**CMD Data Reporting Sheet APP**

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**Reporting date:** 27 January 2001  
**Project title:** APP 8, “Transformations of atmospheric constituents and pollutants induced by S(IV) autoxidation – chemistry and kinetics”  
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<table>
<thead>
<tr>
<th>Reaction</th>
<th>A-factor (M$^{-1}$ s$^{-1}$)</th>
<th>E/R (K)</th>
<th>k(298K) (M$^{-1}$ s$^{-1}$)</th>
<th>References, remarks *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPO + SO$_3^-$ → inactive products</td>
<td>—</td>
<td>—</td>
<td>1×10$^9$</td>
<td>1b, 2c</td>
</tr>
<tr>
<td>TEMPO + Mn(III) → Mn(II) + inactive products</td>
<td>—</td>
<td>—</td>
<td>5×10$^9$</td>
<td>1b, 2c</td>
</tr>
<tr>
<td>Mn(III) + SO$_3^-$ → Mn(II) + SO$_3^-$</td>
<td>—</td>
<td>—</td>
<td>0.1</td>
<td>1b</td>
</tr>
</tbody>
</table>

**Mechanistic information**  
The above reactions constituted the mechanism of inhibition of S(IV) autoxidation by TEMPO (2,2,6,6–tetramethylpiperidine–N–oxyl)

**Experimental details**  
Non-stationary autoxidation of S(IV) in a perfectly mixed reactor, with and without TEMPO added; initial concentrations: [Na$_2$SO$_3$]$_o$ = 1 mM, [O$_2$]$_o$ = 0.20 ÷ 0.25 mM, [MnSO$_4$]$_o$ = 0.01 mM, [TEMPO]$_o$ = 0, 2×10$^{-4}$ ÷ 6×10$^{-3}$ mM; pH = 8.5 ÷ 8.9

**Modelling**  
The rate constants were obtained from the analysis of the overall autoxidation process, using a chemical-kinetic model built by inserting the above reactions into the radical mechanism of S(IV) autoxidation. The model accurately reproduced the experiments.

**Ref., remarks**


2c TEMPO was a model representative of nitroxyl radicals present in the atmosphere.

*) Use **index a** for peer-reviewed publications; **index b** for “grey literature”, **index c** for remarks etc.