CHAPTER 3 – SUPPLEMENT 1

Evaluation of Atmospheric Loss Processes: OH Kinetics Supplement

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Rate coefficients for the reaction of the OH radical with the compounds included in the SPARC Lifetime report have received various amounts of attention. The figures included in this supplement contain (1) a summary of the available literature data for each reaction, (2) the SPARC recommendation for the OH reaction-rate coefficient (solid line) and the basis of the recommendation, and (3) the 2σ uncertainty range in the recommended reaction-rate coefficient shown as the shaded area. The original (un-normalized) experimental data are plotted in the figures unless noted otherwise. The recommended temperature dependence, $E/R$, was determined from fits of data normalized to the recommended $k(298 \text{ K})$, hence, some of the plotted data used in the fits may not appear to be in agreement with the shaded area of the recommended fit.

The uncertainties quoted herein follow the format given in the NASA/JPL\(^1\) data evaluation where the uncertainty factor $f(T)$ corresponds to the 1σ estimated uncertainty range in the rate coefficient, $k(T)$ at temperature $T$

$$f(T) = f(298 \text{ K}) \exp \left[ g \left( \frac{1}{T} - \frac{1}{298} \right) \right]$$

with the $f(298 \text{ K})$ factor corresponding to the 1σ estimated uncertainty range in the room-temperature rate coefficient, $k(298 \text{ K})$, and $g$ is a parameter used to describe the possible increase in uncertainty at temperatures other than 298 K. Therefore, the uncertainty factor corresponding to the 2σ estimated uncertainty at any temperature is calculated as the square of $f(T)$, i.e., $f(T)^2$.

Fully halogenated compounds do not undergo measurable reaction with OH at atmospheric temperatures. Upper limits of the rate coefficients for the reactions of CFCs (CCl$_3$F, CCl$_2$F$_2$, CCl$_2$FCCIF$_2$, CClF$_2$CCIF$_2$, CF$_3$CCIF$_2$, and CCl$_4$) were estimated based on thermochemistry by equating the activation energy with the reaction endothermicity\(^1,2\) for the abstraction of a Cl atom and assuming an Arrhenius pre-exponential factor of $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The corresponding estimations for the reactions of Halons (CBrClF$_2$, CBrF$_3$, CBr$_2$F$_2$, and CBrF$_2$CBrF$_2$) are based on the upper limits of the rate coefficients experimentally obtained above room temperature assuming an Arrhenius pre-exponential factor of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

References


### Table 3.1. Reaction-rate coefficients and estimated uncertainties for the OH + compound gas-phase reactions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Formula</th>
<th>Temperature Range (K) **</th>
<th>$A^*$</th>
<th>$E/R$ (K)</th>
<th>$k(298 \text{ K})^*$</th>
<th>$f(298 \text{ K})$</th>
<th>$g$</th>
<th>Footnotes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CFC - 11</td>
<td>CCl$_3$F</td>
<td>–</td>
<td>10</td>
<td>9695</td>
<td>$&lt; 1$ (-25)</td>
<td>–</td>
<td>–</td>
<td>1,2</td>
</tr>
<tr>
<td>2. CFC - 12</td>
<td>CCl$_2$F$_2$</td>
<td>–</td>
<td>10</td>
<td>11910</td>
<td>$&lt; 1$ (-28)</td>
<td>–</td>
<td>–</td>
<td>1,2</td>
</tr>
<tr>
<td>3. CFC - 113</td>
<td>CCl$_3$FCCIF$_2$</td>
<td>–</td>
<td>10</td>
<td>$&gt; 6220$</td>
<td>$&lt; 1$ (-20)</td>
<td>–</td>
<td>–</td>
<td>3,4</td>
</tr>
<tr>
<td>4. CFC - 114</td>
<td>CClF$_2$CCIF$_2$</td>
<td>–</td>
<td>10</td>
<td>$&gt; 6220$</td>
<td>$&lt; 1$ (-20)</td>
<td>–</td>
<td>–</td>
<td>3,4</td>
</tr>
<tr>
<td>5. CFC - 115</td>
<td>CF$_2$CCIF$_2$</td>
<td>–</td>
<td>10</td>
<td>$&gt; 6220$</td>
<td>$&lt; 1$ (-20)</td>
<td>–</td>
<td>–</td>
<td>3,4</td>
</tr>
<tr>
<td>6. Carbon Tetrachloride</td>
<td>CCl$_4$</td>
<td>–</td>
<td>10</td>
<td>6220</td>
<td>$&lt; 1$ (-20)</td>
<td>–</td>
<td>–</td>
<td>1,2</td>
</tr>
<tr>
<td>7. Nitrous oxide</td>
<td>N$_2$O</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>$&lt; 5.0$ (-17)</td>
<td>–</td>
<td>–</td>
<td>3,a</td>
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<tr>
<td>8. Halon - 1202</td>
<td>CBr$_2$F$_2$</td>
<td>–</td>
<td>1</td>
<td>$&gt; 2200$</td>
<td>$5$ (-16)</td>
<td>–</td>
<td>–</td>
<td>5</td>
</tr>
<tr>
<td>9. Halon - 1211</td>
<td>CBrClF$_2$</td>
<td>–</td>
<td>1</td>
<td>$&gt; 3500$</td>
<td>$8$ (-18)</td>
<td>–</td>
<td>–</td>
<td>2,b</td>
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<tr>
<td>10. Halon - 1301</td>
<td>CBrF$_3$</td>
<td>–</td>
<td>1</td>
<td>$&gt; 3600$</td>
<td>$6$ (-18)</td>
<td>–</td>
<td>–</td>
<td>5</td>
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<tr>
<td>11. Halon - 2402</td>
<td>CBrF$_2$CBrF$_2$</td>
<td>–</td>
<td>1</td>
<td>$&gt; 3600$</td>
<td>$6$ (-18)</td>
<td>–</td>
<td>–</td>
<td>5</td>
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<tr>
<td>12. Methane</td>
<td>CH$_4$</td>
<td>195 – 300</td>
<td>1.85</td>
<td>1690</td>
<td>6.4 (-15)</td>
<td>1.05</td>
<td>50</td>
<td>2,c</td>
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<tr>
<td>13. Methyl Chloroform</td>
<td>CH$_3$CCl$_3$</td>
<td>233 – 379</td>
<td>1.64</td>
<td>1520</td>
<td>1.0 (-14)</td>
<td>1.10</td>
<td>50</td>
<td>5,6</td>
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<td>14. Methyl Chloride</td>
<td>CH$_3$Cl</td>
<td>224 – 298</td>
<td>1.96</td>
<td>1200</td>
<td>3.5 (-14)</td>
<td>1.10</td>
<td>50</td>
<td>2,6,d</td>
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<tr>
<td>15. Methyl Bromide</td>
<td>CH$_3$Br</td>
<td>233 – 300</td>
<td>1.40</td>
<td>1150</td>
<td>3.0 (-14)</td>
<td>1.07</td>
<td>100</td>
<td>2,6,e</td>
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<tr>
<td>16. HCFC - 22</td>
<td>CHClF$_2$</td>
<td>250 – 391</td>
<td>1.03</td>
<td>1600</td>
<td>4.8 (-15)</td>
<td>1.07</td>
<td>100</td>
<td>2,6</td>
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<tr>
<td>17. HCFC - 141b</td>
<td>CH$_2$CClF$_2$</td>
<td>250 – 400</td>
<td>1.25</td>
<td>1600</td>
<td>5.8 (-15)</td>
<td>1.07</td>
<td>100</td>
<td>5,6,f</td>
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<tr>
<td>18. HCFC - 142b</td>
<td>CH$_2$CCIF$_2$</td>
<td>223 – 400</td>
<td>1.30</td>
<td>1770</td>
<td>3.4 (-15)</td>
<td>1.15</td>
<td>50</td>
<td>5,6</td>
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<tr>
<td>19. HFC - 23</td>
<td>CHF$_3$</td>
<td>252 – 298</td>
<td>0.52</td>
<td>2210</td>
<td>3.1 (-16)</td>
<td>1.15</td>
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<td>20. HFC - 32</td>
<td>CH$_2$F$_2$</td>
<td>222 – 384</td>
<td>1.70</td>
<td>1500</td>
<td>1.1 (-14)</td>
<td>1.07</td>
<td>100</td>
<td>5,6</td>
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<tr>
<td>21. HFC - 125</td>
<td>CHF$_2$CF$_3$</td>
<td>220 – 364</td>
<td>0.60</td>
<td>1700</td>
<td>2.0 (-15)</td>
<td>1.10</td>
<td>100</td>
<td>5,6,g</td>
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<tr>
<td>22. HFC - 134a</td>
<td>CH$_3$FCF$_3$</td>
<td>223 – 400</td>
<td>0.95</td>
<td>1600</td>
<td>4.4 (-15)</td>
<td>1.10</td>
<td>100</td>
<td>2,6,h</td>
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<tr>
<td>23. HFC - 143a</td>
<td>CF$_3$CH$_3$</td>
<td>261 – 403</td>
<td>1.06</td>
<td>2010</td>
<td>1.25 (-15)</td>
<td>1.10</td>
<td>100</td>
<td>2,i</td>
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<tr>
<td>24. HFC - 152a</td>
<td>CH$_3$CHF$_2$</td>
<td>210 – 300</td>
<td>0.87</td>
<td>975</td>
<td>3.3 (-14)</td>
<td>1.05</td>
<td>50</td>
<td>5,6,j</td>
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<tr>
<td>25. HFC - 227ea</td>
<td>CF$_3$CHFCCF$_3$</td>
<td>250 – 400</td>
<td>0.48</td>
<td>1680</td>
<td>1.7 (-15)</td>
<td>1.15</td>
<td>75</td>
<td>2,6,k</td>
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<tr>
<td>26. HFC - 245fa</td>
<td>CHF$_3$CH$_2$CF$_3$</td>
<td>273 – 370</td>
<td>0.61</td>
<td>1330</td>
<td>7.0 (-15)</td>
<td>1.15</td>
<td>100</td>
<td>5,6</td>
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<tr>
<td>27. Nitrogen Trifluoride</td>
<td>NF$_3$</td>
<td>–</td>
<td>10</td>
<td>$&gt; 17500$</td>
<td>$&lt; 3$ (-37)</td>
<td>–</td>
<td>–</td>
<td>1,3,1</td>
</tr>
</tbody>
</table>

Footnotes

* Estimated values are given in italics; $A$ is in units of $10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; $k(298$ K) is in units of cm$^3$ molecule$^{-1}$ s$^{-1}$ and $(\times x)$ represents $\times 10^{-x}$; $k(T) = A \exp(-E/RT)$.

** Temperature range of available experimental data considered in the evaluation of the reaction-rate coefficient parameters and uncertainty limits.

1 The recommendation given here was obtained by setting the pre-exponential factor ($A$) to $1 \times 10^{11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and equating the activation energy ($E$) to the reaction endothermicity using the thermochemical parameters reported in JPL10-6 and IUPAC. The JPL10-6 recommendation was derived from experimentally determined rate-coefficient upper limits.

2 $A$ and/or $E/R$ recommendation is revised from JPL10-6.

3 Not evaluated in JPL10-6.

4 The recommended kinetic parameters are taken to be equal to those for the OH + CCl$_4$ reaction.

5 $A$ and $E/R$ recommendation is unchanged from JPL10-6.

6 $f(298$ K) and/or $g$ is revised from JPL10-6.

   a Based on the study by Biermann et al. (1976), who measured a rate coefficient of $3.8 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. A more conservative upper limit ($4.0 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) was reported by Chang and Kaufman (1977b).

   b Rate-coefficient expression was estimated using an estimated Arrhenius $A$-factor and the rate-coefficient upper limit reported by Burkholder et al. (1991) at 373 K.

   c $A$ and/or $E/R$ recommendation was taken from IUPAC data evaluation.

   d The recommended $k(298$ K) was obtained from an average of the data of Hsu and DeMore (1994), Orkin et al. (2013), and Herndon et al. (2001). The recommended $E/R$ was obtained from a fit to the data of Herndon et al. below 298 K.

   e The recommended $k(298$ K) was obtained from an average of the data of Hsu and DeMore (1994) (recalculated based on the JPL10-6-recommended rate coefficient for the OH + CH$_3$CHF$_2$ reference reaction), Chichinin et al. (1994), Mellouki et al. (1992), and Zhang et al. (1992). The recommended value for $E/R$ was derived from a fit to the data of Mellouki et al. below 300 K.

   f The data from Lancar et al. (1993) at T<400 K were used in the fit to obtain $E/R$.

   g The recommended $k(298$ K) was obtained from an average of the data of Talukdar et al. (1991), DeMore (1993), and Young et al. (2009). The recommended value for $E/R$ was taken from Talukdar et al.

   h The present analysis differs from that given in JPL10-6 in that the three rate coefficients reported in DeMore (1993) were averaged in the determination of $E/R$.

   i The present analysis differs from that given in JPL10-6 in that the DF-LMR results of Talukdar et al. (1991) were not included in the analysis for $k(298$ K), although their LP-LIF results were included.

   j The site-specific rate coefficients were estimated by Kozlov et al. (2003) to be 33% reaction at the CH$_3$ group and 67% H atom abstraction from the CH$_3$F group.
The recommended $k$ (298 K) was obtained from an average of the results from the absolute-rate studies of Nelson et al. (1993), Zellner et al. (1994), Zhang et al. (1994), and Tokuhashi et al. (2004) and the relative rate studies of Hsu and DeMore (1995) (recalculated based on the JPL10-6-recommended rate coefficients for the OH + CH$_4$ and OH + CHF$_2$CF$_3$ reference reactions) and Wallington et al. (2004) (recalculated based on the JPL10-6-recommended rate coefficient for the OH + C$_2$H$_4$ and OH + C$_2$H$_2$ reference reactions). The recommended value for $E/R$ was based on a fit of the data below 400 K from Nelson et al. (1993), Zellner et al. (1994), Tokuhashi et al. (2004), and Hsu and DeMore (1995) after scaling to the recommended $k$ (298 K) value.

The rate-coefficient parameters were estimated using a G3B3 quantum chemical method (Curtiss et al., 2001) calculation of the reaction activation barrier, $\sim$146 kJ mol$^{-1}$. Assuming a pre-exponential factor of $1 \times 10^{11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $E/R$ equal to the calculated activation barrier provides the basis of the recommendation.

References


Chang, J. S., and F. Kaufman, Upper limits of the rate constants for the reactions of CFCl$_3$(F-II), CF$_2$Cl$_2$(F-12), and N$_2$O with OH. Estimates of corresponding lower limits to their tropospheric lifetimes, Geophys. Res. Lett., 4, 192-194, 1977.


DeMore, W. B., Rate constants for the reactions of OH with HFC-134a (CF$_3$CH$_2$F) and HFC-134 (CHF$_2$CHF$_2$), Geophys. Res. Lett., 20, 1359-1362, 1993.


Chapter 3: Supplement 1


1. CFCl₃ (CFC-11)

**Recommended Rate Coefficient**

\[ k(T) < 1 \times 10^{-11} \exp(-9695/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) < 1 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommendations were revised from JPL10-6.¹

The current recommendation was obtained by equating the activation energy \((E)\) to the endothermicity for the abstraction of a Cl atom following IUPAC (Atkinson et al., 2008) and setting the pre-exponential factor \((A)\) to \(1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). The JPL10-6 recommendation was derived from typically less-sensitive rate-coefficient upper limits estimated from instrumental sensitivity towards reaction rate measurements.

2. CF₂Cl₂ (CFC-12)

**Recommended Rate Coefficient**

\[ k(T) < 1 \times 10^{-11} \exp(-11910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) < 1 \times 10^{-28} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommendations were revised from JPL10-6.¹

The current recommendation was obtained by equating the activation energy \((E)\) to the endothermicity for the abstraction of a Cl atom following IUPAC (Atkinson et al., 2008) and setting the pre-exponential factor \((A)\) to \(1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). The JPL10-6 recommendation was derived from typically less-sensitive rate-coefficient upper limits estimated from instrumental sensitivity towards reaction rate measurements.

3. CF₂ClCFCl₂ (CFC-113)

**Recommended Rate Coefficient**

\[ k(T) = 1 \times 10^{-11} \exp(-6220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) = 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Not evaluated in JPL10-6¹ or IUPAC.²

The recommended kinetic parameters are taken to be equal to those estimated for the OH + CCl₄ reaction.
4. CF₂ClCF₂Cl (CFC-114)

**Recommended Rate Coefficient**

\[ k(T) < 1 \times 10^{-11} \exp(-6220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) < 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Not evaluated in JPL10-6\textsuperscript{1} or IUPAC.\textsuperscript{2}

The recommended kinetic parameters are taken to be equal to those estimated for the OH + CCl₄ reaction.

5. CF₃CF₂Cl (CFC-115)

**Recommended Rate Coefficient**

\[ k(T) = 1 \times 10^{-11} \exp(-6220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) = 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Not evaluated in JPL10-6\textsuperscript{1} or IUPAC\textsuperscript{2}.

The recommended kinetic parameters are taken to be equal to those estimated for the OH + CCl₄ reaction.

6. CCl₄ (Carbon Tetrachloride)

**Recommended Rate Coefficient**

\[ k(T) < 1 \times 10^{-11} \exp(-6220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) < 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommendations were revised from JPL10-6\textsuperscript{1}.

The current recommendation was obtained by equating the activation energy \((E)\) to the endothermicity for the abstraction of a Cl atom following IUPAC and setting the pre-exponential factor \((A)\) to \(1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). The JPL10-6 recommendation was derived from typically less-sensitive rate-coefficient upper limits estimated from instrumental sensitivity towards reaction-rate measurements.
7. N$_2$O

**Recommended Rate Coefficient**

\[ k(298 \text{ K}) < 5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Not evaluated in JPL10-6.$^1$

The current recommendation is based on the study by Biermann *et al.* (1976), who measured a rate constant of $3.8 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. A more conservative upper limit $(4.0 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) was reported by Chang and Kaufman (1977).

**References**


8. CF$_2$Br$_2$ (Halon-1202)

**Recommended Rate Coefficient**

\[ k(T) < 1 \times 10^{-12} \exp(-2200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) < 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommendations are unchanged from JPL10-6.$^1$

The rate coefficient was estimated using an estimated Arrhenius $A$-factor and the rate-coefficient upper limit reported by Burkholder *et al.* (1991) at 298 K.

**Reference**

9. CF₂ClBr (Halon-1211)

Recommended Rate Coefficient

\[ k(T) < 1 \times 10^{-12} \exp(-3500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
\[ k(298 \text{ K}) < 8 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommendations were revised from JPL10-6.¹

The rate coefficient was estimated using an estimated Arrhenius \( A \)-factor and the rate-coefficient upper limit reported by Burkholder et al. (1991) at 373 K.

Reference

10. CF₃Br (Halon-1301)

Recommended Rate Coefficient

\[ k(T) < 1 \times 10^{-12} \exp(-3600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
\[ k(298 \text{ K}) < 6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommendations are unchanged from JPL10-6.¹

The rate coefficient was estimated using an estimated Arrhenius \( A \)-factor and the rate-coefficient upper limit reported by Orkin and Khamaganov (1993) at 460 K.

Reference

11. CF₂BrCF₂Br (Halon-2402)

Recommended Rate Coefficient

\[ k(T) < 1 \times 10^{-12} \exp(-3600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
\[ k(298 \text{ K}) < 6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommendations are unchanged from JPL10-6.¹

The rate coefficient was estimated using an estimated Arrhenius \( A \)-factor and the rate-coefficient upper limit reported by Orkin and Khamaganov (1993) at 460 K.

Reference
12. CH₄ (Methane)

Results of the temperature-dependence studies

The SPARC recommendation (solid line) over the temperature range 200 to 300 K was taken from the IUPAC data evaluation. The JPL10-6 recommendation (black dashed line) is lower by 15% at 200 K, 3% at 272 K, and 0.4% at 298 K is included for comparison.
History of $k(298 \text{ K})$ measurements

The $k(298 \text{ K})$ values are from the Arrhenius fits obtained from the studies of temperature dependences. The results obtained only at room temperature, near 298 K, were corrected slightly to obtain $k(298 \text{ K})$ using the recommended $E/R$. The more recent studies are believed to be free from the influence of secondary reactions involving OH.

**Recommended Rate Coefficient**

\[
\begin{align*}
    k(T) &= 1.85 \times 10^{-12} \exp(-1690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
    k(298 \text{ K}) &= 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\end{align*}
\]

$A$ and $E/R$ recommendations are unchanged from IUPAC.

The $f(298 \text{ K})$ and $g$ were revised.

**References**


13. \( \text{CH}_3\text{CCl}_3 \) (Methyl Chloroform)

**Recommended Rate Coefficient**

\[
k(T) = 1.64 \times 10^{-12} \exp(-1520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k(298 \text{ K}) = 1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

A and E/R recommendations are unchanged from JPL10-6.¹

\( f(298 \text{ K}) = 1.1 \)

\( g = 50 \)

**References**


Clyne, M. A. A., and P. M. Holt, Reaction kinetics involving ground \( \chi^2\Pi \) and excited \( \Delta^2\Sigma^+ \) hydroxyl radicals. Part 2. Rate constants for reactions of \( \text{OH} \chi^2\Pi \) with halogenomethanes and halogenoethanes, *J. Chem. Soc. Faraday Trans.* 2, 75, 582-591, 1979.


14. CH₃Cl (Methyl Chloride)

**Recommended Rate Coefficient**

\[
k(T) = 1.96 \times 10^{-12} \exp(-1200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k(298 \text{ K}) = 3.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[k(298 \text{ K})\] is an average of room temperature data of Hsu and DeMore, Orkin et al. (1994), and Herndon et al. (2001)

**Recommended Uncertainty Factors**

\[f(298 \text{ K}) = 1.1\]

\[g = 50\]

\[f(298 \text{ K})\] and \(g\) were revised from JPL10-6.¹

**References**


Perry, R. A., R. Atkinson, and J. N. Pitts, Jr., Rate constants for the reaction of OH radicals with CHFCl₂ and CH₃Cl over the temperature range 298-423 °K, and with CH₂Cl₂ at 298 °K, *J. Chem. Phys.*, 64, 1618-1620, 1976.

15. CH$_3$Br (Methyl Bromide)

**Recommended Rate Coefficient:**

\[
k(T) = 1.4 \times 10^{-12} \exp(-1150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k(298 \text{ K}) = 3.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\(k(298 \text{ K})\) is an average of room temperature data of Mellouki et al. (1992), Zhang et al. (1992), Chichinin et al. (1994), and Hsu and DeMore (1994)

**Recommended Uncertainty Factors**

\[f(298 \text{ K}) = 1.07\]

\[g = 100\]

\(f(298 \text{ K})\) was revised from JPL10-6;\(^1\) \(g\) is unchanged from JPL10-6.\(^1\)

**References**


Recommended Rate Coefficient

\[ k(T) = 1.03 \times 10^{-12} \exp(-1600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
\[ k(298 \text{ K}) = 4.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

A recommendation changed and E/R recommendations are unchanged from JPL10-6.\(^1\)

Recommended Uncertainty Factors

\[ f(298 \text{ K}) = 1.07 \]
\[ g = 100 \]

\( f(298 \text{ K}) \) and \( g \) were revised from JPL10-6.\(^1\)

References


17. CH$_3$CFC$_2$ (HCFC-141b)

**Recommended Rate Coefficient**

\[
k(T) = 1.25 \times 10^{-12} \exp(-1600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k(298 \text{ K}) = 5.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\( \mathcal{A} \) and \( E/R \) recommendations are unchanged from JPL10-6.$^1$

\( f(298 \text{ K}) \) and \( g \) were revised from JPL10-6.$^1$

**Recommended Uncertainty Factors**

\[
f(298 \text{ K}) = 1.07
\]

\[
g = 100
\]

**References**


Chapter 3: Supplement 1


Zhang, Z., R. E. Huie, and M. J. Kurylo, Rate constants for the reactions of OH with CH₃CFCl₂ (HCFC-141b), CH₃CF₂Cl (HCFC-142b), and CH₂FCF₃ (HFC-134a), *J. Phys. Chem.*, 96, 1533-1535, 1992.
18. CH$_3$CF$_2$Cl (HCFC-142b)

**Recommended Rate Coefficient**

\[
k(T) = 1.30 \times 10^{-12} \exp(-1770/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k(298 K) = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

**Recommended Uncertainty Factors**

\[
f(298 K) = 1.15
\]

\[
g = 50
\]

References


Chapter 3: Supplement 1


Zhang, Z., R. E. Huie, and M. J. Kurylo, Rate constants for the reactions of OH with CH$_3$CFCI$_2$ (HCFC-141b), CH$_3$CF$_2$Cl (HCFC-142b), and CH$_3$FCF$_3$ (HFC-134a), *J. Phys. Chem.*, 96, 1533-1535, 1992.
19. CHF₃ (HFC-23)

Recommended Rate Coefficient
\[ k(T) = 0.52 \times 10^{-12} \exp(-2210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
\[ k(298 \text{ K}) = 3.1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommended Uncertainty Factors
\[ f(298 \text{ K}) = 1.15 \]
\[ g = 100 \]

A and E/R recommendations are unchanged from JPL10-6.¹

f(298 K) and g are unchanged from JPL10-6.¹

References


Clyne, M. A. A., and P. M. Holt, Reaction kinetics involving ground \( X^2\Pi \) and excited \( A^2\Sigma^+ \) hydroxyl radicals. Part 2. Rate constants for reactions of OH \( X^2\Pi \) with halogenomethanes and halogenoethanes, *J. Chem. Soc. Faraday Trans.* 2, 75, 582-591, 1979.


20. CH$_2$F$_2$ (HFC-32)

Recommended Rate Coefficient

\[ k(T) = 1.7 \times 10^{-12} \exp(-1500/T) \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1} \]

\[ k(298 \text{ K}) = 1.1 \times 10^{-14} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1} \]

\( A \) and \( E/R \) recommendations are unchanged from JPL10-6.$^1$

\[ f(298 \text{ K}) = 1.07 \]

\[ g = 100 \]

Recommended Uncertainty Factors

\( f(298 \text{ K}) \) and \( g \) were revised from JPL10-6.$^1$

References


Clyne, M. A. A., and P. M. Holt, Reaction kinetics involving ground \( \lambda^2\Pi \) and excited \( \lambda^2\Sigma^+ \) hydroxyl radicals. Part 2. Rate constants for reactions of OH \( \lambda^2\Pi \) with halogenomethanes and halogenoethanes, *J. Chem. Soc. Faraday Trans.*, 2, 75, 582-591, 1979.


21. CHF₂CF₃ (HFC-125)

Recommended Rate Coefficient

\[ k(T) = 0.60 \times 10^{-12} \exp(-1700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Recommended Uncertainty Factors

\[ f(298 \text{ K}) = 1.1 \]

\[ g = 100 \]

\[ A \text{ and } E/R \text{ recommendations are unchanged from JPL10-6.}^1 \]

\[ f(298 \text{ K}) \text{ and } g \text{ were revised from JPL10-6.}^1 \]

References


Clyne, M. A. A., and P. M. Holt, Reaction kinetics involving ground \( X^2\Pi \) and excited \( A^3\Sigma^+ \) hydroxyl radicals. Part 2. Rate constants for reactions of \( OH \) \( X^2\Pi \) with halogenomethanes and halogenoethanes, *J. Chem. Soc. Faraday Trans.*, 2, 75, 582-591, 1979.

DeMore, W. B., Rate constants for the reactions of OH with HFC-134a (CF₃CH₂F) and HFC-134 (CHF₂CHF₂), *Geophys. Res. Lett.*, 20, 1359-1362, 1993.


22. CH₂FCF₃ (HFC-134a)

Recommended Rate Coefficient

\[
k(T) = 0.95 \times 10^{-12} \exp(-1600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k(298 \text{ K}) = 4.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

E/R is an average of E/R (T < 400 K) from Liu et al. (1990), Gierczak et al. (1991) (2 studies), Orkin and Khamaganov (1993), Leu and Lee (1994), and DeMore (1993) (3 studies were averaged to give a single E/R).

\[
f(298 \text{ K}) = 1.1
\]

\[
g = 100
\]

\[
g \text{ was revised from JPL10-6.}^1
\]

References


---

DeMore, W. B., Rate constants for the reactions of OH with HFC-134a (CF$_3$CH$_2$F) and HFC-134 (CHF$_2$CHF$_2$), Geophys. Res. Lett., 20, 1359-1362, 1993.


Zhang, Z., R. E. Huie, and M. J. Kurylo, Rate constants for the reactions of OH with CH$_2$CFCl$_2$ (HCFC-141b), CH$_3$CF$_2$Cl (HCFC-142b), and CH$_2$FCF$_3$ (HFC-134a), J. Phys. Chem., 96, 1533-1535, 1992.
23. CH$_3$CF$_3$ (HFC-143a)

![Graph showing rate coefficient vs. temperature for CH$_3$CF$_3$.]

**Recommended Rate Coefficient**

\[
k(T) = 1.06 \times 10^{-12} \exp(-2010/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}
\]

\[
k(298 \text{ K}) = 1.25 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}
\]

Recommended \(k(298 \text{ K})\) is an average of room temperature data from Talukdar *et al.* (1991), (LP-LIF), Hsu and DeMore (1995) (2 studies), and Orkin *et al.* (1996). The Talukdar *et al.* (DF-LMR) data appear to be systematically high.

Recommended \(E/R\) is an average of values from Talukdar *et al.* (2 values), Hsu and DeMore (2 values), and Orkin *et al.*

\(f(298 \text{ K})\) and \(g\) are unchanged from JPL10-6.$^1$

**References**


24. CH$_3$CHF$_2$ (HFC-152a)

\begin{align*}
\text{Recommended Rate Coefficient} \\
k(T) &= 0.87 \times 10^{-12} \exp(-975/T) \text{ cm$^3$ molecule$^{-1}$ s$^{-1}$} \\
k(298 \text{ K}) &= 3.3 \times 10^{-14} \text{ cm$^3$ molecule$^{-1}$ s$^{-1}$} \\
A \text{ and } E/R \text{ recommendations are unchanged from JPL10-6.}^1 \\
f(298 \text{ K}) \text{ was revised from JPL10-6;}^1 \\
g \text{ is unchanged from JPL10-6.}^1 \\
\text{Recommended Uncertainty Factors} \\
f(298 \text{ K}) &= 1.05 \\
g &= 50
\end{align*}

\textbf{References}


### Recommended Rate Coefficient

\[ k(T) = 0.48 \times 10^{-12} \exp(-1680/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) = 1.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ f(298 \text{ K}) = 1.15 \]

\[ g = 75 \]

\[ f(298 \text{ K}) \text{ is unchanged from JPL10-6} \]

\[ g \text{ was revised from JPL10-6} \]

### References


Wallington, T. J., M. D. Hurley, O. J. Nielsen, and M. P. S. Andersen, Atmospheric chemistry of CF\textsubscript{3}CFHCF\textsubscript{2}OCF\textsubscript{3} and CF\textsubscript{3}CFHCF\textsubscript{2}OCF\textsubscript{2}H: Reaction with Cl atoms and OH radicals, degradation mechanism, and global warming potentials, *J. Phys. Chem. A*, 108, 11333-11338, 2004.


Zhang, Z., S. Padmaja, R. D. Saini, R. E. Huie, and M. J. Kurylo, Reactions of hydroxyl radicals with several hydrofluorocarbons: The temperature dependencies of the rate constants for CHF\textsubscript{2}CF\textsubscript{2}CH\textsubscript{2}F (HFC-245ca), CF\textsubscript{3}CHFCHF\textsubscript{2} (HFC-236ea), CF\textsubscript{3}CHFCF\textsubscript{3} (HFC-227ea), and CF\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CF\textsubscript{3} (HFC-356ffa), *J. Phys. Chem.*, 98, 4312-4315, 1994.
Recommended Rate Coefficient

\[ k(T) = 0.61 \times 10^{-12} \exp(-1330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) = 7.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

A and E/R recommendations are unchanged from JPL10-6.\(^1\)

\[ f(298 \text{ K}) \text{ and } g \text{ were revised from JPL10-6.} \]

References


Chapter 3: Supplement 1

27. NF$_3$

**Recommended Rate Coefficient**

\[ k(T) < 1 \times 10^{-11} \exp(-17500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) < 3 \times 10^{-37} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Not evaluated in JPL10-6.

Dillon et al. (2011) reported a room temperature rate-coefficient upper limit of $4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for this reaction. F atom abstraction from NF$_3$ by the OH radical is endothermic by $\approx 42 \text{ kJ mol}^{-1}$ (Gurvich et al., 1998; Karton et al., 2009; Ruscic et al., 2005). Equating the activation energy to this endothermicity and assuming a pre-exponential factor of $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ yields a lower upper-limit rate coefficient of

\[ k(T) < 1 \times 10^{-11} \exp(-5000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) < 5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

A G3B3 quantum chemical method (Curtiss et al., 2001) calculation yields a similar reaction endothermicity (43 kJ mol$^{-1}$) and an activation barrier of $\approx 146 \text{ kJ mol}^{-1}$. Assuming a pre-exponential factor of $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ an even more restrictive upper-limit rate coefficient is obtained with this activation energy and provides the basis of the present recommendation

\[ k(T) < 1 \times 10^{-11} \exp(-17500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k(298 \text{ K}) < 3 \times 10^{-37} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

**References**


Karton, A., S. Parthiban, and J. M. L. Martin, Post-CCSD(T) *ab initio* thermochemistry of halogen oxides and related hydrides XOX, XOOX, HOX, XO$_n$, and HXO$_n$ (X = F, Cl), and evaluation of DFT methods for these systems, *J. Phys. Chem. A*, 113, 4802-4816, 2009.