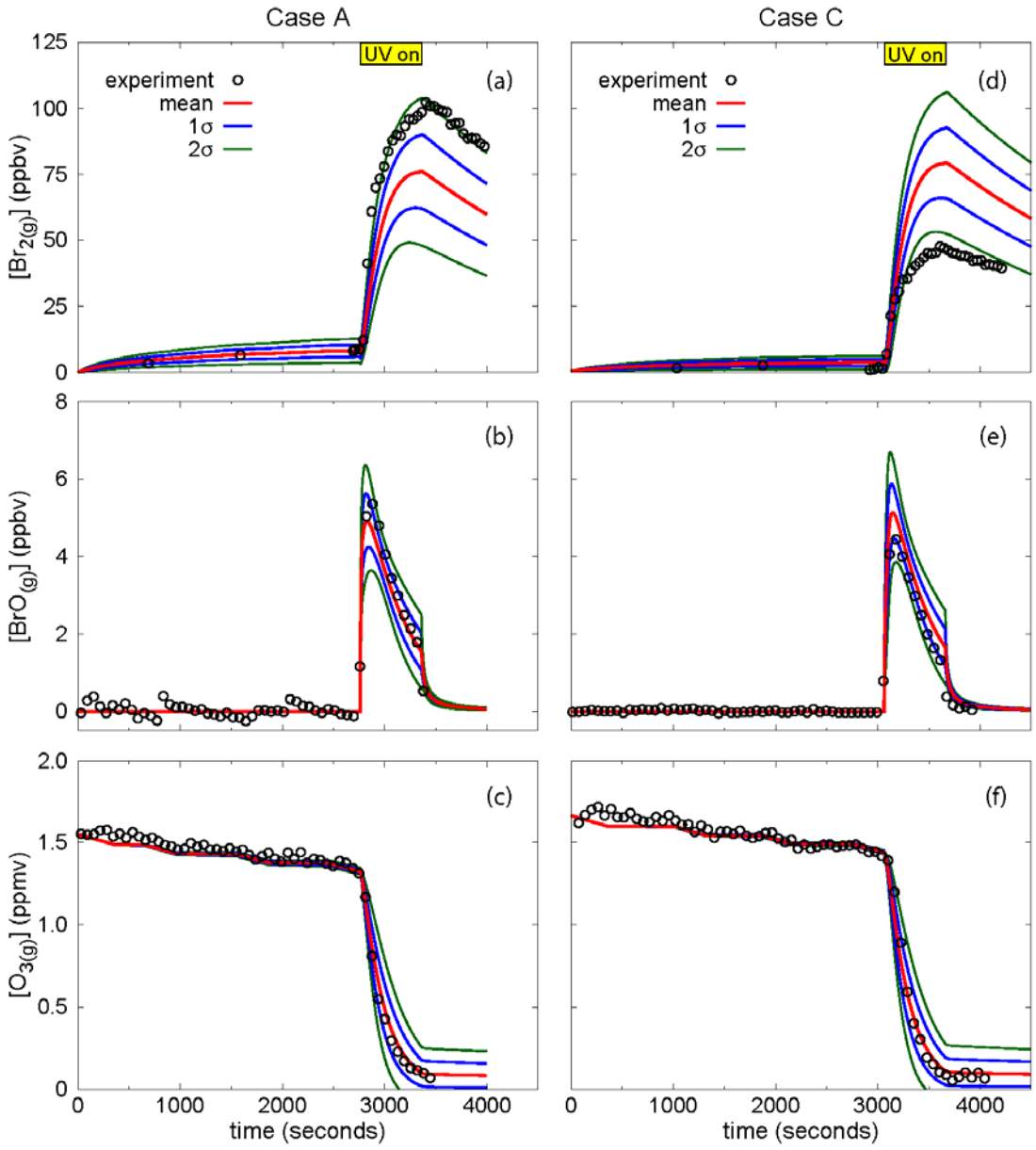
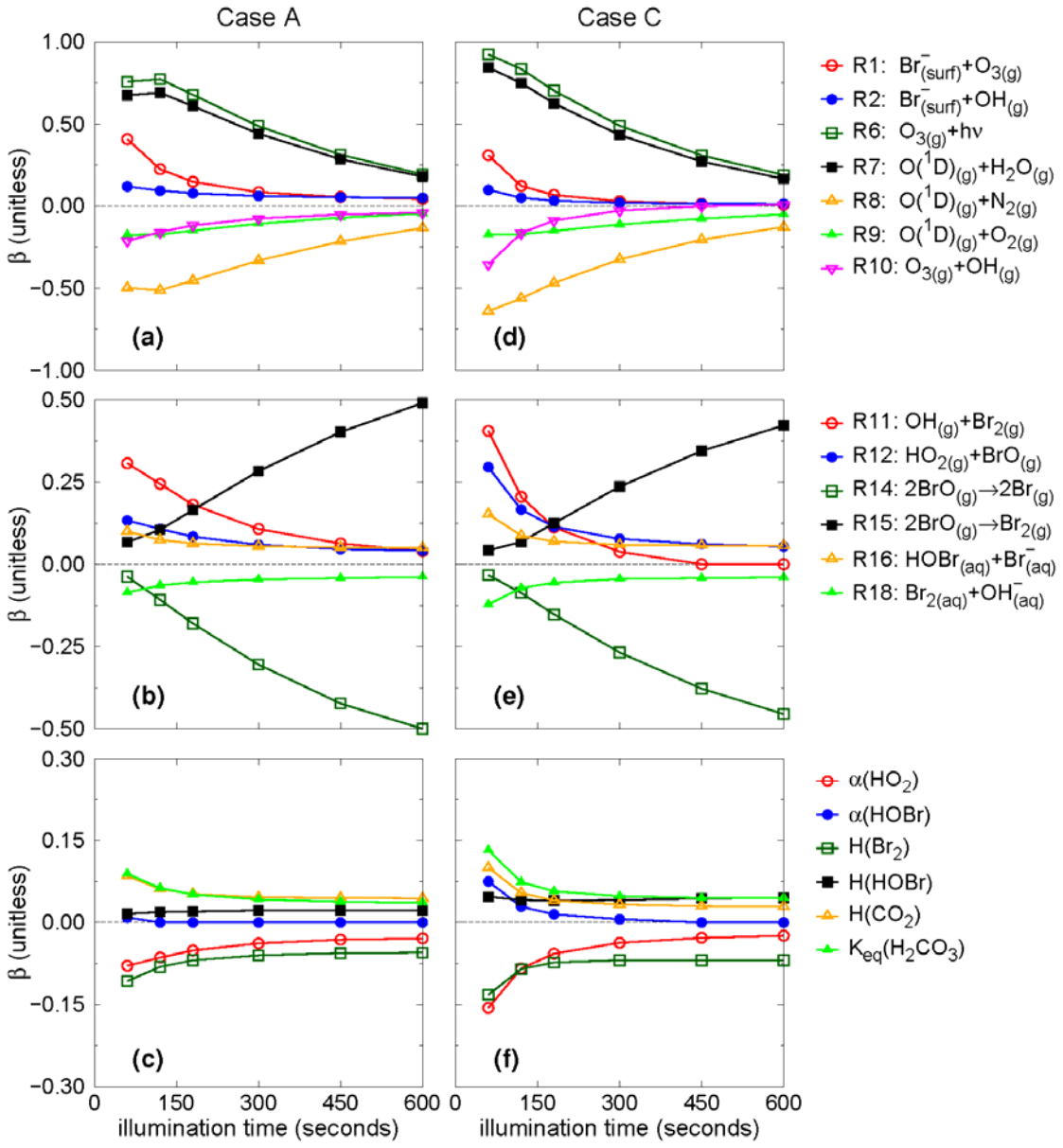
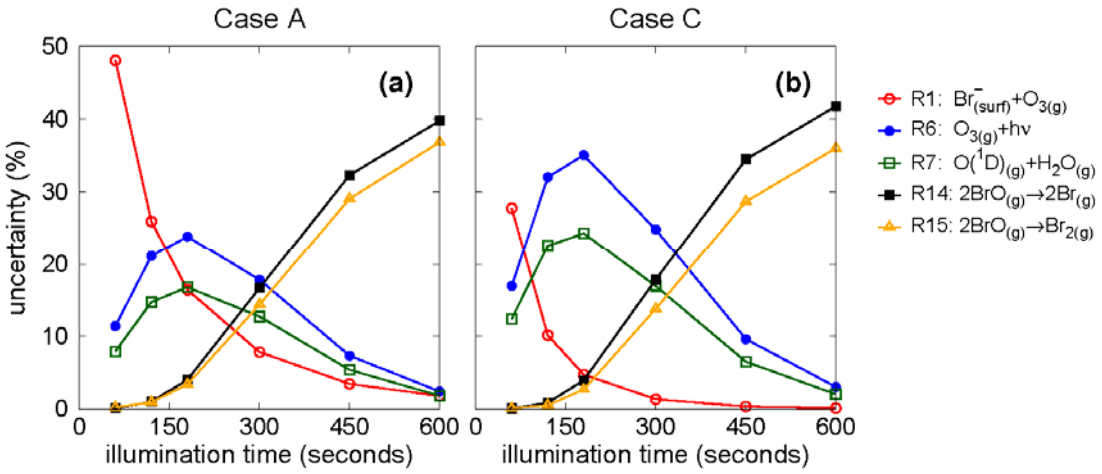
# Supplementary Figures



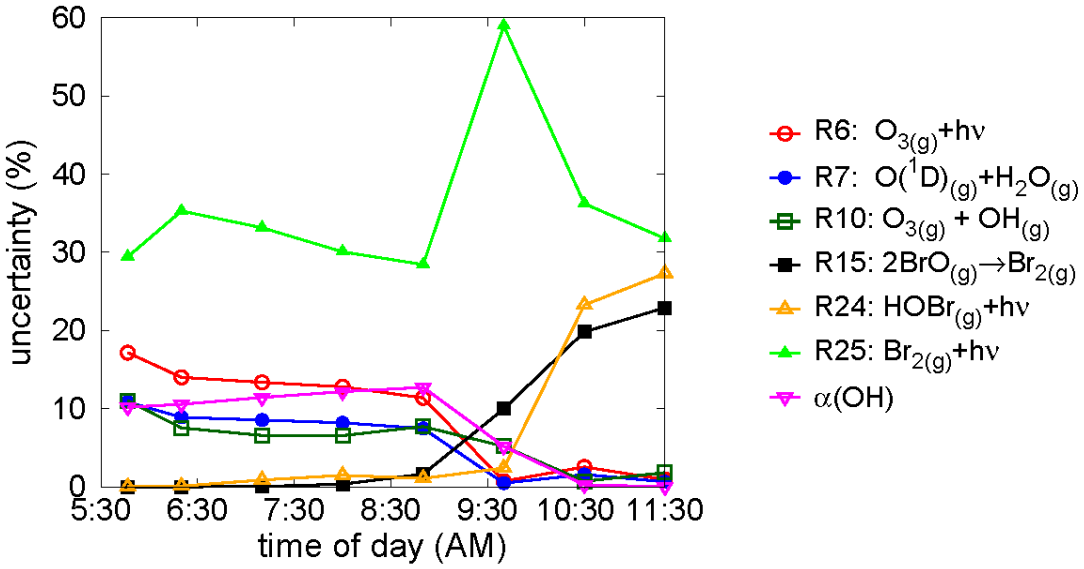

Supplementary Figure 1: A comparison of experimental data (empty circles) with results from the MAGIC model for case A (a-c) and case C (d-f). The mean, 1σ, and 2σ lines are based on the 5000 simulations from the sensitivity analysis performed on MAGIC for each case. The UV lamps are turned on for 600 s in both cases.




Supplementary Figure 2: Sensitivity of [$Br_{2(g)}$] to input parameters at various times during photolysis for cases A (a-c) and C (d-f). The input parameters are significant at the 0.05 level and have either a regression coefficient greater than 0.2 for at least one analysis time or are deemed interesting by the authors. Zero seconds corresponds to when the UV lamps are turned on. Reaction rate constants are represented by R followed by the chemical reaction number from the text. $K_{eq}(X)$, H(X), and α(X) represent the acid-base equilibrium constant, Henry's law constant, and mass accommodation coefficient of species X, respectively.



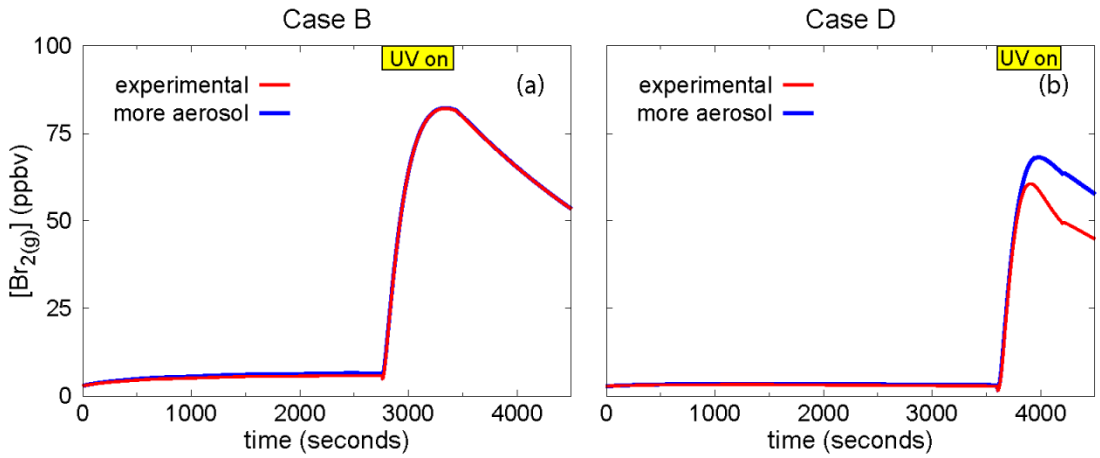

Supplementary Figure 3: Input parameters' contribution to the uncertainty in MAGIC's predictions of $Br_{2(g)}$ levels for case A (a) and case C (b). Input parameters that contribute at least 10% to the uncertainty in $[Br_{2(g)}]$ at one or more analysis times are shown in the figure. Reaction rate constants are represented by R followed by the chemical reaction number from the text.




Supplementary Figure 4: Input parameters' contribution to the uncertainty in MAGIC's predictions of $Br_{2(g)}$ levels for the MBL case. Input parameters that contribute at least 10% to the uncertainty in $[Br_{2(g)}]$ for at least one analysis time are shown in the figure. Reaction rate constants are represented by R followed by the chemical reaction number from the text. α(OH) represents the mass accommodation coefficient of OH.

**Additional simulations examining the impact of aerosol number concentration, surface area, and volume on bromine production (see Section 3.2.2):**

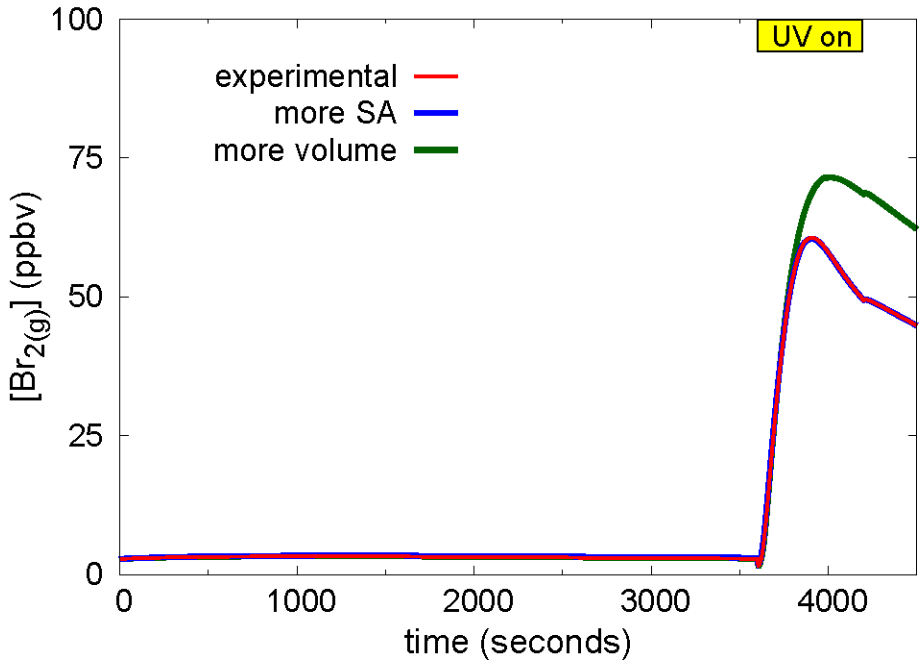
The sensitivity of peak $[Br_{2(g)}]$ to initial bromide in case B (ozone-limited system) and case D (bromide-limited system) is examined further by varying the aerosol number concentration, which affects the total amount of bromide in the system. Supplementary Figure 5 shows that raising the aerosol number concentration by 20% (without adjusting the shape of the aerosol size distribution) leads to an increase in peak $Br_{2(g)}$ of ~12% in case D but <1% in an case B.




Supplementary Figure 5: Concentration of $Br_{2(g)}$ for (a) case B and (b) case D predicted by the MAGIC model using the nominal (mean) values for the input parameters. The "experimental" simulations use the aerosol size distribution derived from data obtained by the SMPS, while the "more aerosol" simulations increase the aerosol number concentration by 20% without adjusting the shape of the aerosol size distribution. The UV lamps are turned on for 660 s in case B and 600 s in case D.

The $Br_{2(g)}$ explosion pathway involves both mass transfer and aqueous-phase reactions, both of which may be influenced by the aerosol properties. Additional simulations are conducted to assess the sensitivity of $[Br_{2(g)}]_{peak}$ to variations in aerosol surface area and aerosol volume in case D, which is bromide-limited. In the first simulation, the total surface area is held constant and the volume increases by 20% by adjusting the aerosol radius and number concentration. In the second simulation, the total surface area increases by 20% and the volume is held constant. Supplementary Figure 6 shows that $[Br_{2(g)}]_{peak}$ is much more sensitive to changes in total aerosol volume ($[Br_{2(g)}]_{peak}$ increases by 18%) than changes in total aerosol surface area ($[Br_{2(g)}]_{peak}$ increases by less than 1%). These simulations are in agreement with the sensitivity analysis showing $[Br_{2(g)}]$ is weakly correlated with the reaction of $OH_{(g)}$ and interfacial $Br^-$; i.e., reaction (2) is too slow to compete with aqueous-phase bromide oxidation during UV photolysis. Therefore, it is the reduction in aerosol volume (the total bromide in the system), not surface area,

that causes the rate-limiting steps in the bromine explosion mechanism to shift from gas-phase reactions in cases A-C to aqueous reactions and mass transfer parameters in case D.




Supplementary Figure 6: Concentration of $Br_{2(g)}$ predicted by the MAGIC model (with nominal values for the input parameters) using different aerosol size distributions for case D. The "experimental" simulation uses the same aerosol distribution as in case D, which is derived using data from the SMPS. The "more SA" simulation increases total aerosol surface area by 20% above the surface area in the "experimental" simulation, while leaving total aerosol volume unchanged. The "more volume" simulation leaves total aerosol surface area unchanged while increasing total aerosol volume by 20% above the volume in the "experimental" simulation. The UV lamps are turned on for 600 s.

**Additional experimental details on the comparison of the chamber walls as a reactive sink relative to NaBr particles (see Section 2.1):**

As discussed in the main text, the chamber was cleaned frequently to remove wall contamination. Of the four experimental cases presented, three were carried out in a freshly cleaned chamber (cases A, C, and D). The fourth case (case B) had only one NaBr aerosol experiment carried out before, which our initial characterization experiments established would not produce significant amounts of $Br_{2(g)}$. The results from case B are in agreement with cases A and C, confirming that carryover from one experiment does not significantly alter the results.

Other species such as HOBr can react rapidly with $Br^-$ on surfaces. If sufficient bromide were present on the chamber walls to initiate this chemistry, significant amounts of gas-phase $Br_2$ would have been observed in the control experiments. For example, the

$HO_2$ reaction with BrO forms HOBr, which would lead to $Br_2$ through reaction with bromide on the walls. BrO formation was measured during the control runs and was found to be <3% of the BrO concentration during aerosol experiments.

In the main text, a discussion of the relative loss of OH to NaBr particles versus loss of OH to the chamber walls is presented. If NaBr and other brominated species are present on the walls and an OH radical collides with those species each time it strikes the wall, the reaction probability for OH on the halocarbon wax-coated walls could be much larger than the value cited in the main text, $\gamma = 2 \times 10^{-4}$. If this were the case, significant amounts of $Br_{2(g)}$ would have been generated in the control experiments. However, significant quantities of $Br_{2(g)}$ were not measured until at least four experiments had been carried out without cleaning the chamber. As stated above, three of the four experiments used for modeling were conducted immediately after cleaning, and the fourth experiment occurred following only one NaBr aerosol experiment. The authors also note that the comparison of OH loss pathways presented in the main text is an overestimate of the contribution of wall reactions versus reactions with particles, as it treats the particle surfaces and the chamber walls as being equally available to OH (or other species such as HOBr). A reactive species in the middle of the chamber must first diffuse to the walls in order to be removed there. At a typical particle concentration of $10^5$ $cm^{-3}$, the average distance between particles is only ~0.02 cm. This is much smaller than the 22 cm that an OH radical must travel from the middle of the chamber to the walls. Only in a thin layer of air immediately adjacent to the chamber walls can loss of OH to the wall be significant compared to reactions with particles. However, the volume of the chamber contents that fall into this category is such a small fraction of the total volume that wall reactions have little impact on the overall gas phase composition.

# Supplementary Tables

Supplementary Table 1: Chemical species included in the MAGIC model

| Group | Gas-phase species[(a)] | Aqueous-phase species[(a)] |
|---|---|---|
| $HO_x$ | $O(^1D)$, $O(^3P)$, **$O_2$**, **$O_3$**, **OH**, **$HO_2$**, **$H_2O_2$**, $H_2O$ | $O(^3P)$, **$O_2$**, **$O_3$**, **OH**/$O^-$, **$HO_2$**/$O_2^-$, **$H_2O_2$**/$HO_2^-$, $HO_3$, $O_3^-$, $H^+$/$OH^-$ |
| $BrO_x$ | Br, **$Br_2$**, **HBr**, BrO, **HOBr** | Br, **$Br_2$**, **HBr**/$Br^-$, $Br_2^-$, $Br_2O_4$, $Br_3^-$, BrO, **HOBr**/$BrO^-$, $BrO_2$, $HBrO_2$/$BrO_2^-$, $BrO_3^-$, $HOBr^-$ |
| $CO_2$ | **$CO_2$** | **$CO_2$•$H_2O$**/$HCO_3^-$/$CO_3^{2-}$, $HCO_3$/$CO_3^-$ |
| other | $N_2$ | $Na^+$ |

(a) Species in bold may transfer between the two phases.

Supplementary Table 2: Mean and uncertainty ranges of the input parameters used in MAGIC for Cases A-D.

Numbered reactions in main text

| Interface reaction rate parameters | | | $(x^* \pm \sigma)$ [a] | references | notes |
|---|---|---|---|---|---|
| R1 | $\gamma'\ O_{3(g)} + Br^-_{(surf)} \rightarrow\rightarrow 0.5\ Br_{2(g)} + O_{3(aq)}$ | | $(9.00 \pm 5.15)\ 10^{-7}$ | This study | b |
| R2 | $\gamma'\ OH_{(g)} + Br^-_{(surf)} \rightarrow\rightarrow 0.5\ Br_{2(g)} + OH_{(aq)}$ | | $(6.00 \pm 4.00)\ 10^{-1}$ | Laskin et al., 2006; Thomas et al., 2006 | c |
| **Gas-phase reaction rate constants ($k_{298}$)** | | **O [d]** | **( $x^* \pm \sigma$ ) [e]** | **references** | **notes** |
| R6 | $O_3 + h\nu \rightarrow O(^1D) + O_2$ | 1 | $(3.15 \pm 0.47)\ 10^{-3}$ | Atkinson et al., 2004 | f |
| R7 | $O(^1D) + H_2O \rightarrow 2OH$ | 2 | $(1.99 \pm 0.28)\ 10^{-10}$ | Sander et al., 2006 | |
| R8 | $O(^1D) + N_2 \rightarrow O(^3P) + N_2$ | 2 | $(3.11 \pm 0.30)\ 10^{-11}$ | Sander et al., 2006 | |
| R9 | $O(^1D) + O_2 \rightarrow O(^3P) + O_2$ | 2 | $(3.97 \pm 0.38)\ 10^{-11}$ | Sander et al., 2006 | |
| R10 | $O_3 + OH \rightarrow HO_2 + O_2$ | 2 | $(7.25 \pm 1.33)\ 10^{-14}$ | Sander et al., 2006 | |
| R11 | $OH + Br_2 \rightarrow HOBr + Br$ | 2 | $(4.70 \pm 0.45)\ 10^{-11}$ | Sander et al., 2006 | |
| R12 | $HO_2 + BrO \rightarrow HOBr + O_2$ | 2 | $(2.11 \pm 0.30)\ 10^{-11}$ | Sander et al., 2006 | |
| R13 | $Br + O_3 \rightarrow BrO + O_2$ | 2 | $(1.16 \pm 0.21)\ 10^{-12}$ | Sander et al., 2006 | |
| R14 | $2BrO \rightarrow 2Br + O_2$ | 2 | $(2.70 \pm 0.63)\ 10^{-12}$ | Atkinson et al., 2006 | |
| R15 | $2BrO \rightarrow Br_2 + O_2$ | 2 | $(4.86 \pm 1.13)\ 10^{-13}$ | Atkinson et al., 2006 | |
| R25 | $Br_2 + h\nu \rightarrow Br + Br$ | 1 | $(1.36 \pm 0.27)\ 10^{-6}$ | Atkinson et al., 2004 | f |
| R26 | $BrO + h\nu \rightarrow Br + O(^3P)$ | 1 | $(4.26 \pm 0.54)\ 10^{-5}$ | Atkinson et al., 2004 | f |
| R24 | $HOBr + h\nu \rightarrow OH + Br$ | 1 | $(1.94 \pm 0.58)\ 10^{-5}$ | Atkinson et al., 2004 | f |
| R27 | $OH + HO_2 \rightarrow O_2 + H_2O$ | 2 | $(1.11 \pm 0.25)\ 10^{-10}$ | Sander et al., 2006 | |
| **Aqueous-phase reaction rate constants** | | **O [d]** | **( $x^* \pm \sigma$ ) [i]** | **references** | **notes** |
| R16 | $HOBr + Br^- + H_2O \rightarrow Br_2 + OH^- + H_2O$ | 2 | $(3.20 \pm 1.76)\ 10^{+4}$ | Beckwith et al., 1996 | l,m |
| R17 | $HOBr + Br^- + HCO_3^- \rightarrow Br_2 + CO_3^{2-} + H_2O$ | 3 | $(1.10 \pm 0.57)\ 10^{+5}$ | Beckwith et al., 1996 | l,m |
| R18 | $Br_2 + OH^- + H_2O \rightarrow HOBr + Br^- + H_2O$ | 2 | $(7.00 \pm 3.57)\ 10^{+9}$ | Beckwith et al., 1996 | l,m |
| R18 | $Br_2 + OH^- + H_2O \rightarrow HOBr + Br^- + H_2O$ | 2 | $(7.00 \pm 3.57)\ 10^{+9}$ | Beckwith et al., 1996 | l,m |
| R19 | $Br_2 + CO_3^{2-} + H_2O \rightarrow HOBr + Br^- + HCO_3^-$ | 2 | $(1.50 \pm 0.78)\ 10^{+7}$ | Beckwith et al., 1996 | l,m |
| R20 | $HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$ | 3 | $(1.60 \pm 0.20)\ 10^{+10}$ | Beckwith et al., 1996 | |
| R21 | $Br^- + OH \rightarrow HOBr^-$ | 2 | $(1.06 \pm 0.08)\ 10^{+10}$ | Zehavi and Rabani, 1972 | |
| R22 | $HOBr^- + Br^- \rightarrow Br_2^- + OH^-$ | 2 | $(1.90 \pm 0.30)\ 10^{+8}$ | Zehavi and Rabani, 1972 | |
| R23 | $Br_2^- + HO_2 \rightarrow Br_2 + HO_2^-$ | 2 | $(3.80 \pm 0.95)\ 10^{+9}$ | Sutton et al., 1965 | |

# Other input parameters in MAGIC

| Gas-phase reaction rate constants ($k_{298}$) | | O [d] | ( $x^* \pm \sigma$ ) [e] | references | notes |
|---|---|---|---|---|---|
| 1 | $O_3 + h\nu \rightarrow O(^3P) + O_2$ | 1 | $(3.50 \pm 0.53)\ 10^{-4}$ | Atkinson et al., 2004 | f |
| 2 | $H_2O_2 + h\nu \rightarrow 2OH$ | 1 | $(2.04 \pm 0.31)\ 10^{-5}$ | Atkinson et al., 2004 | f |
| 3 | $O(^1D) + O_3 \rightarrow O_2 + O_2$ | 2 | $(1.20 \pm 0.22)\ 10^{-10}$ | Sander et al., 2006 | |
| 4 | $O(^1D) + O_3 \rightarrow O(^3P) + O(^3P) + O_2$ | 2 | $(1.20 \pm 0.22)\ 10^{-10}$ | Sander et al., 2006 | |
| 5 | $O(^3P) + O_2 + M \rightarrow O_3 + M$ | 2 | $(1.50 \pm 0.14)\ 10^{-14}$ | Sander et al., 2006 | |
| 6 | $O(^3P) + O_3 \rightarrow O_2 + O_2$ | 2 | $(7.96 \pm 1.12)\ 10^{-15}$ | Sander et al., 2006 | |
| 7 | $O(^3P) + HO_2 \rightarrow OH + O_2$ | 2 | $(5.87 \pm 0.29)\ 10^{-11}$ | Sander et al., 2006 | |
| 8 | $O(^3P) + H_2O_2 \rightarrow OH + HO_2$ | 2 | $(1.70 \pm 0.45)\ 10^{-15}$ | Sander et al., 2006 | |
| 9 | $OH + OH \rightarrow O(^3P) + H_2O$ | 2 | $(1.80 \pm 0.48)\ 10^{-12}$ | Sander et al., 2006 | |
| 10 | $OH + OH + M \rightarrow H_2O_2 + M$ | 3 | $(6.29 \pm 2.62)\ 10^{-12}$ | Sander et al., 2006 | |
| 11 | $H_2O_2 + OH \rightarrow HO_2 + H_2O$ | 2 | $(1.70 \pm 0.39)\ 10^{-12}$ | Atkinson et al., 2004 | |
| 12 | $O_3 + HO_2 \rightarrow OH + 2O_2$ | 2 | $(1.93 \pm 0.27)\ 10^{-15}$ | Sander et al., 2006 | |
| 13 | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | 2 | $(1.81 \pm 0.33)\ 10^{-12}$ | Sander et al., 2006 | |
| 14 | $HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$ | 3 | $(4.86 \pm 0.89)10^{-32}[M]$ | Sander et al., 2006 | |
| 15 | $CO + OH + O_2 \rightarrow CO_2 + HO_2$ | 3 | $(2.10 \pm 0.24)\ 10^{-13}$ | Atkinson et al., 2004 | |
| 16 | $O + BrO \rightarrow Br + O_2$ | 2 | $(4.11 \pm 1.71)\ 10^{-11}$ | Sander et al., 2006 | |
| 17 | $O + HBr \rightarrow OH + Br$ | 2 | $(3.80 \pm 1.00)\ 10^{-14}$ | Sander et al., 2006 | |
| 18 | $O + HOBr \rightarrow OH + BrO$ | 2 | $(2.84 \pm 3.78)\ 10^{-11}$ | Sander et al., 2006 | |
| 19 | $OH + BrO \rightarrow Br + HO_2$ | 2 | $(5.65 \pm 2.56)\ 10^{-12}$ | Sander et al., 2006 | g |
| 20 | $OH + HBr \rightarrow H_2O + Br$ | 2 | $(1.08 \pm 0.10)\ 10^{-11}$ | Sander et al., 2006 | |
| 21 | $HO_2 + Br \rightarrow HBr + O_2$ | 2 | $(1.70 \pm 0.45)\ 10^{-12}$ | Sander et al., 2006 | |
| 22 | $Br + H_2O_2 \rightarrow HBr + HO_2$ | 2 | $(5.00 \pm 1.25)\ 10^{-16}$ | Sander et al., 2006 | h |
| 23 | $BrO + O_3 \rightarrow Br + 2O_2$ | 2 | $(2.00 \pm 0.28)\ 10^{-17}$ | Sander et al., 2006 | h |
| 24 | $Br_2 \rightarrow$ wall loss | 1 | $(2.98 \pm 0.73)\ 10^{-4}$ | This study | f |

| Aqueous-phase reaction rate constants | | O [d] | ( $x^* \pm \sigma$ ) [i] | references | notes |
|---|---|---|---|---|---|
| 25 | $H_2O_2 + h\nu \rightarrow 2OH$ | 1 | $(1.99 \pm 0.45)\ 10^{-5}$ | Zellner et al., 1990; Atkinson et al., 2004 | f |
| 26 | $O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2$ | 1 | $(1.51 \pm 0.49)\ 10^{-3}$ | Gurol and Akata, 1996; Atkinson et al., 2004 | f |
| 27 | $O_3 + h\nu \rightarrow O(^3P) + O_2$ | 1 | $(2.24 \pm 0.62)\ 10^{-4}$ | Reisz et al., 2003; Atkinson et al., 2004 | f |
| 28 | $O_3 \rightarrow O(^3P) + O_2$ | 1 | $(3.00 \pm 0.50)\ 10^{-6}$ | Sehested et al., 1992 | |
| 29 | $OH + OH \rightarrow H_2O_2$ | 2 | $(4.98 \pm 0.85)\ 10^{+9}$ | Thomas, 1965; Rabani and Matheson, 1966; Pagsberg et al., 1969; Christensen and Sehested, 1981; Buxton et al., 1988; Elliot, 1989; Elliot et al., 1990 | |
| 30 | $OH + HO_2 \rightarrow O_2 + H_2O$ | 2 | $(7.53 \pm 1.76)\ 10^{+9}$ | Thomas, 1963; Sehested et al., 1968; Elliot and Buxton, 1992 | |

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|---|---|---|---|---|---|
| 31 | $OH + O_2^- \rightarrow OH^- + O_2$ | 2 | $(9.10 \pm 1.24)\ 10^{+9}$ | Sehested et al., 1968; Beck, 1969; Christensen et al., 1989; Elliot and Buxton, 1992 | |
| 32 | $OH + H_2O_2 \rightarrow HO_2 + H_2O$ | 2 | $(2.72 \pm 0.60)\ 10^{+7}$ | Greenstock and Wiebe, 1981; Christensen et al., 1982; Buxton et al., 1988 | |
| 33 | $OH + HO_2^- \rightarrow HO_2 + OH^-$ | 2 | $(7.05 \pm 0.99)\ 10^{+9}$ | Rabani, 1968; Buxton, 1969; Merenyi and Lind, 1980; Christensen et al., 1982 | |
| 34 | $OH + O_3 \rightarrow HO_2 + O_2$ | 2 | $(1.10 \pm 0.20)\ 10^{+8}$ | Sehested et al., 1984 | |
| 35 | $OH + O_3^- \rightarrow O_2^- + HO_2$ | 2 | $(6.00 \pm 1.00)\ 10^{+9}$ | Sehested et al., 1984 | |
| 36 | $OH + O_3^- \rightarrow O_3 + OH^-$ | 2 | $(2.50 \pm 0.50)\ 10^{+9}$ | Sehested et al., 1984 | |
| 37 | $O^- + O_2 \rightarrow O_3^-$ | 2 | $(3.54 \pm 0.49)\ 10^{+9}$ | Adams et al., 1966; Rabani and Matheson, 1966; Buxton, 1969; Kläning et al., 1981; Buxton et al., 1988; Elliot and McCracken, 1989 | |
| 38 | $O^- + HO_2^- \rightarrow O_2^- + OH^-$ | 2 | $(4.00 \pm 0.50)\ 10^{+8}$ | Christensen et al., 1982 | |
| 39 | $O^- + O_2^- + H_2O \rightarrow 2OH^- + O_2$ | 2 | $(6.00 \pm 1.00)\ 10^{+8}$ | Sehested et al., 1982 | |
| 40 | $O^- + OH \rightarrow HO_2^-$ | 2 | $(1.00 \pm 1.00)\ 10^{+10}$ | Rabani and Matheson, 1966 | j |
| 41 | $O^- + H_2O \rightarrow OH + OH^-$ | 2 | $(9.40 \pm 1.52)\ 10^{+7}$ | Buxton, 1970; Zehavi and Rabani, 1971 | |
| 42 | $O^- + O_3 \rightarrow O_2^- + O_2$ | 2 | $(1.00 \pm 0.50)\ 10^{+8}$ | Gonzalez and Mártire, 1997 | j |
| 43 | $O^- + O_3^- \rightarrow 2O_2^-$ | 2 | $(8.00 \pm 1.00)\ 10^{+8}$ | Sehested et al., 1982; Gonzalez and Mártire, 1997 | |
| 44 | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | 2 | $(8.60 \pm 0.62)\ 10^{+5}$ | Bielski, 1978 | |
| 45 | $HO_2 + O_2^- \rightarrow HO_2^- + O_2$ | 2 | $(1.02 \pm 0.49)\ 10^{+8}$ | Bielski, 1978 | |
| 46 | $HO_2 + H_2O_2 \rightarrow OH + O_2 + H_2O$ | 2 | $(5.00 \pm 0.90)\ 10^{-1}$ | Weinstein and Bielski, 1979 | |
| 47 | $HO_2 + O_3 \rightarrow OH + 2O_2$ | 2 | $(5.00 \pm 5.00)\ 10^{+3}$ | Sehested et al., 1984 | j |
| 48 | $O_2^- + O_2^- + 2\ H_2O \rightarrow H_2O_2 + 2OH^- + O_2$ | 2 | $(1.75 \pm 1.75)\ 10^{-1}$ | Bielski, 1978 | j |
| 49 | $O_2^- + H_2O_2 \rightarrow OH + OH^- + O_2$ | 2 | $(1.30 \pm 0.70)\ 10^{-1}$ | Weinstein and Bielski, 1979 | |
| 50 | $O_2^- + O_3 \rightarrow O_3^- + O_2$ | 2 | $(1.52 \pm 0.05)\ 10^{+9}$ | Sehested et al., 1983 | |
| 51 | $O_2^- + O_3^- \rightarrow 2OH^- + 2O_2$ | 2 | $(5.00 \pm 2.50)\ 10^{+4}$ | Gonzalez and Mártire, 1997 | j |
| 52 | $O_3^- \rightarrow O^- + O_2$ | 1 | $(4.28 \pm 1.41)\ 10^{+3}$ | Behar and Czapski, 1968; Gall and Dorfman, 1969; Bobrowski et al., 1976; Elliot and McCracken, 1989 | |
| 53 | $O_3^- + H^+ \rightarrow OH + O_2$ | 2 | $(9.00 \pm 1.00)\ 10^{+10}$ | Sehested et al., 1984 | |
| 54 | $O_3^- + H^+ \rightarrow HO_3$ | 2 | $(5.20 \pm 0.60)\ 10^{+10}$ | Bühler et al., 1984 | |
| 55 | $HO_3 \rightarrow OH + O_2$ | 1 | $(1.00 \pm 0.10)\ 10^{+5}$ | Bühler et al., 1984 | |
| 56 | $HO_3 \rightarrow O_3^- + H^+$ | 1 | $(3.70 \pm 0.30)\ 10^{+4}$ | Bühler et al., 1984 | |
| 57 | $O_3 + OH^- \rightarrow HO_2^- + O_2$ | 2 | $(5.27 \pm 1.27)\ 10^{+1}$ | Forni et al., 1982; Staehelin and Hoigné, 1982; Gordon | |

| | | | | | |
|---|---|---|---|---|---|
| | | | | et al., 1987 | |
| 58 | $O_3 + OH^- \rightarrow HO_2 + O_2^-$ | 2 | $(7.00 \pm 0.70)\ 10^{+1}$ | Staehelin and Hoigné, 1982 | |
| 59 | $O_3 + H_2O_2 \rightarrow OH + HO_2 + O_2$ | 2 | $(3.75 \pm 2.75)\ 10^{-2}$ | Taube and Bray, 1940; Sehested et al., 1982; Staehelin and Hoigné, 1982 | |
| 60 | $O_3 + HO_2^- \rightarrow HO_3 + O_2^-$ | 2 | $(5.50 \pm 1.00)\ 10^{+6}$ | Staehelin and Hoigné, 1982 | |
| 61 | $O(^3P) + O_2 \rightarrow O_3$ | 2 | $(4.00 \pm 2.00)\ 10^{+9}$ | Kläning et al., 1984 | j |
| 62 | $O(^3P) + OH^- \rightarrow HO_2^-$ | 2 | $(4.20 \pm 0.73)\ 10^{+8}$ | Sauer et al., 1984 | |
| 63 | $O(^3P) + H_2O_2 \rightarrow OH + HO_2$ | 2 | $(1.60 \pm 0.32)\ 10^{+9}$ | Sauer et al., 1984 | |
| 64 | $O(^3P) + HO_2^- \rightarrow OH + O_2^-$ | 2 | $(5.30 \pm 2.12)\ 10^{+9}$ | Sauer et al., 1984 | |
| 65 | $O^- + H_2O_2 \rightarrow O_2^- + H_2O$ | 2 | $(2.50 \pm 2.50)\ 10^{+8}$ | Buxton et al., 1988 | j |
| 66 | $HCO_3^- + OH \rightarrow CO_3^- + H_2O$ | 2 | $(9.25 \pm 0.75)\ 10^{+6}$ | Keene et al., 1965; Buxton et al., 1988 | |
| 67 | $CO_3^{2-} + OH \rightarrow CO_3^- + OH^-$ | 2 | $(3.79 \pm 0.32)\ 10^{+8}$ | Thomas, 1965; Weeks and Rabani, 1966; Buxton, 1969; Behar et al., 1970; Buxton et al., 1988; Buxton et al., 1988 | |
| 68 | $HCO_3^- + O_2^- \rightarrow CO_3^- + HO_2^-$ | 2 | $(1.50 \pm 0.50)\ 10^{+6}$ | Schmidt, 1972 | |
| 69 | $CO_3^{2-} + O^- + H_2O \rightarrow CO_3^- + 2OH^-$ | 2 | $(2.50 \pm 2.50)\ 10^{+5}$ | Gonzalez and Mártire, 1997 | j |
| 70 | $CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2$ | 2 | $(5.77 \pm 1.60)\ 10^{+5}$ | Behar et al., 1970; Draganic et al., 1991 | |
| 71 | $CO_3^- + HO_2^- \rightarrow CO_3^{2-} + HO_2$ | 2 | $(3.20 \pm 1.88)\ 10^{+7}$ | Behar et al., 1970; Eriksen et al., 1983; Draganic et al., ; Gonzalez and Mártire, 1997 | |
| 72 | $CO_3^- + HO_2 \rightarrow HCO_3^- + O_2$ | 2 | $(3.53 \pm 2.97)\ 10^{+8}$ | Behar et al., 1970; Herrmann et al., 2000 | |
| 73 | $CO_3^- + O_2^- \rightarrow CO_3^{2-} + O_2$ | 2 | $(5.25 \pm 0.71)\ 10^{+8}$ | Behar et al., 1970; Eriksen et al., 1985 | |
| 74 | $CO_3^- + O_3^- \rightarrow CO_3^{2-} + O_3$ | 2 | $(6.00 \pm 2.00)\ 10^{+7}$ | Holcman et al., 1982 | |
| 75 | $2CO_3^- + O_2 + 2H_2O \rightarrow 2CO_2{\bullet}H_2O + 2O_2^-$ | 2 | $(1.50 \pm 1.29)\ 10^{+7}$ | Weeks and Rabani, 1966; Chen et al., 1973; Zhestkova and Pikaev, 1976; McGinniss and Kah, 1977; Mulac et al., 1984; Eriksen et al., 1985; Saini and Bhattacharyya, 1986; Mandal et al., 1991; Czapski et al., 1994 | |
| 76 | $CO_2{\bullet}H_2O + OH \rightarrow CO_3^- + H^+ + H_2O$ | 2 | $(0.70 \pm 1.68)\ 10^{+6}$ | | j |
| 77 | $Br^- + H_2O + O_3 \rightarrow HOBr + O_2 + OH^-$ | 3 | $(2.58 \pm 1.29)\ 10^{+2}$ | Liu et al., 2001 | m |
| 78 | $Br^- + O_3 \rightarrow O_2 + BrO^-$ | 2 | $(2.39 \pm 0.59)\ 10^{+2}$ | Taube, 1942; Garland et al., 1980; Haruta and Takeyama, 1981; Haag and Hoigné, 1983 | k |

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| 79 | $BrO^- + O_3 \rightarrow Br^- + 2O_2$ | 2 | $(3.30 \pm 0.60) 10^{+2}$ | Haag and Hoigné, 1983 | |
| 80 | $BrO^- + 2O_3 \rightarrow BrO_3^- + 2O_2$ | 3 | $(1.00 \pm 0.20) 10^{+2}$ | Haag and Hoigné, 1983 | |
| 81 | $HOBr + O_3 \rightarrow BrO_2^- + O_2 + H^+$ | 2 | $(1.30 \pm 0.78) 10^{+2}$ | Haag and Hoigné, 1983 | h |
| 82 | $BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$ | 2 | $(1.00 \pm 0.55) 10^{+6}$ | Hoigné et al., 1985 | h |
| 83 | $Br_2 + Br^- \rightarrow Br_3^-$ | 2 | $(1.50 \pm 0.38) 10^{+9}$ | Ruasse et al., 1986 | |
| 84 | $Br_3^- \rightarrow Br_2 + Br^-$ | 1 | $(5.00 \pm 1.25) 10^{+7}$ | Ruasse et al., 1986 | |
| 85 | $Br_2 + H_2O \rightarrow HOBr + Br^- + H^+$ | 1 | $(9.70 \pm 1.22) 10^{+1}$ | Beckwith et al., 1996 | |
| 86 | $Br_2 + HCO_3^- + H_2O \rightarrow HOBr + Br^- + CO_2H_2O$ | 2 | $(1.60 \pm 0.83) 10^{+5}$ | Beckwith et al., 1996 | l,m |
| 87 | $HOBr + Br^- + CO_2H_2O \rightarrow Br_2 + HCO_3^- + H_2O$ | 3 | $(1.20 \pm 0.62) 10^{+7}$ | Beckwith et al., 1996 | l,m |
| 88 | $BrO^- + HCO_3^- \rightarrow HOBr + CO_3^{2-}$ | 2 | $(3.90 \pm 2.18) 10^{+7}$ | Troy and Margerum, 1991 | m |
| 89 | $HOBr + CO_3^{2-} \rightarrow BrO^- + HCO_3^{2-}$ | 2 | $(3.00 \pm 1.53) 10^{+8}$ | Troy and Margerum, 1991 | m |
| 90 | $Br_2 + HO_2^- + H_2O \rightarrow HOBr + Br^- + H_2O_2$ | 2 | $(8.80 \pm 4.49) 10^{+7}$ | Beckwith et al., 1996 | l,m |
| 91 | $HOBr + Br^- + H_2O_2 \rightarrow Br_2 + HO_2^- + H_2O$ | 3 | $(3.90 \pm 1.99) 10^{+4}$ | Beckwith et al., 1996 | l,m |
| 92 | $HOBr + H_2O_2 \rightarrow Br^- + O_2 + H^+ + H_2O$ | 2 | $(1.50 \pm 0.17) 10^{+4}$ | Taube, 1942 | |
| 93 | $HOBr + HO_2^- \rightarrow Br^- + O_2 + H^+ + H_2O$ | 2 | $(7.60 \pm 1.30) 10^{+8}$ | von Gunten and Oliveras, 1997 | |
| 94 | $Br^- + H_2O_2 + H^+ \rightarrow HOBr + H_2O$ | 3 | $(1.41 \pm 0.01) 10^{-2}$ | Mohammad and Liebhafsky, 1934 | n |
| 95 | $Br^- + H_2O_2 \rightarrow HOBr + OH^-$ | 2 | $(2.14 \pm 0.13) 10^{-5}$ | Mohammad and Liebhafsky, 1934 | n |
| 96 | $2BrO^- \rightarrow BrO_2^- + Br^-$ | 2 | $(6.00 \pm 4.00) 10^{-7}$ | Beckwith and Margerum, 1997 | |
| 97 | $HBrO_2 + BrO_2 \rightarrow HOBr + BrO_3^-$ | 2 | $(3.91 \pm 0.26) 10^{+1}$ | de Barros Faria et al., 1994 | |
| 98 | $2HOBr + CO_3^{2-} \rightarrow HBrO_2 + Br^- + HCO_3^-$ | 3 | $(3.20 \pm 1.70) 10^{-1}$ | Beckwith and Margerum, 1997 | m |
| 99 | $2HOBr + OH^- \rightarrow HBrO_2 + Br^- + H_2O$ | 3 | $(1.50 \pm 0.75) 10^{-1}$ | Beckwith and Margerum, 1997 | m |
| 100 | $2HOBr \rightarrow HBrO_2 + Br^- + H^+$ | 2 | $(2.30 \pm 1.70) 10^{-3}$ | Beckwith and Margerum, 1997 | |
| 101 | $2HBrO_2 \rightarrow HBr + BrO_3^- + H^+$ | 2 | $(8.00 \pm 1.00) 10^{+2}$ | de Barros Faria et al., 1994 | |
| 102 | $Br_2O_4 + OH^- \rightarrow BrO_3^- + BrO_2^- + H^+$ | 2 | $(7.45 \pm 4.02) 10^{+8}$ | Buxton and Dainton, 1968 | m |
| 103 | $BrO_2^- + O(^3P) \rightarrow BrO^- + O_2$ | 2 | $(1.24 \pm 0.67) 10^{+9}$ | Amichai and Treinin, 1970 | m,o |
| 104 | $BrO_3^- + O(^3P) \rightarrow BrO_2^- + O_2$ | 2 | $(4.25 \pm 2.75) 10^{+7}$ | Hart and Brown, 1980; Kläning et al., 1984 | k |
| 105 | $HOBr^- \rightarrow Br^- + OH$ | 1 | $(3.30 \pm 0.40) 10^{+7}$ | Zehavi and Rabani, 1972 | |
| 106 | $HOBr^- \rightarrow Br + OH^-$ | 1 | $(4.20 \pm 0.60) 10^{+6}$ | Zehavi and Rabani, 1972 | |
| 107 | $Br + OH^- \rightarrow HOBr^-$ | 2 | $(2.50 \pm 1.57) 10^{+11}$ | Mamou et al., 1977 | |
| 108 | $HOBr^- + H^+ \rightarrow Br + H_2O$ | 2 | $(4.40 \pm 0.80) 10^{+10}$ | Zehavi and Rabani, 1972 | |
| 109 | $Br + H_2O \rightarrow HOBr^- + H^+$ | 1 | $(1.36 \pm 0.71) 10^{+0}$ | Kläning and Wolff, 1985 | m |
| 110 | $Br_2^- + OH^- \rightarrow HOBr^- + Br^-$ | 2 | $(5.14 \pm 2.23) 10^{+7}$ | Mamou et al., 1977 | p |
| 111 | $Br + Br^- \rightarrow Br_2^-$ | 2 | $(1.17 \pm 0.28) 10^{+10}$ | Lilie and Koskikallio, 1984; Nagarajan and Fessenden, 1985; Lal et al., 1986; Lind et al., 1991; Scaiano et al., | j |

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| | | | | 1993; Merenyi and Lind, 1994; Weldon et al., 1995 | |
| 112 | $Br_2^- \rightarrow Br + Br^-$ | 1 | $(4.71 \pm 0.47)\ 10^{+4}$ | Lind et al., 1991 | n |
| 113 | $2Br_2^- \rightarrow Br_3^- + Br^-$ | 2 | $(2.04 \pm 0.42)\ 10^{+9}$ | Cercek et al., 1965; Sutton et al., 1965; Matheson et al., 1966; Buxton and Dainton, 1968; Thornton and Laurence, 1970; Thornton and Laurence, 1973; Broszkiewicz, 1976; Morliere and Patterson, 1982; D'Angelantonio et al., 1988; Ferraudi, 1993 | k |
| 114 | $2Br \rightarrow Br_2$ | 2 | $(1.50 \pm 0.20)\ 10^{+10}$ | Zhu and Harris, 1991 | q |
| 115 | $Br + Br_2^- \rightarrow Br_2 + Br^-$ | 2 | $(5.00 \pm 2.70)\ 10^{+9}$ | Merenyi and Lind, 1994 | m |
| 116 | $Br + BrO^- \rightarrow Br^- + BrO$ | 2 | $(4.10 \pm 2.17)\ 10^{+9}$ | Kläning and Wolff, 1985 | m |
| 117 | $Br_2^- + BrO \rightarrow BrO + 2Br^-$ | 2 | $(8.00 \pm 0.70)\ 10^{+7}$ | Buxton and Dainton, 1968 | |
| 118 | $Br_2^- + BrO_2^- \rightarrow BrO + BrO^- + Br^-$ | 2 | $(8.00 \pm 0.80)\ 10^{+7}$ | Buxton and Dainton, 1968 | |
| 119 | $2BrO + H_2O \rightarrow BrO^- + BrO_2^- + 2H^+$ | 2 | $(2.60 \pm 0.38)\ 10^{+9}$ | Amichai and Treinin, 1970; Kläning and Wolff, 1985 | k |
| 120 | $2BrO_2 \rightarrow Br_2O_4$ | 2 | $(6.00 \pm 3.18)\ 10^{+9}$ | Field et al., 1982 | m |
| 121 | $Br_2O_4 \rightarrow 2BrO_2$ | 1 | $(3.10 \pm 1.67)\ 10^{+5}$ | Field et al., 1982 | m |
| 122 | $BrO + BrO_2^- \rightarrow BrO^- + BrO_2$ | 2 | $(3.40 \pm 0.70)\ 10^{+8}$ | Buxton and Dainton, 1968 | |
| 123 | $BrO^- + CO_3^- \rightarrow BrO + CO_3^{2-}$ | 2 | $(4.30 \pm 0.40)\ 10^{+7}$ | Buxton and Dainton, 1968 | |
| 124 | $BrO_2^- + CO_3^- \rightarrow BrO_2 + CO_3^{2-}$ | 2 | $(8.00 \pm 3.00)\ 10^{+7}$ | Kläning et al., 1975 Buxton and Dainton, 1968 | k |
| 125 | $Br + H_2O_2 \rightarrow Br^- + HO_2 + H^+$ | 2 | $(2.50 \pm 1.35)\ 10^{+9}$ | Sutton et al., 1965 | h |
| 126 | $Br_2^- + H_2O_2 \rightarrow 2Br^- + HO_2 + H^+$ | 2 | $(1.00 \pm 0.52)\ 10^{+3}$ | Hasegawa and Neta, 1978 | h |
| 127 | $Br_2 + HO_2 \rightarrow Br_2^- + O_2 + H^+$ | 2 | $(1.30 \pm 0.16)\ 10^{+8}$ | Sutton and Downes, 1972; Schwarz and Bielski, 1986 | k |
| 128 | $Br_3^- + HO_2 \rightarrow Br_2^- + Br^- + O_2 + H^+$ | 2 | $(1.00 \pm 0.50)\ 10^{+8}$ | Cercek et al., 1965 | |
| 129 | $Br_2 + O_2 \rightarrow Br_2^- + O_2$ | 2 | $(5.30 \pm 0.30)\ 10^{+9}$ | Sutton and Downes, 1972; Schwarz and Bielski, 1986 | k |
| 130 | $Br_3^- + O_2 \rightarrow Br_2^- + Br^- + O_2$ | 2 | $(2.65 \pm 1.15)\ 10^{+9}$ | Sutton and Downes, 1972; Schwarz and Bielski, 1986 | k |
| 131 | $BrO^- + O_2 + H_2O \rightarrow Br + O_2 + 2OH^-$ | 2 | $(2.00 \pm 1.04)\ 10^{+8}$ | Schwarz and Bielski, 1986 | h,r |
| 132 | $HOBr + O_2^- \rightarrow Br + O_2 + OH^-$ | 2 | $(2.23 \pm 1.28)\ 10^{+9}$ | Sutton and Downes, 1972; Schwarz and Bielski, 1986 | k |
| 133 | $HOBr + OH \rightarrow BrO + H_2O$ | 2 | $(2.00 \pm 1.04)\ 10^{9}$ | Kläning and Wolff, 1985 | m |
| 134 | $BrO^- + OH \rightarrow BrO + OH^-$ | 2 | $(3.00 \pm 1.65)\ 10^{+9}$ | Buxton and Dainton, 1968 | m |
| 135 | $BrO_2 + OH \rightarrow BrO_3^- + H^+$ | 2 | $(2.00 \pm 1.10)\ 10^{+9}$ | Field et al., 1982 | m |
| 136 | $BrO_2^- + OH \rightarrow BrO_2 + OH^-$ | 2 | $(2.05 \pm 0.25)\ 10^{+9}$ | Buxton and Dainton, 1968; Amichai et al., 1969 | k |
| 137 | $BrO^- + O^- \rightarrow BrO + OH^-$ | 2 | $(3.55 \pm 0.65)\ 10^{+9}$ | Buxton and Dainton, 1968; Amichai et al., 1969 | k |
| 138 | $BrO_2^- + O^- + H_2O \rightarrow BrO_2 + 2OH^-$ | 2 | $(2.05 \pm 0.25)\ 10^{+9}$ | Buxton and Dainton, 1968; | k |

| | | | Amichai et al., 1969 | |
|---|---|---|---|---|
| Mass accommodation coefficients | | ( $x^* \pm \sigma$ ) [s] | references | notes |
| 139 | $\alpha(O_3)$ | $(5.01 \pm 4.99)\ 10^{-1}$ | Utter et al., 1992 | j |
| 140 | $\alpha(O_2)$ | $(5.05 \pm 4.95)\ 10^{-1}$ | Sander and Crutzen, 1996 | j |
| 141 | $\alpha(OH)$ | $(5.05 \pm 4.95)\ 10^{-1}$ | Takami et al., 1998 | j |
| 142 | $\alpha(HO_2)$ | $(5.55 \pm 3.16)\ 10^{-1}$ | Mozurkewich et al., 1987; Hanson et al., 1992; Kanaya et al., 2000; Carslaw et al., 2002 | j |
| 143 | $\alpha(H_2O_2)$ | $(1.00 \pm 0.20)\ 10^{-1}$ | Worsnop et al., 1989 | |
| 144 | $\alpha(CO_2)$ | $(5.00 \pm 5.00)\ 10^{-2}$ | Sander and Crutzen, 1996; Herrmann et al., 2000; Sander et al., 2006 | j |
| 145 | $\alpha(Br_2)$ | $(3.80 \pm 1.14)\ 10^{-2}$ | Hu et al., 1995 | t |
| 146 | $\alpha(HBr)$ | $(5.00 \pm 0.09)\ 10^{-2}$ | Sander et al., 2006 | u |
| 147 | $\alpha(HOBr)$ | $(6.00 \pm 2.00)\ 10^{-1}$ | Wachsmuth et al., 2002 | |
| Henry's law coefficients ($H_{298}$) | | ( $x^* \pm \sigma$ ) [v] | references | notes |
| 148 | $H(O_3)$ | $(1.09 \pm 0.15)\ 10^{-2}$ | Sander, 1999 | |
| 149 | $H(O_2)$ | $(1.25 \pm 0.05)\ 10^{-3}$ | Sander, 1999 | |
| 150 | H(OH) | $(1.55 \pm 3.33)\ 10^{+3}$ | Sander, 1999 | |
| 151 | $H(HO_2)$ | $(4.90 \pm 2.53)\ 10^{+3}$ | Sander, 1999 | |
| 152 | $H(H_2O_2)$ | $(9.45 \pm 2.17)\ 10^{+4}$ | Sander, 1999 | |
| 153 | $H(CO_2)$ | $(3.54 \pm 0.42)\ 10^{-2}$ | Sander, 1999 | |
| 154 | $H(Br_2)$ | $(7.79 \pm 0.87)\ 10^{-1}$ | Sander, 1999 | k,w |
| 155 | H(HBr) | $(9.13 \pm 2.73)\ 10^{-1}$ | Sander, 1999 | k, x |
| 156 | H(HOBr) | $(6.10 \pm 4.20)\ 10^{+3}$ | Blatchley et al., 1992; Frenzel et al., 1998 | k, y |
| Acid/base equilibrium constants ($K_{eq,298}$) | | ( $x^* \pm \sigma$ ) [z] | references | notes |
| 157 | $K(H_2O)$ | $(1.07 \pm 0.13)\ 10^{-14}$ | Sillén and Martell, 1964 | |
| 158 | $K(H_2O_2)$ | $(1.96 \pm 0.55)\ 10^{-12}$ | Sauer et al., 1984 | |
| 159 | $K(HO_2)$ | $(1.82 \pm 1.43)\ 10^{-5}$ | Bielski, 1978; Bielski et al., 1985 | |
| 160 | K(OH) | $(1.26 \pm 0.63)\ 10^{-12}$ | Buxton et al., 1988 | j |
| 161 | $K(CO_2 \bullet H_2O)$ | $(3.80 \pm 0.78)\ 10^{-7}$ | Sillén and Martell, 1964 | |
| 162 | $K(HCO_3^-)$ | $(4.88 \pm 0.60)\ 10^{-11}$ | Sillén and Martell, 1964 | |
| 163 | $K(HCO_3)$ | $(3.98 \pm 3.97)\ 10^{+4}$ | Czapski et al., 1999 | j |
| 164 | K(HBr) | $(1.00 \pm 0.10)\ 10^{+9}$ | Hunt et al., 2004 | aa |
| 165 | K(HOBr) | $(1.63 \pm 0.37)\ 10^{-9}$ | Troy and Margerum, 1991 | |
| 166 | $K(HBrO_2)$ | $(3.70 \pm 0.90)\ 10^{-4}$ | Faria et al., 1994 | |

| | Kinetic salt effect parameter | ( $x^{*} \pm \sigma$ ) [bb] | references | notes |
|---|---|---|---|---|
| 167 | Ψ | $(7.50 \pm 2.50)\ 10^{-1}$ | | cc |

(a) Unitless. A log-normal probability distribution is used for all input parameters except the kinetic salt effect parameter, Ψ. The σ of each input parameter determines the shape of the probability distribution and may be larger than the mean. (b) The interface reaction rate constant is determined by adjusting this parameter in the simulations during the initial dark period until the $Br_{2(g)}$ curve fits the experimental observations. (c) Measurement by Laskin et al. (2006) for interfacial reaction between gas-phase OH and surface-bound $Cl^-$ taken as a lower-bound, with unity as an upper-bound. (d) Reaction order. (e) Dimensions of $cm^{3\times(Order-1)}$ molecules $^{-(Order-1)}$ $seconds^{-1}$. (f) Photolysis rate constants are based entirely or in part on the experiments in this study. (g) We take the rate constant of this reaction to be the rate constant for OH + BrO → products minus the rate constant for $HO_2$ + Br → HBr + $O_2$, which are both listed in Sander et al. (2006), and assume that the overall error factor used by Sander et al. is the product of the error factors for these two reactions. (h) This mean as an upper bound or lower bound in the reference, so it may be a misestimate. The standard deviation was assigned from the log-normal random sampling technique; see section 2.1 for details. (i) Dimensions of $M^{(1-Order)}$ $seconds^{-1}$. (j) It was not possible to establish an uncertainty range from the source. The mean and uncertainty range of this input parameter are chosen to be consistent with Nissenson et al. (2008). (k) Mean and standard deviation calculated from mean values given in references. (l) Mean calculated with the Alternate Bronsted Extrapolation. See Hunt et al. (2004) for details. (m) Standard deviation assigned from log-normal random sampling technique; see section 2.1 for details. (n) Rate constant recalculated from data in reference. (o) Calculated with $k = 0.31 k_{O(^3P)+O_2}$, where $k_{O(^3P)+O_2} = 4.0\times10^9\ M^{-1}\ s^{-1}$, as in Kläning et al. (1984). Also see footnote for this reaction in Hunt et al. (2004). (p) Rate constant calculated using equilibrium constant from referenced paper, as well as rate constant for backward reaction (parameter 54). (q) Non-geminate recombination data in $CCl_4$. (r) Rate constant estimated in reference from a similar reaction. (s) Dimensionless. (t) Arbitrary standard deviation of ± 30% set, due to lack of available data. (u) This mean is an upper bound or lower bound in the reference, so it may be a misestimate. Arbitrary standard deviation of ± 30% set, due to lack of available data. (v) Dimensions of M $atm^{-1}$. (w) Did not include value published by Dubik et al., 1987, in calculation. (x) p$K_a$ of HBr taken to be -9, as given by Atkins and de Paula, 2006. (y). These are the only two consistent references given by Sander (1999). The first gives H(HOBr) > $1.9\times10^3$ M $atm^{-1}$, whereas the second gives H(HOBr) = $6.1\times10^3$ M $atm^{-1}$. We take the latter as the mean, and set the former equal to μ - σ. (z) Units in M. (aa) Arbitrary standard deviation of ± 10%. (bb) Unitless. (cc) Allowed to vary from 0 to 1.

## References for Supplementary Table 2


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