IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_4

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This data sheet updated: 3\textsuperscript{rd} July 2005.

\[ n\text{-C}_3\text{H}_7\text{O}_2 + \text{NO} \rightarrow n\text{-C}_3\text{H}_7\text{O} + \text{NO}_2 \quad \text{(1)} \]
\[ n\text{-C}_3\text{H}_7\text{O}_2 + \text{NO} + \text{M} \rightarrow n\text{-C}_3\text{H}_7\text{ONO}_2 + \text{M} \quad \text{(2)} \]

Rate coefficient data \( (k = k_1 + k_2) \)

<table>
<thead>
<tr>
<th>( k )/cm(^3) molecule(^{-1}) s(^{-1})</th>
<th>Temp./K</th>
<th>Reference</th>
<th>Technique/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute Rate Coefficients</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2.9 \times 10^{-12} \exp[(350 \pm 60)/T] )</td>
<td>201-402</td>
<td>Eberhard and Howard, 1996</td>
<td>F-CIMS(a)</td>
</tr>
<tr>
<td>( (9.4 \pm 1.6) \times 10^{-12} )</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 4.3 \times 10^{-12} \exp[(268 \pm 56)/T] )</td>
<td>213-298</td>
<td>Chow et al., 2003</td>
<td>F-CIMS (b)</td>
</tr>
<tr>
<td>( (1.05 \pm 0.14) \times 10^{-11} )</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Branching Ratio</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_2/k = 0.020 \pm 0.009 )\ (1 bar)</td>
<td>299</td>
<td>Atkinson et al., 1982</td>
<td>(c)</td>
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<td></td>
<td></td>
<td>Carter and Atkinson, 1989</td>
<td></td>
</tr>
</tbody>
</table>

Comments

(a) \( n\text{-C}_3\text{H}_7\text{O}_2 \) radicals were produced by pyrolysis of \( n\text{-C}_3\text{H}_7\text{ONO}_2 \) in the presence of \( \text{O}_2 \) and detected by CIMS. Pseudo-first order kinetics with excess NO.

(b) Turbulent flow reactor at 133 mbar \( \text{N}_2 \) total pressure. \( \text{C}_3\text{H}_7\text{O}_2 \) radicals were generated by the reaction of \( \text{Cl} \) atoms with \( \text{C}_3\text{H}_8 \) in the presence of \( \text{O}_2 \), thus both \( n\text{-C}_3\text{H}_7\text{O}_2 \) and i-\( \text{C}_3\text{H}_7\text{O}_2 \) were present and the rate coefficients measured are overall values for both isomers, which were detected as \( \text{C}_3\text{H}_7\text{OOH}^+\text{(H}_2\text{O})_3 \) following reaction with \( \text{H}^+\text{(H}_2\text{O})_4 \) ions.

(c) Based on yield of \( n\text{-C}_3\text{H}_7\text{ONO}_2 \) product from photo-oxidation of \( \text{C}_3\text{H}_8 \) in \( \text{NO}_x\)-air mixtures. Carter and Atkinson (1989) revised the analysis of original data to provide the values quoted.

Preferred Values

\[ k = 9.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] at 298 K.
\[ k = 2.9 \times 10^{-12} \exp(350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] over the temperature range 200 K to 410 K.
\[ k_2/k = 0.020 \] at 298 K and 1 bar pressure.

Reliability

\[ \Delta \log k = \pm 0.2 \] at 298 K.
\[ \Delta (E/R) = \pm 100 \text{ K}. \]
\[ \Delta \log(k_2/k) = \pm 0.3 \] at 298 K and 1 bar pressure.

Comments on Preferred Values

The measurements of Eberhard and Howard (1996) provide the only experimental data on the isomer-specific rate coefficient. The data of Chow et al. (2003), who measured a
weighted average value for \( n{-}\text{C}_3\text{H}_7\text{O}_2 \) and \( i{-}\text{C}_3\text{H}_7\text{O}_2 \) are in good agreement, which confirms that \( n{-}\text{C}_3\text{H}_7\text{O}_2 \) and \( i{-}\text{C}_3\text{H}_7\text{O}_2 \) have similar rate coefficients for reaction with NO. The negative temperature coefficient is consistent with that observed for the rate coefficient for other RO\(_2\) + NO reactions. The recommendation accepts the Arrhenius expression of Eberhard and Howard (1996).

The preferred branching ratio for \( n \)-propyl nitrate formation is that measured by Atkinson et al. (1982), as revised by Carter and Atkinson (1989).

**References**