

Tables S5-S8: Photochemical reactions involving mercury

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The tables listed here give the reactions used to represent atmospheric mercury in the model described by *Sillman et al.* [2007] (Reactive mercury in the troposphere: Model formation and results for Florida, the northeastern U.S. and the Atlantic Ocean, *J. Geophys. Res.*, 10.1029/2006JD008227, 2007).

Aqueous reactions for other species and gas-phase halogen chemistry is described in Tables S1-S4. The mechanism for gas-phase photochemistry (other than mercury or halogens) is described in Appendix A of *Ito et al.* [2007].

This file includes the following tables:

Table S5: Henry's law coefficients for species containing mercury.

Table S6: Aqueous equilibrium coefficients for species containing mercury.

Table S7: Aqueous reactions for species containing mercury.

Table S8: Gas-phase reactions for species containing mercury.

Table S5
Henry's Law coefficients for species containing mercury

Values here represent the physical Henry constants (K_H) and do not take into account enhanced solubilities due to dissociation equilibria.

Abbreviations and units:

K_{H298} =Henry's law coefficient at 298 K, expressed in $M \text{ atm}^{-1}$.

ΔH = enthalpy of solution, expressed as $\Delta H/R$ (where R represents the gas constant) in units $^{\circ}K$.

The temperature dependence is represented by $K_H = K_{H298} \exp[-\Delta H/R(1/T - 1/298)]$ for temperature T in $^{\circ}K$.

Species	K_{H298}	$\Delta H/R$	Reference
Hg	0.11E+00	0.	
Hg(OH) ₂	1.2E+04	0.	
HgO	1.4E+06	0.	
HgCl ₂	1.4E+06	0.	
HgBr ₂	1.4E+06	0.	
Hg(SO ₃) ₂ ¹	1.0E+08 ¹		see note 1.

1. Species such as Hg(SO₃)₂ that form soluble aerosols are represented by a gas-phase pseudo-species with a very high Henry constant, which insures rapid incorporation into the aqueous phase. This is used in model calculations that do not include explicit treatment of aerosols.

Table S6
Aqueous equilibrium coefficients for species containing mercury

K_{aq} represents the equilibrium constant for reactions with the form $C \rightleftharpoons A+B$, with format $K_{aq} = [A][B]/[C]$, in M.

Abbreviations and units:

K_{aq298} =equilibrium constant at 298 K, in M.

ΔH = reaction enthalpy, expressed as $\Delta H/R$ (where R represents the gas constant) in units $^{\circ}K$.

The temperature dependence is represented by $K_{aq} = K_{aq298} \exp[-\Delta H/R(1/T - 1/298)]$ for temperature T in $^{\circ}K$.

Reaction	K_{aq298}	$\Delta H/R$	Reference
$Hg(OH)_2 \rightleftharpoons OH^- + HgOH^+$	2.344E-11	0.	<i>Lin, 1997, 1998a, 2005</i>
$HgOH^+ \rightleftharpoons OH^- + Hg^{+2}$	2.455E-12	0.	<i>Lin, 1997, 1998a, 2005,</i> see note 1
$HgOHCl \rightleftharpoons OH^- + HgCl^+$	1.122E-11	0.	<i>Lin, 1997, 1998a, 2005</i> see note 2
$HgCl^+ \rightleftharpoons Cl^- + Hg^{+2}$	6.012E-08	0.	<i>Lin, 1997, 1998a, 2005</i>
$HgCl_2 \rightleftharpoons Cl^- + HgCl^+$	1.995E-07	0.	<i>Lin, 1997, 1998a, 2005,</i> see note 3
$HgOHBr \rightleftharpoons OH^- + HgBr^+$	1.122E-11	0.	<i>Lin, 1997, 1998a, 2005,</i> see note 2
$HgBr^+ \rightleftharpoons Br^- + Hg^{+2}$	6.012E-08	0.	<i>Lin, 1997, 1998a, 2005</i>
$HgBr_2 \rightleftharpoons Br^- + HgBr^+$	1.995E-07	0.	<i>Lin, 1997, 1998a, 2005,</i> see note 3
$HgSO_3 \rightleftharpoons SO_3^{-2} + Hg^{+2}$	1.995E-13	0.	<i>van Loon, 2001</i>
$Hg(SO_3)_2^{-2} \rightleftharpoons SO_3^{-2} + HgSO_3$	3.981E-12	0.	<i>van Loon, 2001</i>

Notes

1. The equilibrium coefficient K_e for $\text{HgOH}^+ \leftrightarrow \text{OH}^- + \text{Hg}^{+2}$ was derived from reported coefficients for $\text{Hg}(\text{OH})_2 \leftrightarrow 2\text{OH}^- + \text{Hg}^{+2}$ (K_1) and $\text{Hg}(\text{OH})_2 \leftrightarrow \text{OH}^- + \text{HgOH}^+$ (K_2). The value shown here for K_e is K_1/K_2 and is mathematically equivalent to the reported values.
2. The equilibrium coefficient K_e for $\text{HgOHCl} \leftrightarrow \text{OH}^- + \text{HgCl}^+$ was derived from reported coefficients for $\text{HgOHCl} \leftrightarrow \text{OH}^- + \text{Hg}^{+2} + \text{Cl}^-$ (K_1) and $\text{HgCl}^+ \leftrightarrow \text{Cl}^- + \text{Hg}^{+2}$ (K_2). The value shown here for K_e is K_1/K_2 and is mathematically equivalent to the reported values. The equivalent derivation was used for HgOHBr .
3. The equilibrium coefficient K_e for $\text{HgCl}_2 \leftrightarrow \text{Cl}^- + \text{HgCl}^+$ was derived from reported coefficients for $\text{HgCl}_2 \leftrightarrow 2\text{Cl}^- + \text{HgCl}^+$ (K_1) and $\text{HgCl}^+ \leftrightarrow \text{Cl}^- + \text{Hg}^{+2}$ (K_2). The value shown here for K_e is K_1/K_2 and is mathematically equivalent to the reported values. The equivalent derivation was used for HgBr_2 .

Table S7
Aqueous reactions of species containing mercury

k_{298} : rate constant at 298 K, in $M s^{-1}$ (for reactions involving two species) or s^{-1} for reactants involving a single species.

E_a : activation energy, expressed as E_a/R (where R represents the gas constant) in units $^{\circ}K$.

The temperature dependence is represented by $k_T = k_{298} \exp[-E_a/R(1/T - 1/298)]$ for temperature T in $^{\circ}K$.

Reaction	k_{298}	E_a/R	References
$Hg^0 + O_3 \rightarrow Hg^{+2} + 2OH^-$	4.7E+07	0.	<i>Munthe, 1992</i>
$Hg^0 + OH \rightarrow Hg^{+2} + 2OH^-$	2.0E+09	0	<i>Lin, 1997.</i> see note 1.
$HgSO_3 \rightarrow Hg + SO_2$	1.06E-02	0.	<i>van Loon, 2000</i>
$HgO + H^+ \rightarrow Hg^{+2} + OH^-$	1.0E+10	0.	<i>Pleijel and Munthe, 1995; Hedgecock, 2005</i>
$Hg^0 + HOCl \rightarrow Hg^{+2} + 2OH^-$	2.09E+06	0.	<i>Lin, 1998b</i>
$Hg^0 + OCl^- \rightarrow Hg^{+2} + OH^-$	1.990E+06	0.	<i>Lin, 1998b</i>
$Hg^{+2} + HO_2 \rightarrow Hg^0 + 2H^+$	1.7E+04		<i>Pekkonen, 1998;</i> challenged by <i>Gartfeldt, 2003</i>
$Hg^{+2} + O_2^- \rightarrow Hg^0 + H^+$	1.7E+04		<i>Pekkonen, 1998;</i> challenged by <i>Gartfeldt, 2003</i>

$\text{HgCl}^+ + \text{HO}_2 \rightarrow \text{Hg}^0 + \text{Cl}^- + 2\text{H}^+$	1.7E+04		<i>Pekkonen</i> , 1998; challenged by <i>Gartfeldt</i> , 2003 see note 2
$\text{HgCl}^+ + \text{O}_2^- \rightarrow \text{Hg}^0 + \text{Cl}^- + \text{H}^+$	1.7E+04		<i>Pekkonen</i> , 1998; challenged by <i>Gartfeldt</i> , 2003. see note 2.
$\text{HgSO}_3 + \text{HO}_2 \rightarrow \text{Hg}^0 + \text{SO}_3^{-2} + 2\text{H}^+$	1.7E+04		<i>Pekkonen</i> , 1998; challenged by <i>Gartfeldt</i> , 2003. see note 2
$\text{HgSO}_3 + \text{O}_2^- \rightarrow \text{Hg}^0 + \text{SO}_3^{-2} + \text{H}^+$	1.7E+04		<i>Pekkonen</i> , 1998; challenged by <i>Gartfeldt</i> , 2003. see note 2.

1. It is unclear how to include the reaction of Hg with OH(aq). *Lin and Pekkonen* [1997] report this reaction in two stages: $\text{Hg}^0 + \text{OH} \rightarrow \text{Hg}^+$; $\text{Hg}^+ + \text{OH} \rightarrow \text{Hg}^{+2}$. However, *Pekkonen and Lin* [1998] also report the reaction $\text{Hg}^+ + \text{O}_2^- \rightarrow \text{Hg}^0$, and the equivalent reaction with HO₂, both with an indeterminate fast rate. *Hedgecock et al* [2005] omit this reaction. If included, the result of the reaction sequence would depend on the relative rate of the two pathways for H₊. Other models have approximated the forward reaction as $\text{Hg}^0 + \text{OH} \rightarrow \text{Hg}^{+2}$ [*Ryaboshapko et al.*, 2002], which is what we have done here. See also the summary in *Lin et al.*, 2006.

2. Analogous reactions are included for all species containing Hg^{II}.

Table S8
Gas-phase reactions for species containing mercury

Units are molec. cm⁻³ s⁻¹ for reactions involving two species and s⁻¹ for reactants involving a single species.

Abbreviations:

k_0 =equilibrium constant at 0 K, in M.

E_a = activation energy, expressed as E_a/R (where R represents the gas constant) in units °K.

The temperature dependence is represented by $k_T = k_0 \exp[-E_a/R(1/T)]$ for temperature T in °K.

Reaction	k_0	E_a/R	References
Hg+ O ₃ → HgO	2.1E-18	1256.	<i>Hall, 1995</i>
Hg+ Cl ₂ → HgCl ₂	2.6E-18	0.	<i>Ariya, 2002</i>
Hg+ Cl→ HgCl ¹	1.0E-11	0.	<i>Ariya, 2002, Hedgecock et al., 2005; see note 1</i>
Hg+ HCl→ HgCl ¹	1.0E-19	0.	<i>Hall and Bloom, 1993</i>
Hg+ Br ₂ → HgBr ₂	9.0E-17	0.	<i>Ariya, 2002</i>
Hg+ Br→ HgBr ¹	3.2E-12	0.	<i>Ariya, 2002, Hedgecock et al., 2005; see note 1</i>
Hg+ HBr→ HgBr ¹	1.0E-19	0.	<i>Hall and Bloom, 1993</i>
Hg+ H ₂ O ₂ → HgO	1.0E-19	0.	<i>Tokos, 1998; Hedgecock, 2005</i>
Hg+ OH→ HgO	8.0E-14	0.	<i>Sommar, 2001; Hedgecock, 2005</i>

1. The reactions Hg+Cl and Hg+Br are represented as forming HgCl₂ and HgBr₂ in most studies. We have represented them by the pseudo-species HgCl and HgBr in order to insure mass conservation for Cl and Br.

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