Hydroxyl Radical Reactions with Halogenated Ethanols
in Aqueous Solution

S. Gligorovski (1), I. Morozov (2), P. Barzaghi (1) and H. Herrmann (1)

(1) Leibniz-Institut für Troposphärenforschung, Leipzig, Germany, (2) Semenov Institute of Chemical Physics, Moscow, Russia, saso@tropos.de

Motivation

Halogenated alcohols have been suggested as alternative to CFCs and HCFCs, therefore their atmospheric concentrations are expected to increase in the near future. Due to their polarity, uptake by cloud water and rain might be a significant sink for these chemicals in the atmosphere. In the aqueous phase, fluorinated and chlorinated alcohols are suggested to react mainly with OH radical. However, only few kinetic data are available in the literature, thus the reactions of OH radical with the following organic compounds have been studied: (1) 2-fluoroethanol, (2) 2,2-difluoroethanol, (3) 2,2,2-trifluoroethanol, (4) 2-chloroethanol, (5) 2,2-dichloroethanol, and (6) 2,2,2-trichloroethanol. In the present study, a laser-photolysis long-path absorption (LP-LPA) set-up (Figure 1) was used for indirect kinetic studies of OH radical reactions with halogenated alcohols in the aqueous phase. The kinetic data obtained here will be used as input parameters in forthcoming versions of the multiphase reaction mechanism CAPRAM.

Experimental

Because the OH radical absorbs weakly in the UV region of the spectrum with only a small extinction coefficient of \( \epsilon = 600 \, \text{mol}^{-1} \, \text{cm}^{-1} \) at \( \lambda = 235 \, \text{nm} \) and due to the overlapping of the organic peroxy radicals formed in parallel to the OH decay an OH radical absorption measurement is difficult. Thus, the OH radical concentration is followed indirectly by using the common competition kinetics method. A much-applied competition kinetic system for the study of OH reactions in aqueous solution is the thioacetonitrite system which has been applied in this work. This competition kinetic system is based on the reactions (R-1) - (R-4):

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{hv} (\lambda \approx 248 \, \text{nm}) & \rightarrow 2 \, \text{OH} \\
\text{OH} + \text{SCN}^{-} & \rightarrow \text{SCNOH}^{-} \\
\text{SCNOH}^{-} + \text{OH}^{-} & \rightarrow \text{SCN} + \text{OH} \\
\text{SCN} + \text{SCN}^{-} & \rightarrow (\text{SCN})_2
\end{align*}
\]

The product (SCN)₂ absorbs strongly in the blue region of the spectrum with peak absorbance at \( \lambda = 475 \, \text{nm} \) and extinction coefficient of \( \epsilon = 7600 \, \text{mol}^{-1} \, \text{cm}^{-1} \). In this work the temperature-dependent rate constant of reaction (R-2) reported by Chin and Wine \((k = 1.24 \cdot 10^{10} \, \text{mol}^{-1} \, \text{s}^{-1} \) at 298 K was applied as reference data.

Results and Discussions

In Table 1 the observed rate constants at 298 K and the activation parameters obtained from the temperature dependent measurements of OH radical reactions towards halogenated alcohols are summarized.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( k(298K) ) [( \text{mol}^{-1} , \text{s}^{-1} )]</th>
<th>( A ) [( \text{mol}^{-1} , \text{s}^{-1} )]</th>
<th>( E_A ) [kJ mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-fluoroethanol</td>
<td>( 5.4 \pm 1.8 ) ( \times 10^8 )</td>
<td>( 1.2 \pm 0.1 ) ( \times 10^{12} )</td>
<td>( 18 \pm 8 )</td>
</tr>
<tr>
<td>2,2-difluoroethanol</td>
<td>( 2.8 \pm 0.7 ) ( \times 10^9 )</td>
<td>( 4.5 \pm 0.5 ) ( \times 10^{10} )</td>
<td>( 7 \pm 7 )</td>
</tr>
<tr>
<td>2,2,2-trifluoroethanol</td>
<td>( 8.5 \pm 2.5 ) ( \times 10^9 )</td>
<td>( 2.0 \pm 0.1 ) ( \times 10^{11} )</td>
<td>( 20 \pm 7 )</td>
</tr>
<tr>
<td>2-chloroethanol</td>
<td>( 8.6 \pm 0.7 ) ( \times 10^9 )</td>
<td>( 3.0 \pm 0.2 ) ( \times 10^{10} )</td>
<td>( 9 \pm 4 )</td>
</tr>
<tr>
<td>2,2-dichloroethanol</td>
<td>( 3.9 \pm 0.8 ) ( \times 10^9 )</td>
<td>( 2.1 \pm 0.2 ) ( \times 10^{10} )</td>
<td>( 10 \pm 4 )</td>
</tr>
<tr>
<td>2,2,2-trichloroethanol</td>
<td>( 1.7 \pm 0.8 ) ( \times 10^9 )</td>
<td>( 1.6 \pm 0.1 ) ( \times 10^{10} )</td>
<td>( 10 \pm 5 )</td>
</tr>
</tbody>
</table>

The rate constant data show clearly that the halogenated ethanols are less reactive than the parent compound, ethanol \((k = 2.1 \cdot 10^9 \, \text{mol}^{-1} \, \text{s}^{-1})\). The available kinetic data suggest that the H abstraction occurs predominately from the CH₂ group of the ethanols. It is proposed that the relatively large reductions in reactivity of the halogenated ethanols are mainly due to the inductive effects in the transition states. Halogen substitution in the CH₃ group will reduce the electron density on the H atoms in the CH₃ group and thus destabilize the transition state compared to that formed with CH₃CH₂OH. These transition states will be increasingly destabilized as the degree of charge separation increases.

Summary and Conclusions

References


Figure 1: Laser photolysis long-path absorption (LP-LPA) set-up for kinetic investigation

Figure 2: Plot of the logarithm of rate constant vs. sum of Pauling electronegativities of terminal Cₓ group

Acknowledgement

Supports of this study by the EC within the project “Impact of Fluorinated Alcohols and Ethers on the Environment (IAFAEE)” under contract EVK2-CT-1999-00009, grant NATO CLG 979421, and INTAS 03-51-56-98 are gratefully acknowledged.