{\rightarrow} SO_3 + CH_3OO$	$k_{uni} = 1.1 \times 10^{17} \exp(-12057/T)$	67
G543	$CH_3SO_3 + HO_2 \rightarrow CH_3SO_3H + O_2$	4.00×10^{-11}	68
G544	$CH_3SO_3 + HCHO \overset{O_2}{\rightarrow} CH_3SO_3H + CO + HO_2$	1.60×10^{-15}	69
G545	$CH_3SO_3 + H_2O_2 \rightarrow CH_3SO_3H + HO_2$	3.00×10^{-16}	69
G546	$OH + SO_2 \overset{M,O_2}{\rightarrow} SO_3 + HO_2$		
		$F_c = 0.45,\ k_0 = 4.0 \times 10^{-31}(T/300)^{-3.33},\ k_\infty = 2.0 \times 10^{-12}$	3
G547	$SO_3 + H_2O \overset{M}{\rightarrow} H_2SO_4$	2.40×10^{-15}	43
G548	$CH_3SO_3H \rightarrow$ MSA (fine-mode aerosols)	$k_{uni} = 1.55 \times 10^{-4}$	see note[i]
G549	$H_2SO_4 \rightarrow$ sulfate (fine-mode aerosols)	$k_{uni} = 8.50 \times 10^{-4}$	see note[i]

References: 1, Sander et al. (2000); 2, DeMore et al. (1997); 3, Atkinson et al. (1997); 4, Atkinson et al. (1999); 5, Kondo and Benson (1984); 6, Veyret et al. (1982); 7, Saunders et al. (2003); 8, Jenkin et al. (1997); 9, Atkinson et al. (2000); 10, Orlando and Tyndall (1996); 11, Aranda et al. (1997); 12, Baulch et al. (1981); 13, Dolson and Leone (1987); 14, Clyne and Cruse (1972), 15, Carl et al. (1996); 16, Anderson and Fahey (1990); 17, Villenave and Lesclaux (1996); 18, Wallington et al. (1989a); 19, Tyndall et al. (1997); 20, D'Anna and Nielsen (1997); 21, Ramacher et al. (2000); 22, Sehested et al. (1998); 23, Green et al. (1990); 24, Orlando et al. (1999); 25, Ramacher et al. (2001); 26, Aschmann and Atkinson (1998); 27, Niki et al. (1987); 28, Niki et al. (1985); 29, Wallington et al. (1990); 30, Lightfoot et al. (1992) 31, Yarwood et al. (1992); 32, Wallington et al. (1988); 33, Wallington et al. (1996); 34, Bilde et al. (1999); 35, Tyndall et al. (1993); 36, Villenave et al. (2003); 37, Chen et al. (1996); 38, Baulch et al. (1992); 39, Maricq et al. (1997); 40, Villenave and Lesclaux (1995); 41, Chen et al. (1995); 42, Orlando et al. (1996); 43, DeMore et al. (1994); 44, Atkinson (1990); 45, Atkinson (1989); 46, Kaiser and Wallington (1996b); 47, Lee and Rowland (1977); 48, Bedjanian et al. (1998); 49, Barnes et al. (1989); 50, Wallington et al. (1989b); 51, Notario et al. (2000); 52, Maricq et al. (1993); 53, Bierbach et al. (1997); 54, Eberhard and Howard (1997); 55, Boyd et al. (1996); 56, Jenkin et al. (1993); 57, Orlando and Tyndall (2002); 58, Canosa-Mas et al. (2001); 59, Sauer et al. (1999); 60, Yarwood et al. (1991); 61, Francisco (1992); 62, McGivern et al. (2002), 63, Kambanis et al. (1997); 64, Nakano et al. (2001); 65, Urbanski et al. (1998); 66, Kukui et al. (2002); 67, Ayers et al. (1996); 68, Koga and Tanaka (1999); 69, Yin et al. (1990).

[a] Units of bimolecular reaction rate constants are $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

[b] Units of termolecular reaction rate constants (k_0) are $\mathrm{cm^6\ molecule^{-2}\ s^{-1}}$. Where a pressure fall-off correction is necessary, an additional entry (k_∞) gives the limiting high-pressure rate constant. In this case, the following formula is used to obtain an effective second-order rate constant (k):

$$k = \frac{k_0[M]}{1 + (k_0[M]/k_\infty)} F_c^{\{1+[\log_{10}(k_0[M]/k_\infty)]^2\}^{-1}}$$

In some cases, effective second-order rate constants at $\sim$1 atm of air are directly taken from the literature.

[c] Decomposition and thermalization reaction rates are given as first-order decomposition constants (k_{uni}) in $\mathrm{s^{-1}}$.

[d] Product yields are assumed to be identical to those of Reaction (G209).

[e] $(k_{G230} + k_{G231})/k_{G134} = 1.1$ (Niki et al., 1987)

[f] Since the SAR method (Kwok and Atkinson, 1995) is found to overestimate the rate constant (k_{G272}) for analogous reaction $ClCH_2CHO$ + OH by a factor of two compared with a recommended value based on the critical evaluation of measured data (Atkinson et al., 1997), a slightly modified approach is taken to estimate the rate constant (k_{G316}) for reaction $BrCH_2CHO$ + OH; At first the ratio of k_{G316} to k_{G272} is estimated to be 1.255 by the SAR method and then k_{G316} is obtained by multiplying this ratio and k_{G272} value recommended by Atkinson et al. (1997).

[g] $k_{G399}/k_{G192} = 1.144$ (Notario et al., 2000)

[h] Br-atom elimination is assumed to occur spontaneously.

[i] First-order rate constants for uptake onto fine-mode aerosols with a number concentration of 280 $\mathrm{cm^{-3}}$, volume geometric median diameter of 0.214 μm, and geometric standard deviation of 1.29 (Kim et al., 1995) are estimated using γ for H_2SO_4 in Table S5 or α for CH_3SO_3H in Table S6.

Table S4. Photolysis Reactions in the Gas- and Aqueous-Phases and their Calculated J Values [a,b]

No.	Phase	Reaction	J, s^{-1}	Reference
P1	gas	$O_3 \rightarrow O(^1D) + O_2$	6.18×10^{-6}	1, 2, 3
P2	gas	$O_3 \rightarrow O(^3P) + O_2$	1.63×10^{-4}	1, 2, 3
P3	aq	$O_3 \overset{H_2O}{\rightarrow} H_2O_2 + O_2$	1.12×10^{-5}	4
P4	gas	$H_2O_2 \rightarrow 2\,OH$	1.59×10^{-6}	5
P5	aq	$H_2O_2 \rightarrow 2\,OH$	6.18×10^{-7}	4
P6	gas	$NO_2 \rightarrow NO + O(^3P)$	2.40×10^{-3}	5
P7	gas	$NO_3 \rightarrow NO + O_2$	9.39×10^{-3}	6
P8	gas	$NO_3 \rightarrow NO_2 + O(^3P)$	7.17×10^{-2}	5
P9	gas	$N_2O_5 \rightarrow NO_3 + NO_2$	9.87×10^{-6}	5
P10	gas	$HONO \rightarrow OH + NO$	4.98×10^{-4}	5
P11	aq	$HONO \rightarrow NO + OH$	5.76×10^{-5}	4
P12	aq	$NO_2^- \overset{H_2O}{\rightarrow} NO + OH + OH^-$	9.77×10^{-6}	4
P13	gas	$HNO_3 \rightarrow OH + NO_2$	1.09×10^{-7}	5
P14	aq	$NO_3^- \overset{H_2O}{\rightarrow} NO_2 + OH + OH^-$	8.08×10^{-8}	4, 7
P15	aq	$NO_3^- \rightarrow NO_2^- + O(^3P)$	5.80×10^{-9}	4, 8
P16	gas	$HO_2NO_2 \rightarrow 0.33 \times (OH + NO_3) + 0.67 \times (HO_2 + NO_2)$	7.47×10^{-7}	5
P17	gas	$OClO \rightarrow ClO + O(^3P)$	2.30×10^{-2}	9
P18	gas	$Cl_2O_2 \rightarrow 2\,Cl + O_2$	3.28×10^{-4}	5
P19	gas	$HOCl \rightarrow Cl + OH$	6.78×10^{-5}	10
P20	aq	$HOCl \rightarrow Cl + OH$	1.36×10^{-4}	$= J_{P19} \times 2$
P21	gas	$CH_3OCl \overset{O_2}{\rightarrow} HCHO + HO_2 + Cl$	2.21×10^{-5}	5
P22	aq	$CH_3OCl \overset{O_2}{\rightarrow} HCHO + HO_2 + Cl$	4.43×10^{-5}	$= J_{P21} \times 2$
P23	gas	$ClNO_2 \rightarrow Cl + NO_2$	8.24×10^{-5}	5
P24	gas	$ClONO_2 \rightarrow Cl + NO_3$	7.14×10^{-6}	5
P25	gas	$ClONO_2 \rightarrow ClO + NO_2$	4.76×10^{-6}	5
P26	gas	$Cl_2 \rightarrow 2\,Cl$	6.03×10^{-4}	5
P27	aq	$Cl_2 \rightarrow 2\,Cl$	1.21×10^{-3}	$= J_{P26} \times 2$
P28	gas	$BrO \rightarrow Br + O(^3P)$	9.09×10^{-3}	5
P29	gas	$HOBr \rightarrow Br + OH$	6.32×10^{-4}	10
P30	aq	$HOBr \rightarrow Br + OH$	1.26×10^{-3}	$= J_{P29} \times 2$
P31	gas	$BrNO_2 \rightarrow Br + NO_2$	5.67×10^{-4}	see note[c]
P32	gas	$BrONO_2 \rightarrow 0.71 \times (BrO + NO_2) + 0.29 \times (Br + NO_3)$	3.53×10^{-4}	5
P33	gas	$Br_2 \rightarrow 2\,Br$	1.08×10^{-2}	11
P34	aq	$Br_2 \rightarrow 2\,Br$	2.15×10^{-2}	$= J_{P33} \times 2$
P35	gas	$BrCl \rightarrow Br + Cl$	3.30×10^{-3}	5
P36	aq	$BrCl \rightarrow Br + Cl$	6.60×10^{-3}	$= J_{P35} \times 2$
P37	gas	$CHBr_3 \rightarrow 2\,Br + HBr$ + products	2.24×10^{-7}	5, 12, 13
P38	gas	$HCHO \overset{O_2}{\rightarrow} CO + 2\,HO_2$	6.02×10^{-6}	5
P39	gas	$HCHO \rightarrow H_2 + CO$	1.08×10^{-5}	5
P40	gas	$CH_3OOH \overset{O_2}{\rightarrow} HCHO + HO_2 + OH$	1.14×10^{-6}	5
P41	gas	$CH_3CHO \overset{O_2}{\rightarrow} CH_3OO + HO_2 + CO$	7.98×10^{-7}	14
P42	gas	$HOCH_2CHO \overset{O_2}{\rightarrow} HCHO + CO + 2\,HO_2$	1.69×10^{-6}	15, 16
P43	gas	$ClCH_2CHO \rightarrow CH_3Cl + CO$	4.26×10^{-10}	17[d]
P44	gas	$ClCH_2CHO \overset{O_2}{\rightarrow} ClCH_2OO + CO + HO_2$	3.63×10^{-6}	17[d]
P45	gas	$BrCH_2CHO \rightarrow CH_3Br + CO$	3.04×10^{-8}	see note[e]
P46	gas	$BrCH_2CHO \overset{O_2}{\rightarrow} BrCH_2OO + CO + HO_2$	9.98×10^{-6}	see note[e]
P47	gas	$C_2H_5CHO \overset{O_2}{\rightarrow} C_2H_5OO + HO_2 + CO$	3.07×10^{-6}	14
P48	gas	$CH_3CH(OH)CHO \overset{O_2}{\rightarrow} CH_3CHO + CO + 2\,HO_2$	2.57×10^{-7}	see note[f]

Table S4. (continued)

No.	Phase	Reaction	J, s^{-1}	Reference
P49	gas	$CH_3CHClCHO \overset{O_2}{\rightarrow} CH_3CHClOO + CO + HO_2$	9.85×10^{-6}	see note[g]
P50	gas	$CH_3CHBrCHO \overset{O_2}{\rightarrow} CH_3CHBrOO + CO + HO_2$	2.09×10^{-5}	see note[g]
P51	gas	$CH_3COCH_3 \overset{O_2}{\rightarrow} CH_3C(O)OO + CH_3OO$	8.37×10^{-8}	14
P52	gas	$CH_3COCH_2OH \overset{O_2}{\rightarrow} 0.5 \times (CH_3C(O)OO + HCHO + HO_2) + 0.5 \times (HOCH_2C(O)OO + CH_3OO)$	1.70×10^{-7}	18
P53	gas	$CH_3COCH_2Cl \overset{O_2}{\rightarrow} 0.5 \times (CH_3C(O)OO + ClCH_2OO) + 0.5 \times (ClCH_2C(O)OO + CH_3OO)$	8.82×10^{-6}	19
P54	gas	$CH_3COCH_2Br \overset{O_2}{\rightarrow} 0.5 \times (CH_3C(O)OO + BrCH_2OO) + 0.5 \times (BrCH_2CO + CH_3OO)$	4.09×10^{-5}	19
P55	gas	$CH_3COCHO \overset{O_2}{\rightarrow} CH_3C(O)OO + CO + HO_2$	2.61×10^{-5}	20
P56	gas	$HCOCHO \overset{O_2}{\rightarrow} 2\,CO + 2\,HO_2$	1.54×10^{-5}	20
P57	gas	$HCOCOOH \overset{O_2}{\rightarrow} CO + 2\,HO_2 + CO_2$	2.61×10^{-5}	$= J_{P55}$
P58	gas	$HCOCO_3H \overset{O_2}{\rightarrow} CO + HO_2 + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P59	gas	$HCOCO_3H \overset{O_2}{\rightarrow} CO + HO_2 + OH + CO_2$	2.61×10^{-5}	$= J_{P55}$
P60	gas	$CH_2{=}CHCHO \rightarrow C_2H_4 + CO$	2.05×10^{-7}	16
P61	gas	$CH_2{=}CHCHO \overset{O_2}{\rightarrow} HCHO + 2\,CO + 2\,HO_2$	1.27×10^{-7}	16
P62	gas	$CH_2{=}CHCHO \overset{O_2}{\rightarrow} CH_3CHOO^* + CO$	3.83×10^{-7}	16
P63	gas	$CH_2{=}CHCHO \overset{O_2}{\rightarrow} CH_2{=}CHC(O)OO + HO_2$	1.40×10^{-7}	16
P64	gas	$HCOCl \overset{O_2}{\rightarrow} HO_2 + CO + Cl$	2.55×10^{-8}	20
P65	gas	$CH_3COCl \overset{O_2}{\rightarrow} CH_3C(O)OO + Cl$	1.79×10^{-10}	17
P66	gas	$CH_3COCOCl \overset{O_2}{\rightarrow} CH_3C(O)OO + CO + Cl$	1.79×10^{-10}	$= J_{P65}$
P67	gas	$HCOBr \overset{O_2}{\rightarrow} HO_2 + CO + Br$	1.79×10^{-6}	17
P68	gas	$CBr_2O \rightarrow CO + 2\,Br$	2.83×10^{-7}	17
P69	gas	$CH_3COBr \overset{O_2}{\rightarrow} CH_3C(O)OO + Br$	1.79×10^{-6}	$= J_{P67}$
P70	gas	$CH_3COCOBr \overset{O_2}{\rightarrow} CH_3C(O)OO + CO + Br$	1.79×10^{-6}	$= J_{P67}$
P71	gas	$HOCH_2OOH \overset{O_2}{\rightarrow} HCOOH + HO_2 + OH$	1.12×10^{-6}	21
P72	gas	$C_2H_5OOH \overset{O_2}{\rightarrow} CH_3CHO + HO_2 + OH$	1.14×10^{-6}	$= J_{P40}$
P73	gas	$n\text{-}PrOOH \overset{O_2}{\rightarrow} C_2H_5CHO + HO_2 + OH$	1.14×10^{-6}	$= J_{P40}$
P74	gas	$i\text{-}PrOOH \overset{O_2}{\rightarrow} CH_3COCH_3 + HO_2 + OH$	1.14×10^{-6}	$= J_{P40}$
P75	gas	$CH_3COCH_2OOH \overset{O_2}{\rightarrow} CH_3C(O)OO + HCHO + OH$	1.14×10^{-6}	$= J_{P40}$
P76	gas	$CH_3CO_3H \overset{O_2}{\rightarrow} CH_3OO + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P77	gas	$C_2H_5CO_3H \overset{O_2}{\rightarrow} C_2H_5OO + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P78	gas	$HOCH_2CO_3H \overset{O_2}{\rightarrow} HCHO + HO_2 + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P79	gas	$HOCH_2CH_2OOH \rightarrow HOCH_2CH_2O + OH$	1.14×10^{-6}	$= J_{P40}$
P80	gas	$ClCH_2CH_2OOH \overset{O_2}{\rightarrow} ClCH_2CHO + HO_2 + OH$	1.14×10^{-6}	$= J_{P40}$
P81	gas	$BrCH_2CH_2OOH \overset{O_2}{\rightarrow} BrCH_2CHO + HO_2 + OH$	1.14×10^{-6}	$= J_{P40}$
P82	gas	$ClCH_2CO_3H \overset{O_2}{\rightarrow} ClCH_2OO + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P83	gas	$BrCH_2CO_3H \overset{O_2}{\rightarrow} BrCH_2OO + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P84	gas	$ClCH_2OOH \rightarrow ClCH_2O + OH$	1.14×10^{-6}	$= J_{P40}$
P85	gas	$BrCH_2OOH \rightarrow BrCH_2O + OH$	1.14×10^{-6}	$= J_{P40}$
P86	gas	$CH_3CH(OOH)CH_2OH \overset{O_2}{\rightarrow} CH_3CHO + HCHO + HO_2 + OH$	1.14×10^{-6}	$= J_{P40}$
P87	gas	$CH_3CH(OH)CO_3H \overset{O_2}{\rightarrow} CH_3CHO + HO_2 + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P88	gas	$CH_3CH(OH)CH_2OOH \overset{O_2}{\rightarrow} CH_3CHO + HCHO + HO_2 + OH$	1.14×10^{-6}	$= J_{P40}$
P89	gas	$CH_3CH(OOH)CH_2Cl \overset{O_2}{\rightarrow} CH_3CHOCH_2Cl + OH$	1.14×10^{-6}	$= J_{P40}$

Table S4. (continued)

No.	Phase	Reaction	J, s^{-1}	Reference
P90	gas	$CH_3COCHClOOH \overset{O_2}{\rightarrow} CH_3C(O)OO + CO + HCl + OH$	1.14×10^{-6}	$= J_{P40}$
P91	gas	$CH_3CHClCH_2OOH \overset{O_2}{\rightarrow} CH_3CHClOO + HCHO + OH$	1.14×10^{-6}	$= J_{P40}$
P92	gas	$CH_3CHClCO_3H \overset{O_2}{\rightarrow} CH_3CHClOO + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P93	gas	$CH_3CHClOOH \overset{O_2}{\rightarrow} CH_3C(O)OO + HCl + OH$	1.14×10^{-6}	$= J_{P40}$
P94	gas	$CH_3CH(OOH)CH_2Br \rightarrow CH_3CHOCH_2Br + OH$	1.14×10^{-6}	$= J_{P40}$
P95	gas	$CH_3COCHBrOOH \rightarrow CH_3COCHBrO + OH$	1.14×10^{-6}	$= J_{P40}$
P96	gas	$CH_3CHBrCH_2OOH \overset{O_2}{\rightarrow} CH_3CHBrOO + HCHO + OH$	1.14×10^{-6}	$= J_{P40}$
P97	gas	$CH_3CHBrCO_3H \overset{O_2}{\rightarrow} CH_3CHBrOO + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P98	gas	$CH_3CHBrOOH \rightarrow CH_3CHBrO + OH$	1.14×10^{-6}	$= J_{P40}$
P99	gas	$CH_2{=}CHCH_2OOH \overset{O_2}{\rightarrow} CH_2{=}CHCHO + HO_2 + OH$	1.14×10^{-6}	$= J_{P40}$
P100	gas	$CH_2{=}CHCO_3H \overset{O_2}{\rightarrow} HCHO + CO + HO_2 + OH + CO_2$	1.14×10^{-6}	$= J_{P40}$
P101	gas	$PAN \rightarrow CH_3C(O)OO + NO_2$	1.43×10^{-7}	20
P102	gas	$PHAN \rightarrow HOCH_2C(O)OO + NO_2$	3.43×10^{-8}	see note[h]
P103	gas	$GLYPAN \overset{O_2}{\rightarrow} 2\,CO + HO_2 + O_2 + NO_2$	1.43×10^{-7}	$= J_{P101}$
P104	gas	$PClAN \rightarrow ClCH_2C(O)OO + NO_2$	4.12×10^{-7}	see note[i]
P105	gas	$PBrAN \rightarrow BrCH_2C(O)OO + NO_2$	1.15×10^{-6}	see note[j]
P106	gas	$PPN \rightarrow C_2H_5C(O)OO + NO_2$	1.43×10^{-7}	$= J_{P101}$
P107	gas	i-PROPOLPAN $\rightarrow CH_3CH(OH)C(O)OO + NO_2$	3.43×10^{-8}	see note[h]
P108	gas	i-ClACETPAN $\rightarrow CH_3CHClC(O)OO + NO_2$	4.12×10^{-7}	see note[i]
P109	gas	i-BrACETPAN $\rightarrow CH_3CHBrC(O)OO + NO_2$	1.15×10^{-6}	see note[j]
P110	gas	$ACRPAN \rightarrow CH_2{=}CHC(O)OO + NO_2$	1.43×10^{-7}	$= J_{P101}$

References for absorption cross sections and quantum yields: 1, WMO (1986); 2, Molina and Molina (1986); 3, Matsumi et al. (2002); 4, Graedel and Weschler (1981), 5, DeMore et al. (1997); 6, Wayne et al. (1991); 7, Zellner et al. (1990); 8, Warneck and Wurzinger (1988); 9, Wahner et al. (1987); 10, Sander et al. (2000); 11, Hubinger and Nee (1995); 12, Weller et al. (1992); 13, McGivern et al. (2000); 14, Atkinson et al. (1997); 15, Bacher et al. (2001); 16, Calvert et al. (2002); 17, Libuda (1992); 18, Orlando et al. (1999); 19, Burkholder et al. (2002); 20, Atkinson et al. (1999); 21, Bauerle and Moortgat (1999).

[a] 24-hour average on an equinox day at 40° latitude with 340 DU column ozone and at T = 293 K.

[b] Actinic flux inside aerosol particles is assumed to be a factor of two greater than that in the gas phase (Ruggaber et al., 1997).

[c] Absorption cross sections are assumed to be red-shifted by 50 nm relative to $ClNO_2$.

[d] Wavelength-dependent quantum yields of CH_3Cl + CO and $ClCH_2$ + HCO are assumed to be red-shifted by 10 nm relative to those of CH_4 + CO and CH_3 + HCO, respectively, for CH_3CHO photolysis.

[e] Absorption cross sections are assumed to be red-shifted by 10 nm relative to $ClCH_2CHO$; Wavelength-dependent quantum yields of CH_3Cl + CO and $ClCH_2$ + HCO are assumed to be red-shifted by 20 nm relative to those of CH_4 + CO and CH_3 + HCO, respectively, for CH_3CHO photolysis.

[f] Absorption cross sections and wavelength-dependent quantum yields of $CH_3CH(OH)CHO$ photolysis are assumed to be blue-shifted by 15 nm relative to those of C_2H_5CHO photolysis.

[g] Absorption cross sections and wavelength-dependent quantum yields of $CH_3CHClCHO$ and $CH_3CHBrCHO$ photolysis are assumed to be red-shifted by 10 nm and 20 nm, respectively, relative to those of C_2H_5CHO photolysis.

[h] Absorption cross sections are assumed to be blue-shifted by 15 nm relative to PAN.

[i] Absorption cross sections are assumed to be red-shifted by 10 nm relative to PAN.

[j] Absorption cross sections are assumed to be red-shifted by 20 nm relative to PAN.

Table S5. Heterogeneous Reactions and their Reactive Uptake Coefficients (γ)[a]

No.	Reaction	γ	Reference
H1[b]	N_2O_5 + H_2O → 2 HNO_3	0.032	Behnke et al. (1997)
H2[b]	N_2O_5 + Cl^- → $ClNO_2$ + NO_3^-	0.032	Behnke et al. (1997)
H3[b]	N_2O_5 + Br^- → $BrNO_2$ + NO_3^-	0.032	Behnke et al. (1997)
H4[b]	$ClONO_2$ + H_2O → $HOCl$ + HNO_3	0.1	Koch and Rossi (1998)
H5[b]	$ClONO_2$ + Cl^- → Cl_2 + NO_3^-	0.1	Koch and Rossi (1998)
H6[b]	$ClONO_2$ + Br^- → $BrCl$ + NO_3^-	0.1	Koch and Rossi (1998)
H7[b]	$BrONO_2$ + H_2O → $HOBr$ + HNO_3	0.8	Hanson et al. (1996)
H8[b]	$BrONO_2$ + Cl^- → $BrCl$ + NO_3^-	0.8	Hanson et al. (1996)
H9[b]	$BrONO_2$ + Br^- → Br_2 + NO_3^-	0.8	Hanson et al. (1996)
H10	H_2SO_4 + H_2O → SO_4^{2-} + 2 H^+	0.65	Pöschl et al. (1998)
H11	$CH_3C(O)OO$ + H_2O → CH_3COOH + HO_2	0.001	DeMore et al. (1997)
H12	$HCOCl$ + H_2O → CO + HCl + H_2O	0.1	Sander et al. (1997)[c]
H13	$HCOBr$ + H_2O → CO + HBr + H_2O	0.1	Sander et al. (1997)[c]
H14	CH_3COCl + H_2O → CH_3COOH + HCl	8×10^{-4}	see note[d]
H15	$CH_3COCOCl$ + H_2O → $CH_3COCOOH$ + HCl	8×10^{-4}	see note[d]
H16	CH_3COBr + H_2O → CH_3COOH + HBr	8×10^{-4}	see note[d]
H17	$CH_3COCOBr$ + H_2O → $CH_3COCOOH$ + HBr	8×10^{-4}	see note[d]

[a] It is assumed that reaction products are diffused into the bulk of aerosol volume and then subject to either aqueous-phase reactions or release to the gas phase.

[b] N_2O_5, $ClONO_2$, and $BrONO_2$ can react with either H_2O or halide ions on aerosol surface. Their relative reactivities towards H_2O, Cl^-, and Br^- are assumed to be 3.3×10^{-6}, 1.7×10^{-3}, and 1, respectively (Sander et al., 1999).

[c] In their modeling study Sander et al. (1997) tentatively assigned this value for reactive uptake of formyl halides, which appears quite reasonable considering the rapid non-hydrolytic decay of $HCOCl$ to give CO + HCl that occurs in aqueous solution (Dowideit et al., 1996). The latter authors also found that hydrolysis of $HCOCl$ to give $HCOOH$ + HCl occurs negligibly slowly as compared with the non-hydrolytic decay (see also discussion in Sects. S1 and 3.2.3).

[d] The value of γ assigned is taken from that for CCl_3COCl uptake onto water determined by George et al. (1994).

Table S6. Henry's Law Constants (K_H) and Mass Accommodation Coefficients (α) for Species Capable of Being Transferred across Gas-Aerosol Interface[a,b]

Species	$K_H^{\ominus}$, M atm^{-1}	$-\Delta H_{soln}/R$, K	Reference	$\alpha^{\ominus}$	$-\Delta H^{\#}_{obs}/R$, K	Reference
O_2	1.70×10^{-3}	1500	1	0.01		2
O_3	1.20×10^{-2}	2560	3	0.002		4
OH	2.50×10^{1}		5	0.2		6
HO_2	9.00×10^{3}		7	0.2		6
H_2O_2	9.90×10^{4}	6300	8	0.115	2769	9
NO	1.90×10^{-3}	1400	1	0.0015		$= \alpha(NO_2)$
NO_2	7.00×10^{-3}		10	0.0015		11
NO_3	1.80×10^{0}		12	0.002		12
HONO	4.90×10^{1}	4780	13	0.05		14
HNO_3	2.10×10^{5}	8700	5	0.06	3323	9
HO_2NO_2	1.26×10^{4}	6868	15	0.115	2769	$= \alpha(H_2O_2)$
NH_3	5.80×10^{1}	4085	3	0.097		6
CH_3OH	2.20×10^{2}	5200	16	0.017	4028	9
CH_3OO	6.00×10^{0}	5586	17	0.01		2
CH_3OOH	3.00×10^{2}	5300	8	0.0046	3273	18
HCHO	3.00×10^{3}	7193	19[c]	0.04		6
CH_3CHO	6.70×10^{0}	6267	19[d]	0.03		20
HCOOH	3.70×10^{3}	5700	3	0.014	3977	9
CH_3COOH	4.10×10^{3}	6300	21	0.02	4078	9
CH_3CO_3H	6.70×10^{2}	5900	8	0.0046	3273	$= \alpha(CH_3COOH)$
C_2H_5COOH	5.70×10^{3}		22	0.02	4078	$= \alpha(CH_3COOH)$
$HOCH_2COOH$	9.00×10^{3}		$= K_H(HCOCOOH)$	0.02	4078	$= \alpha(CH_3COOH)$
HCOCOOH	9.00×10^{3}		23	0.02	4078	$= \alpha(CH_3COOH)$
$CH_3COCOOH$	3.10×10^{5}	5100	22	0.02	4078	$= \alpha(CH_3COOH)$
$CH_2{=}CHCOOH$	2.40×10^{3}		24	0.02	4078	$= \alpha(CH_3COOH)$
$ClCH_2COOH$	1.08×10^{5}	9742	25	0.139		26
$BrCH_2COOH$	1.53×10^{5}	9261	25	0.139		$= \alpha(ClCH_2COOH)$
$CH_3CHClCOOH$	1.08×10^{5}	9742	$= K_H(ClCH_2COOH)$	0.139		$= \alpha(ClCH_2COOH)$
$CH_3CHBrCOOH$	1.53×10^{5}	9261	$= K_H(BrCH_2COOH)$	0.139		$= \alpha(ClCH_2COOH)$
CO_2	3.10×10^{-2}	2423	3	0.01		2
HCl	1.10×10^{0}	2023	27	0.066	3625	28
HOCl	6.60×10^{2}	5900	29	0.066	3625	$= \alpha(HCl)$
CH_3OCl	6.60×10^{1}	5900	$= K_H(HOCl) \times 0.1$	0.066	3625	$= \alpha(HCl)$
Cl_2	9.40×10^{-2}	2109	1	0.038	6545	30
$ClNO_2$	4.60×10^{-2}		31	0.009		32
HBr	1.30×10^{0}	10239	33, 34	0.018	5035	28
HOBr	6.10×10^{3}		31	0.6		35
BrO	6.10×10^{3}		$= K_H(HOBr)$	0.1		36[e]
Br_2	7.70×10^{-1}	229	37	0.038	6545	30
BrCl	9.40×10^{-1}	5629	37	0.33		38
$BrNO_2$	3.00×10^{-1}		31	0.009		$= \alpha(ClNO_2)$

(continued on the next page)

Table S6. (continued)

Species	$K_{\mathrm{H}}^{\ominus}$, $\mathrm{M\,atm^{-1}}$	$-\Delta H_{\mathrm{soln}}/R$, K	Reference	$\alpha^{\ominus}$	$-\Delta H_{\mathrm{obs}}^{\#}/R$, K	Reference
SO_2	1.20×10^{0}	3120	3	0.11		6
CH_3SO_3H	8.90×10^{11}		39	0.076	1762	40

References: 1, Lide (1999); 2, Sander and Crutzen (1996); 3, Chameides (1984); 4, Utter et al. (1992); 5, Lelieveld and Crutzen (1991); 6, DeMore et al. (1997); 7, Weinstein-Lloyd and Schwartz (1991); 8, Lind and Kok (1994); 9, Jayne et al. (1991); 10, Lee and Schwartz (1981); 11, Ponche et al. (1993); 12, Thomas et al. (1998); 13, Schwartz and White (1981); 14, Bongartz et al. (1994); 15, Régimbal and Mozurkewich (1997); 16, Snider and Dawson (1985); 17, Seinfeld and Pandis (1998); 18, Magi et al. (1997); 19, Betterton and Hoffmann (1988b); 20, Jayne et al. (1992); 21, Johnson et al. (1996); 22, Khan et al. (1995); 23, Saxena and Hildemann (1996); 24, Yaws and Yang (1992); 25, Bowden et al. (1998); 26, Hu et al. (1993); 27, Marsh and McElroy (1985); 28, Schweitzer et al. (2000); 29, Huthwelker et al. (1995); 30, Hu et al. (1995); 31, Frenzel et al. (1998); 32, Fickert et al. (1998); 33, Brimblecombe and Clegg (1988); 34, Brimblecombe and Clegg (1989); 35, Wachsmuth et al. (2002); 36, Abbatt (1996); 37, Bartlett and Margerum (1999); 38, Katrib et al. (2001); 39, Clegg and Brimblecombe (1985); 40, De Bruyn et al. (1994).

[a] Temperature dependence of Henry's law constants is given by $K_{\mathrm{H}} = K_{\mathrm{H}}^{\ominus} \times \exp[-\Delta H_{\mathrm{soln}}/R \times (1/T - 1/T^{\ominus})]$, where $K_{\mathrm{H}}^{\ominus}$ is K_{H} at $T^{\ominus}$, $T^{\ominus}$ = 298.15 K, ΔH_{soln} is the enthalpy of solution and R is gas constant.

[b] Temperature dependence of mass accommodation coefficients is given by $\mathrm{d}\ln[\alpha/(1-\alpha)]/\mathrm{d}\,(1/T) = -\Delta H_{\mathrm{obs}}^{\#}/RT$, where $\Delta H_{\mathrm{obs}}^{\#}$ is the enthalpy of transition state between the gas and solvated states and R is gas constant.

[c] Effective Henry's law constant that takes into account the hydrolysis of HCHO in the aqueous phase, as reported by Betterton and Hoffmann (1988b): $K_{\mathrm{H}} = ([\mathrm{HCHO}]_{\mathrm{aq}} + [\mathrm{CH_2(OH)_2}])/p(\mathrm{HCHO})$. Considering a fact that formaldehyde in the aqueous phase predominantly exists as its hydrated form ($[\mathrm{HCHO}]_{\mathrm{aq}} \ll [\mathrm{CH_2(OH)_2}]$; see Table S7), $K_{\mathrm{H}} = [\mathrm{CH_2(OH)_2}]/p(\mathrm{HCHO})$ is assumed to hold at equilibrium of $\mathrm{HCHO(gas)} \rightleftharpoons \mathrm{CH_2(OH)_2}$.

[d] Effective Henry's law constant that takes into account the hydrolysis of $\mathrm{CH_3CHO}$ in the aqueous phase as reported by Betterton and Hoffmann (1988b) is corrected using a hydrolysis constant given in Table S7; $K_{\mathrm{H}} = [\mathrm{CH_3CH(OH)_2}]/p(\mathrm{CH_3CHO})$ at equilibrium of $\mathrm{CH_3CHO(gas)} \rightleftharpoons \mathrm{CH_3CH(OH)_2}$.

[e] Estimated based on the experimental study by Abbatt (1996), who determined reactive uptake coefficients for BrO on the surface of NaCl solutions doped with $\mathrm{Na_2SO_3}$.

Table S7. Aqueous-Phase Equilibrium Constants (K_{eq}) for Acids, Bases, Hydrates, and Other Species that Undergo Ion Dissociation in Water[a]

No.	Reaction	K_{eq}^{298}, M	$-\Delta H/R$, K	Reference
E1	$H_2O \rightleftharpoons H^+ + OH^-$	1.0×10^{-14}	-6716	National Bureau of Standards (1965)
E2	$HO_2 \rightleftharpoons H^+ + O_2^-$	1.60×10^{-5}		Weinstein-Lloyd and Schwartz (1991)
E3	$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	2.2×10^{-12}	-3730	Smith and Martell (1976)
E4	$NH_3 + H_2O \rightleftharpoons OH^- + NH_4^+$	1.70×10^{-5}	-4325	Chameides (1984)
E5	$HONO \rightleftharpoons H^+ + NO_2^-$	5.10×10^{-4}	-1260	Schwartz and White (1981)
E6	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	1.50×10^{1}		Lelieveld and Crutzen (1991)
E7	$HO_2NO_2 \rightleftharpoons H^+ + NO_4^-$	1.41×10^{-6}		Løgager and Sehested (1993)
E8	$HCHO + H_2O \rightleftharpoons CH_2(OH)_2$	2.45×10^{3}	4000	Warneck (1998) and references therein
E9	$CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2$	1.43×10^{0}	2518	Bell (1966); Bell and Evans (1966)
E10	$HCOOH \rightleftharpoons H^+ + HCOO^-$	1.80×10^{-4}		Lide (1999)
E11	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.76×10^{-5}		Lide (1999)
E12	$C_2H_5COOH \rightleftharpoons H^+ + C_2H_5COO^-$	1.34×10^{-5}		Lide (1999)
E13	$HOCH_2COOH \rightleftharpoons H^+ + HOCH_2COO^-$	1.48×10^{-4}		Lide (1999)
E14	$HCOCOOH \rightleftharpoons H^+ + HCOCOO^-$	1.48×10^{-4}		$= K_{eq}(HOCH_2COOH)$
E15	$CH_3COCOOH \rightleftharpoons H^+ + CH_3COCOO^-$	3.39×10^{-3}		Fisher and Warneck (1991)
E16	$CH_2{=}CHCOOH \rightleftharpoons H^+ + CH_2{=}CHCOO^-$	5.60×10^{-5}		Lide (1999)
E17	$ClCH_2COOH \rightleftharpoons H^+ + ClCH_2COO^-$	1.40×10^{-3}		Lide (1999)
E18	$BrCH_2COOH \rightleftharpoons H^+ + BrCH_2COO^-$	2.05×10^{-3}		Lide (1999)
E19	$CH_3CHClCOOH \rightleftharpoons H^+ + CH_3CHClCOO^-$	1.47×10^{-3}		Lide (1999)
E20	$CH_3CHBrCOOH \rightleftharpoons H^+ + CH_3CHBrCOO^-$	2.05×10^{-3}		$= K_{eq}(BrCH_2COOH)$
E21	$CH_3CO_3H \rightleftharpoons H^+ + CH_3CO_3^-$	6.31×10^{-9}		Fortnum et al. (1960)
E22	$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$	4.30×10^{-7}	-913	Chameides (1984)
E23	$HCl \rightleftharpoons H^+ + Cl^-$	1.70×10^{6}	6896	Marsh and McElroy (1985)
E24	$Cl_2^- \rightleftharpoons Cl + Cl^-$	5.20×10^{-6}		Jayson et al. (1973)
E25	$Cl_3^- \rightleftharpoons Cl_2 + Cl^-$	5.56×10^{0}		Wang et al. (1994)
E26	$HOCl \rightleftharpoons H^+ + ClO^-$	3.20×10^{-8}		Lax (1969)
E27	$HBr \rightleftharpoons H^+ + Br^-$	1.00×10^{9}		Lax (1969)
E28	$Br_2^- \rightleftharpoons Br + Br^-$	1.53×10^{-6}		Merényi and Lind (1994)
E29	$HOBr \rightleftharpoons H^+ + BrO^-$	2.30×10^{-9}	-3091	Kelly and Tartar (1956)
E30	$HBrO_2 \rightleftharpoons H^+ + BrO_2^-$	3.70×10^{-4}		Faria et al. (1994)
E31	$Br_3^- \rightleftharpoons Br^- + Br_2$	6.21×10^{-2}		Wang et al. (1994)
E32	$BrCl_2^- \rightleftharpoons Br^- + Cl_2$	2.38×10^{-7}		Liu and Margerum (2001)
E33	$BrCl_2^- \rightleftharpoons BrCl + Cl^-$	2.63×10^{-1}		Liu and Margerum (2001)
E34	$Br_2Cl^- \rightleftharpoons Br^- + BrCl$	5.56×10^{-5}		Wang et al. (1994)
E35	$Br_2Cl^- \rightleftharpoons Cl^- + Br_2$	7.69×10^{-1}		Wang et al. (1994)
E36	$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$	1.70×10^{-2}	2090	Chameides (1984)
E37	$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	6.00×10^{-8}	1120	Chameides (1984)
E38	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.02×10^{-2}	2720	Smith and Martell (1976)
E39	$HSO_5^- \rightleftharpoons H^+ + SO_5^{2-}$	3.98×10^{-10}		Fortnum et al. (1960)
E40	$CH_3SO_3H \rightleftharpoons CH_3SO_3^- + H^+$	7.30×10^{1}		Clarke and Woodward (1966)

[a] Temperature dependence of equilibrium constants is given by $K_{eq} = K_{eq}^{298} \times \exp[-\Delta H/R \times (1/T - 1/298)]$, where ΔH is reaction enthalpy and R is gas constant.

Table S8. Aqueous-Phase Reactions and their Rate Constants[a]

No.	Reaction (of Order n)	n	$k^{298}, \mathrm{M}^{1-n}\,\mathrm{s}^{-1}$	$-E_a/R, \mathrm{K}$	Reference
A1	$O_3 + O_2^- \overset{H_2O}{\rightarrow} OH + OH^- + 2\,O_2$	2	1.50×10^9		1
A2	$O_3 + OH \rightarrow HO_2 + O_2$	2	1.10×10^8		2
A3	$OH + OH \rightarrow H_2O_2$	2	5.50×10^9		3
A4	$OH + HO_2 \rightarrow H_2O + O_2$	2	7.10×10^9		4
A5	$OH + O_2^- \rightarrow OH^- + O_2$	2	1.00×10^{10}		4
A6	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	2	2.70×10^7		5
A7	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2	9.70×10^5	-2500	6
A8	$HO_2 + O_2^- \rightarrow HO_2^- + O_2$	2	1.00×10^8	-900	6
A9	$O_2 + O(^3P) \rightarrow O_3$	2	4.00×10^9		7
A10	$H_2O_2 + O(^3P) \rightarrow OH + HO_2$	2	1.60×10^9		8
A11	$HO_2^- + O(^3P) \rightarrow OH + O_2^-$	2	5.30×10^9		8
A12	$OH^- + O(^3P) \rightarrow HO_2^-$	2	4.20×10^8		8
A13	$NO + NO_2 \overset{H_2O}{\rightarrow} 2\,NO_2^- + 2\,H^+$	2	2.00×10^8		9
A14	$NO + OH \rightarrow NO_2^- + H^+$	2	2.00×10^{10}		10
A15	$NO_2 + NO_2 \overset{H_2O}{\rightarrow} NO_2^- + NO_3^- + 2\,H^+$	2	6.50×10^7		11
A16	$NO_2 + OH \rightarrow NO_3^- + H^+$	2	1.30×10^9		12
A17	$NO_2 + O_2^- \rightarrow NO_2^- + O_2$	2	4.50×10^9		13
A18	$NO_2 + HO_2 \rightarrow HO_2NO_2$	2	1.80×10^9	-2778	13
A19	$HO_2NO_2 + HONO \rightarrow 2\,NO_3^- + 2\,H^+$	2	1.20×10^1		13
A20	$HO_2NO_2 \rightarrow HONO + O_2$	1	7.00×10^{-4}		13
A21	$HO_2NO_2 \rightarrow HO_2 + NO_2$	1	2.60×10^{-2}	-13242	14
A22	$NO_4^- \rightarrow NO_2^- + O_2$	1	1.00×10^0		13
A23	$HONO + OH \rightarrow NO_2 + H_2O$	2	1.00×10^9	-1500	15
A24	$HONO + NO_3 \rightarrow NO_2 + NO_3^- + H^+$	2	8.00×10^6		16
A25	$HONO + H_2O_2 + H^+ \rightarrow NO_3^- + 2\,H^+ + H_2O$	3	6.30×10^3	-6700	17
A26	$NO_2^- + OH \rightarrow NO_2 + OH^-$	2	8.00×10^9		18
A27	$NO_2^- + Cl_2^- \rightarrow NO_2 + 2\,Cl^-$	2	2.50×10^8		19
A28	$NO_2^- + Br_2^- \rightarrow NO_2 + 2\,Br^-$	2	2.00×10^7		20
A29	$NO_2^- + BrO_2 \rightarrow NO_2 + BrO_2^-$	2	2.00×10^6		20
A30	$NO_2^- + NO_3 \rightarrow NO_2 + NO_3^-$	2	1.20×10^9		21
A31	$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	2	3.30×10^5		22
A32	$NO_3^- + O(^3P) \rightarrow NO_2^- + O_2$	2	2.24×10^8		23
A33	$NO_2^- + O(^3P) \rightarrow NO_3^-$	2	1.48×10^9		23
A34	$NO_3 + HO_2 \rightarrow NO_3^- + H^+ + O_2$	2	4.50×10^9	-1500	24
A35	$NO_3 + O_2^- \rightarrow NO_3^- + O_2$	2	1.00×10^9	-1500	24
A36	$NO_3 + H_2O_2 \rightarrow NO_3^- + HO_2 + H^+$	2	7.10×10^6	-241	25
A37	$NO_3 + OH^- \rightarrow NO_3^- + OH$	2	8.20×10^7	-2700	26
A38	$CH_3OO + HO_2 \rightarrow CH_3OOH + O_2$	2	4.30×10^5		24
A39	$CH_3OO + O_2^- \overset{H_2O}{\rightarrow} CH_3OOH + OH^- + O_2$	2	5.00×10^7		24
A40	$CH_3OOH + OH \rightarrow CH_3OO + H_2O$	2	2.70×10^7	-1700	24
A41	$CH_3OOH + OH \rightarrow HCHO + OH + H_2O$	2	1.90×10^7	-1800	24
A42	$CH_3OH + OH \overset{O_2}{\rightarrow} HCHO + HO_2 + H_2O$	2	9.70×10^8		3
A43	$CH_3OH + SO_4^- \overset{O_2}{\rightarrow} HCHO + HO_2 + SO_4^{2-} + H^+$	2	9.00×10^6	-2190	27
A44	$CH_3OH + NO_3 \overset{O_2}{\rightarrow} HCHO + HO_2 + NO_3^- + H^+$	2	5.40×10^5	-4300	28
A45	$CH_3OH + Cl_2^- \overset{O_2}{\rightarrow} HCHO + HO_2 + 2\,Cl^- + H^+$	2	1.00×10^3	-5500	29
A46	$CH_3OH + Br_2^- \overset{O_2}{\rightarrow} HCHO + HO_2 + 2\,Br^- + H^+$	2	4.40×10^3		30
A47	$CH_3OH + CO_3^- \overset{O_2}{\rightarrow} HCHO + HO_2 + HCO_3^-$	2	2.60×10^3		29
A48	$CH_2(OH)_2 + OH \overset{O_2}{\rightarrow} HCOOH + HO_2 + H_2O$	2	2.00×10^9	-1500	31
A49	$CH_2(OH)_2 + SO_4^- \overset{O_2}{\rightarrow} HCOOH + HO_2 + SO_4^{2-} + H^+$	2	1.40×10^7	-1300	32
A50	$CH_2(OH)_2 + NO_3 \overset{O_2}{\rightarrow} HCOOH + HO_2 + NO_3^- + H^+$	2	1.00×10^6	-4500	33

Table S8. (continued)

No.	Reaction (of Order n)	n	$k^{298}, \mathrm{M}^{1-n}\,\mathrm{s}^{-1}$	$-E_a/R, \mathrm{K}$	Reference
A51	$CH_2(OH)_2 + Cl_2^- \overset{O_2}{\rightarrow} HCOOH + HO_2 + 2\,Cl^- + H^+$	2	3.10×10^4	-4400	29
A52	$CH_2(OH)_2 + Br_2^- \overset{O_2}{\rightarrow} HCOOH + HO_2 + 2\,Br^- + H^+$	2	3.00×10^3		34
A53	$CH_2(OH)_2 + CO_3^- \overset{O_2}{\rightarrow} HCOOH + HO_2 + HCO_3^-$	2	1.30×10^4		29
A54	$CH_3CH(OH)_2 + OH \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + H_2O$	2	1.20×10^9		35
A55	$CH_3CHO + OH \overset{H_2O,O_2}{\rightarrow} CH_3COOH + HO_2 + H_2O$	2	3.60×10^9		35
A56	$CH_3CH(OH)_2 + SO_4^- \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + SO_4^{2-} + H^+$	2	1.00×10^7		34
A57	$CH_3CH(OH)_2 + NO_3 \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + NO_3^- + H^+$	2	1.90×10^6		29
A58	$CH_3CH(OH)_2 + Cl_2^- \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + 2\,Cl^- + H^+$	2	4.00×10^4		36
A59	$CH_3CH(OH)_2 + Br_2^- \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + 2\,Br^- + H^+$	2	4.00×10^4		34
A60	$CH_3CH(OH)_2 + CO_3^- \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + HCO_3^-$	2	1.00×10^4		34
A61	$HCOOH + OH \overset{O_2}{\rightarrow} HO_2 + CO_2 + H_2O$	2	1.10×10^8	-991	37
A62	$HCOO^- + OH \overset{O_2}{\rightarrow} OH^- + HO_2 + CO_2$	2	3.10×10^9	-1240	37
A63	$HCOOH + SO_4^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + SO_4^{2-} + H^+$	2	2.50×10^6		38
A64	$HCOO^- + SO_4^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + SO_4^{2-}$	2	2.10×10^7		38
A65	$HCOOH + NO_3 \overset{O_2}{\rightarrow} HO_2 + CO_2 + NO_3^- + H^+$	2	3.80×10^5	-3400	39
A66	$HCOO^- + NO_3 \overset{O_2}{\rightarrow} HO_2 + CO_2 + NO_3^-$	2	5.10×10^7	-2200	39
A67	$HCOOH + Cl_2^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + 2\,Cl^- + H^+$	2	5.50×10^3	-4500	40
A68	$HCOO^- + Cl_2^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + 2\,Cl^-$	2	1.90×10^6		19
A69	$HCOOH + Br_2^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + 2\,Br^- + H^+$	2	4.00×10^3		41
A70	$HCOO^- + Br_2^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + 2\,Br^-$	2	4.90×10^3		36
A71	$HCOO^- + CO_3^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + HCO_3^- + OH^-$	2	1.40×10^5	-3300	29
A72	$HCO_3^- + OH \rightarrow H_2O + CO_3^-$	2	8.50×10^6		3
A73	$HCO_3^- + O_2^- \rightarrow HO_2^- + CO_3^-$	2	0.00×10^0		42
A74	$CO_3^- + O_2^- \overset{H_2O}{\rightarrow} HCO_3^- + OH^- + O_2$	2	6.50×10^8		43
A75	$CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2$	2	4.30×10^5		44
A76	$CO_3^- + HCOO^- \overset{H_2O,O_2}{\rightarrow} 2\,HCO_3^- + HO_2$	2	1.50×10^5		44
A77	$Cl^- + OH \rightarrow ClOH^-$	2	4.30×10^9		45
A78	$Cl^- + NO_3 \rightarrow Cl + NO_3^-$	2	1.00×10^7	-4300	26
A79	$Cl + H_2O \rightarrow ClOH^- + H^+$	1	1.30×10^3		46
A80	$ClOH^- \rightarrow Cl^- + OH$	1	6.10×10^9		45
A81	$ClOH^- + H^+ \rightarrow Cl + H_2O$	2	2.10×10^{10}		45
A82	$Cl_2^- + Cl_2^- \rightarrow Cl_3^- + Cl^-$	2	7.00×10^8		46
A83	$Cl_2^- + OH \rightarrow HOCl + Cl^-$	2	1.00×10^9		47
A84	$Cl_2^- + HO_2 \rightarrow 2\,Cl^- + H^+ + O_2$	2	4.50×10^9		48
A85	$Cl_2^- + O_2^- \rightarrow 2\,Cl^- + O_2$	2	1.00×10^9		49
A86	$Cl_2^- + H_2O_2 \rightarrow 2\,Cl^- + HO_2 + H^+$	2	1.40×10^5		19
A87	$Cl^- + HOCl + H^+ \rightarrow Cl_2 + H_2O$	3	2.20×10^4	-3508	50
A88	$Cl^- + CH_3OCl + H^+ \rightarrow Cl_2 + CH_3OH$	3	2.20×10^4	-3508	$= k_{A87}$
A89	$Cl_2 + H_2O \rightarrow Cl^- + HOCl + H^+$	1	2.20×10^1	-8012	50
A90	$Cl^- + HOCl + HSO_4^- \rightarrow Cl_2 + SO_4^{2-} + H_2O$	3	2.80×10^3		50
A91	$Cl^- + CH_3OCl + HSO_4^- \rightarrow Cl_2 + SO_4^{2-} + CH_3OH$	3	2.80×10^3		$= k_{A90}$
A92	$Cl_2 + SO_4^{2-} \overset{H_2O}{\rightarrow} Cl^- + HOCl + HSO_4^-$	2	3.20×10^1		50
A93	$Cl^- + HOCl + HCOOH \rightarrow Cl_2 + HCOO^- + H_2O$	3	1.20×10^{-1}		50
A94	$Cl^- + CH_3OCl + HCOOH \rightarrow Cl_2 + HCOO^- + CH_3OH$	3	1.20×10^{-1}		$= k_{A93}$
A95	$Cl_2 + HCOO^- \overset{H_2O}{\rightarrow} Cl^- + HOCl + HCOOH$	2	1.20×10^2		50
A96	$Br^- + OH \rightarrow BrOH^-$	2	1.10×10^{10}		51
A97	$Br^- + NO_3 \rightarrow Br + NO_3^-$	2	4.00×10^9		52

Table S8. (continued)

No.	Reaction (of Order n)	n	k^{298}, $\mathrm{M}^{1-n}\,\mathrm{s}^{-1}$	$-E_a/R$, K	Reference
A98	$Br + OH^- \rightarrow BrOH^-$	2	1.30×10^{10}		51
A99	$BrOH^- \rightarrow Br^- + OH$	1	3.30×10^{7}		51
A100	$BrOH^- \rightarrow Br + OH^-$	1	4.20×10^{6}		51
A101	$BrOH^- + H^+ \rightarrow Br + H_2O$	2	4.40×10^{10}		51
A102	$BrOH^- + Br^- \rightarrow Br_2^- + OH^-$	2	2.00×10^{8}		53
A103	$Br_2^- + Br_2^- \rightarrow Br^- + Br_3^-$	2	1.90×10^{9}		54
A104	$Br_2^- + HO_2 \rightarrow Br_2 + HO_2^-$	2	9.10×10^{7}		55
A105	$Br_2^- + HO_2 \rightarrow 2\,Br^- + H^+ + O_2$	2	1.00×10^{8}		55
A106	$Br_2^- + O_2^- \rightarrow 2\,Br^- + O_2$	2	1.70×10^{8}		55
A107	$Br_2^- + H_2O_2 \rightarrow 2\,Br^- + H^+ + HO_2$	2	5.00×10^{2}		56
A108	$HOBr + O_2^- \rightarrow Br + OH^- + O_2$	2	3.50×10^{9}		57
A109	$HOBr + H_2O_2 \rightarrow Br^- + H^+ + O_2 + H_2O$	2	3.40×10^{6}		58
A110	$Br_2 + O_2^- \rightarrow Br_2^- + O_2$	2	5.00×10^{9}		57
A111	$Br_2 + HO_2 \rightarrow Br_2^- + O_2 + H^+$	2	1.30×10^{8}		57
A112	$Br_3^- + O_2^- \rightarrow Br^- + Br_2^- + O_2$	2	1.50×10^{9}		57
A113	$Cl^- + HOBr \rightarrow Br^- + HOCl$	2	1.01×10^{-2}		59, 60
A114	$Br^- + HOCl \rightarrow Cl^- + HOBr$	2	1.55×10^{3}		60
A115	$Br^- + CH_3OCl \xrightarrow{H_2O} Cl^- + HOBr + CH_3OH$	2	1.55×10^{3}		$= k_{\mathrm{A114}}$
A116	$Br^- + HOCl + H^+ \rightarrow BrCl + H_2O$	3	1.32×10^{6}		59
A117	$Br^- + CH_3OCl + H^+ \rightarrow BrCl + CH_3OH$	3	1.32×10^{6}		$= k_{\mathrm{A116}}$
A118	$BrCl + H_2O \rightarrow Br^- + HOCl + H^+$	1	1.15×10^{-3}		61
A119	$Cl^- + HOBr + H^+ \rightarrow BrCl + H_2O$	3	2.31×10^{10}		61
A120	$BrCl + H_2O \rightarrow Cl^- + HOBr + H^+$	1	3.00×10^{6}		61
A121	$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$	3	1.60×10^{10}		62
A122	$Br_2 + H_2O \rightarrow Br^- + HOBr + H^+$	1	9.70×10^{1}		62
A123	$Br^- + HOBr + HSO_4^- \rightarrow Br_2 + SO_4^{2-} + H_2O$	3	3.70×10^{9}		62
A124	$Br_2 + SO_4^{2-} \xrightarrow{H_2O} Br^- + HOBr + HSO_4^-$	2	4.10×10^{2}		62
A125	$BrNO_2 + Br^- \rightarrow Br_2 + NO_2^-$	2	7.11×10^{5}		63
A126	$Br_2 + NO_2^- \rightarrow BrNO_2 + Br^-$	2	1.85×10^{6}		63
A127	$BrNO_2 + NO_2^- \xrightarrow{H_2O} Br^- + NO_3^- + NO_2^- + 2\,H^+$	2	1.27×10^{4}		63
A128	$ClNO_2 + Br^- \rightarrow BrNO_2 + Cl^-$	2	1.18×10^{6}		63
A129	$BrNO_2 + Cl^- \rightarrow ClNO_2 + Br^-$	2	3.00×10^{2}		63
A130	$ClNO_2 + Cl^- \rightarrow Cl_2 + NO_2^-$	2	0.00×10^{0}		63
A131	$Cl_2 + NO_2^- + ClNO_2 + Cl^-$	2	2.50×10^{6}		63
A132	$ClNO_2 + NO_2^- \xrightarrow{H_2O} Cl^- + NO_3^- + NO_2^- + 2\,H^+$	2	7.98×10^{3}		63
A133	$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+ + O_2$	2	3.70×10^{5}	-5500	64
A134	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$	2	1.50×10^{9}	-5300	64
A135	$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O$	2	see note[b]	-3650	65
A136	$HSO_3^- + CH_3OOH + H^+ \rightarrow SO_4^{2-} + CH_3OH + 2\,H^+$	3	1.60×10^{7}	-3800	66
A137	$SO_3^{2-} + CH_3OOH + H^+ \rightarrow SO_4^{2-} + CH_3OH + H^+$	3	1.60×10^{7}	-3800	66
A138	$HSO_3^- + CH_3CO_3H + H^+ \rightarrow SO_4^{2-} + CH_3COOH + 2\,H^+$	3	4.83×10^{7}	-3993	66
A139	$HSO_3^- + CH_3CO_3H \rightarrow SO_4^{2-} + CH_3COOH + H^+$	3	8.42×10^{2}	-3993	66
A140	$HSO_3^- + OH \rightarrow SO_3^- + H_2O$	2	2.70×10^{9}		67
A141	$SO_3^{2-} + OH \rightarrow SO_3^- + OH^-$	2	4.60×10^{9}		67
A142	$HSO_3^- + HO_2 \rightarrow SO_3^- + H_2O_2$	2	3.00×10^{4}		68
A143	$HSO_3^- + O_2^- \rightarrow SO_3^- + HO_2^-$	2	3.00×10^{4}		68
A144	$HSO_3^- + NO_3 \rightarrow SO_3^- + NO_3^- + H^+$	2	1.40×10^{9}	-2000	26
A145	$SO_3^{2-} + NO_3 \rightarrow SO_3^- + NO_3^-$	2	2.00×10^{9}		52
A146	$HSO_3^- + Cl_2^- \rightarrow SO_3^- + 2\,Cl^- + H^+$	2	4.80×10^{8}	-1079	69
A147	$SO_3^{2-} + Cl_2^- \rightarrow SO_3^- + 2\,Cl^-$	2	6.20×10^{7}		70
A148	$HSO_3^- + Br_2^- \rightarrow SO_3^- + 2\,Br^- + H^+$	2	6.40×10^{7}	-779	69
A149	$SO_3^{2-} + Br_2^- \rightarrow SO_3^- + 2\,Br^-$	2	2.20×10^{8}	-647	69

Table S8. (continued)

No.	Reaction (of Order n)	n	k^{298}, $M^{1-n}\,s^{-1}$	$-E_a/R$, K	Reference
A150	HSO_3^- + HCHO → HMS^-	2	4.50×10^{2}	-2660	71
A151	SO_3^{2-} + HCHO $\xrightarrow{H_2O}$ HMS^- + OH^-	2	5.40×10^{6}	-2530	71
A152	HMS^- + OH^- → SO_3^{2-} + $CH_2(OH)_2$	2	4.60×10^{3}	-4880	71
A153	HMS^- + OH $\xrightarrow{H_2O, O_2}$ HSO_3^- + HCOOH + HO_2 + H_2O	2	3.00×10^{8}		72
A154	HMS^- + SO_4^- → SO_4^{2-} + H^+ + HCHO + SO_3^-	2	2.80×10^{6}		72
A155	HMS^- + NO_3 → NO_3^- + H^+ + HCHO + SO_3^-	2	4.20×10^{6}		28
A156	HMS^- + Cl_2^- → 2 Cl^- + H^+ + HCHO + SO_3^-	2	5.00×10^{5}		36
A157	HMS^- + Br_2^- → 2 Br^- + H^+ + HCHO + SO_3^-	2	5.00×10^{4}		34
A158	HSO_3^- + HSO_5^- + H^+ → 2 SO_4^{2-} + 3 H^+	3	7.10×10^{6}		73
A159	HSO_3^- + SO_4^- → SO_3^- + SO_4^{2-} + H^+	2	6.80×10^{8}		67
A160	SO_3^{2-} + SO_4^- → SO_3^- + SO_4^{2-}	2	3.10×10^{8}		67
A161	HSO_3^- + SO_5^- → SO_4^- + SO_4^{2-} + H^+	2	3.60×10^{2}		67
A162	SO_3^{2-} + SO_5^- → SO_4^- + SO_4^{2-}	2	5.50×10^{5}		67
A163	HSO_3^- + SO_5^- → SO_3^- + HSO_5^-	2	8.60×10^{3}		67
A164	SO_3^{2-} + SO_5^- $\xrightarrow{H^+}$ SO_3^- + HSO_5^-	2	2.10×10^{5}		67
A165	SO_3^- + O_2 → SO_5^-	2	2.50×10^{9}		67
A166	SO_4^- + O_2^- → SO_4^{2-} + O_2	2	4.00×10^{9}		67
A167	SO_4^- + NO_3^- → SO_4^{2-} + NO_3	2	2.30×10^{5}		74
A168	SO_4^- + Cl^- → SO_4^{2-} + Cl	2	2.70×10^{8}		46
A169	SO_4^- + Br^- → SO_4^{2-} + Br	2	3.50×10^{9}		75
A170	SO_4^- + SO_4^- → ($S_2O_8^{2-}$)	2	4.50×10^{8}		67
A171	SO_5^- + O_2^- $\xrightarrow{H^+}$ HSO_5^- + O_2	2	2.34×10^{8}		67
A172	SO_5^- + HO_2 → HSO_5^- + O_2	2	5.00×10^{7}		76
A173	SO_5^- + SO_5^- → SO_4^- + SO_4^- + O_2	2	2.20×10^{8}		67
A174	SO_5^- + SO_5^- → O_2 (+ $S_2O_8^{2-}$)	2	4.80×10^{7}		67
A175	BrO^- + SO_3^{2-} → Br^- + SO_4^{2-}	2	1.00×10^{8}		77
A176	HOBr + SO_3^{2-} → Br^- + SO_4^{2-} + H^+	2	5.00×10^{9}		77
A177	HOBr + HSO_3^- → Br^- + SO_4^{2-} + 2 H^+	2	5.00×10^{9}		$= k_{A176}$
A178	HOCl + SO_3^{2-} → Cl^- + SO_4^{2-} + H^+	2	7.60×10^{8}		78
A179	CH_3OCl + SO_3^{2-} $\xrightarrow{H_2O}$ Cl^- + SO_4^{2-} + CH_3OH + H^+	2	7.60×10^{8}		$= k_{A178}$
A180	HOCl + HSO_3^- → Cl^- + SO_4^{2-} + 2 H^+	2	7.60×10^{8}		$= k_{A178}$
A181	CH_3OCl + HSO_3^- $\xrightarrow{H_2O}$ Cl^- + SO_4^{2-} + CH_3OH + 2 H^+	2	7.60×10^{8}		$= k_{A178}$
A182	HO_2NO_2 + HSO_3^- → SO_4^{2-} + NO_3^- + 2 H^+	2	3.30×10^{5}		79
A183	Br^- + HSO_5^- → HOBr + SO_4^{2-}	2	1.04×10^{0}	-5338	80
A184	Cl^- + HSO_5^- → HOCl + SO_4^{2-}	2	1.80×10^{-3}	-7352	80
A185	Br^- + CH_3CO_3H → HOBr + CH_3COO^-	2	2.58×10^{-1}	-6897	80
A186	Cl^- + CH_3CO_3H → HOCl + CH_3COO^-	2	4.47×10^{-4}	-8911	$= k_{A185} \times k_{A184}/k_{A183}$
A187	Br^- + HO_2NO_2 → HOBr + NO_3^-	2	5.44×10^{-1}		81
A188	Cl^- + HO_2NO_2 → HOCl + NO_3^-	2	1.40×10^{-3}	-7216	81
A189	Br^- + O_3 → BrO^- + O_2	2	2.10×10^{2}	-4450	82
A190	BrO^- + O_3 → Br^- + 2 O_2	2	3.30×10^{2}		82
A191	BrO^- + O_3 → BrO_2^- + O_2	2	1.00×10^{2}		82
A192	Br + BrO^- → BrO + Br^-	2	4.00×10^{9}		51
A193	OH + BrO^- → BrO + OH^-	2	4.50×10^{9}		3
A194	OH + HOBr → BrO + H_2O	2	2.00×10^{9}		3
A195	Br_2^- + BrO^- → BrO + 2 Br^-	2	8.00×10^{7}		3
A196	Br + O_3 → BrO + O_2	2	1.50×10^{8}		83
A197	BrO + BrO $\xrightarrow{H_2O}$ BrO^- + BrO_2^- + H^+ + H^+	2	5.00×10^{9}		3
A198	BrO + BrO_2^- → BrO^- + BrO_2	2	3.40×10^{8}		3
A199	Br_2^- + BrO_2^- → BrO^- + BrO + Br^-	2	8.00×10^{7}		3
A200	OH + BrO_2^- → BrO_2 + OH^-	2	1.90×10^{9}		3

Table S8. (continued)

No.	Reaction (of Order n)	n	$k^{298}, \mathrm{M^{1-n}\,s^{-1}}$	$-E_a/R, \mathrm{K}$	Reference
A201	$OH + BrO_2 \rightarrow BrO_3^- + H^+$	2	2.00×10^9		84
A202	$BrO_2 + BrO_2 \rightarrow Br_2O_4$	2	1.40×10^9		85
A203	$Br_2O_4 \rightarrow BrO_2 + BrO_2$	1	7.40×10^4		85
A204	$Br_2O_4 + OH^- \rightarrow BrO_3^- + BrO_2^- + H^+$	2	7.00×10^8		3
A205	$Br_2O_4 + H_2O \rightarrow HBrO_2 + BrO_3^- + H^+$	1	2.20×10^3		85
A206	$BrO_2^- + O_3 \xrightarrow{H_2O} BrO_2 + OH + O_2 + OH^-$	2	8.90×10^4	-6901	86
A207	$BrO_2^- + HOCl \rightarrow BrO_3^- + Cl^- + H^+$	2	1.70×10^1		87
A208	$BrO_2^- + CH_3OCl \xrightarrow{H_2O} BrO_3^- + Cl^- + CH_3OH + H^+$	2	1.70×10^1		$= k_{A207}$
A209	$HBrO_2 + HOCl \rightarrow BrO_3^- + Cl^- + 2\,H^+$	2	5.00×10^7		88
A210	$HBrO_2 + CH_3OCl \xrightarrow{H_2O} BrO_3^- + Cl^- + CH_3OH + 2\,H^+$	2	5.00×10^7		$= k_{A209}$
A211	$HBrO_2 + Br^- + H^+ \rightarrow HOBr + HOBr$	3	3.00×10^6		85
A212	$HOBr + HOBr \rightarrow HBrO_2 + Br^- + H^+$	2	2.00×10^{-5}		85
A213	$BrO_3^- + Br^- + H^+ + H^+ \rightarrow HBrO_2 + HOBr$	4	2.00×10^0		85
A214	$BrO_2^- + HOBr \rightarrow BrO_3^- + Br^- + H^+$	2	1.80×10^{-2}		89
A215	$HBrO_2 + HOBr \rightarrow BrO_3^- + Br^- + 2\,H^+$	2	3.20×10^0		85
A216	$BrO_2^- + HBrO_2 \rightarrow HOBr + BrO_3^-$	2	3.91×10^1		90
A217	$HBrO_2 + HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$	2	8.00×10^2		90
A218	$HOBr + BrO_3^- + H^+ \rightarrow HBrO_2 + HBrO_2$	3	1.00×10^{-8}		85
A219	$HBrO_2 + BrO_3^- + H^+ \rightarrow Br_2O_4 + H_2O$	3	4.20×10^1		85
A220	$BrO + SO_3^{2-} \rightarrow BrO^- + SO_3^-$	2	1.00×10^5		see note[c]
A221	$BrO + HSO_3^- \rightarrow BrO^- + SO_3^- + H^+$	2	1.00×10^5		see note[c]
A222	$BrO_2 + SO_3^{2-} \rightarrow BrO_2^- + SO_3^-$	2	9.50×10^8		20
A223	$BrO_2 + HSO_3^- \rightarrow BrO_2^- + SO_3^- + H^+$	2	9.50×10^8		$= k_{A222}$
A224	$BrO_2^- + SO_3^{2-} \rightarrow BrO^- + SO_4^{2-}$	2	3.00×10^7		91
A225	$BrO_3^- + SO_2 \xrightarrow{H_2O} BrO_2^- + SO_4^{2-} + 2\,H^+$	2	8.50×10^1		92
A226	$BrO_3^- + HSO_3^- \rightarrow BrO_2^- + SO_4^{2-} + H^+$	2	2.70×10^{-2}		92
A227	$BrO_3^- + O(^3P) \rightarrow BrO_2^- + O_2$	2	1.50×10^7		7

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[a] Temperature dependence of rate constants is given by $k = k^{298} \times \exp[-E_a/R \times (1/T - 1/298)]$, where E_a is activation energy and R is gas constant.

[b] The rate constant depends on pH: $k^{298} = 5.2 \times 10^6 \times [H^+]/([H^+] + 0.1M)$.

[c] Estimated based on experimentally determined reactive uptake coefficients of BrO on the surface of S(IV)-doped NaCl solutions as reported by Abbatt (1996).

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