The Fate of Bromoform in the Troposphere and Lower Stratosphere

by

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CHBr₃ and Cl₂ cross sections from JPL 97-4
Vinyl Bromide measured on 9 Jan 2001

Wavelength / nm

Cross Sections / 10⁻²⁰ cm²
Fig. 1

![Graph showing counts/bin over time for curves A and B.](image)
Fig. 2

![Graph showing the relationship between $K_0/m s^{-1}$ and $[C_2H_3Br]/10^{13}$ molecule cm$^{-3}$]
Fig. 3

![Graph showing data points for Method I and Method II against wavelength in nm.](image)

- **Method II**
- **Method I**
CHBr₃ + hv → Br + CHBr₂

CHBr₂ + O₂ → OOCHBr₂

OOCHBr₂ + NO → NO₂ + OCHBr₂

OCHBr₂ + O₂ → HO₂ + OCBr₂

OCHBr₂ → Br + OCHBr

CHBr₃ in air + NO

CHBr₃ in air

Br atom signal vs. t / milliseconds
**Assumed Mechanism**

*Initiation:*

\[
\text{CHBr}_3 + \text{hv} \quad \rightarrow \quad \text{CHBr}_2 + \text{Br}
\]
Assume immediately after the laser pulse, \([\text{Br}] = [\text{CHBr}_2] = S_0\)

*Loss of CHBr\(_2\):*

\[
\begin{align*}
\text{CHBr}_2 + \text{O}_2 & \quad \overset{k_{1a}}{\rightarrow} \quad \text{CHBrO}_2 \\
\text{CHBr}_2 + \text{NO} & \quad \overset{k_{1b}}{\rightarrow} \quad \text{CHBrNO} \\
\text{CHBr}_2 & \quad \overset{k_{1c}}{\rightarrow} \quad \text{diffusional loss}
\end{align*}
\]

let \(\text{CHBr}_2 = \text{R}\), then solving,

\[
[R] = S_0 \exp(-K_1 t) \quad \text{where}
\]

\[K_1 = k_{1a}[\text{O}_2] + k_{1b}[\text{NO}] + k_{1c}\]

*Loss of CHBr\(_2\)O\(_2\):*

\[
\begin{align*}
\text{CHBr}_2\text{O}_2 + \text{NO} & \quad \overset{k_{2a}}{\rightarrow} \quad \text{CHBrO} + \text{NO}_2 \\
\text{CHBr}_2\text{O}_2 & \quad \overset{k_{2c}}{\rightarrow} \quad \text{diffusional loss}
\end{align*}
\]

let \(\text{CHBr}_2\text{O}_2 = \text{RO}_2\) and

\[
[\text{RO}_2] = k_{1a}[\text{O}_2]S_0\{(\exp(-K_2 t) - \exp(-K_1 t) )/(K_1 - K_2)\}
\]

*Formation and loss of Br:*

Will assume that every \(\text{CHBrO}_2\) that is formed rapidly decomposes to \(\text{Br}\) and \(\text{CHBrO}\): \(^{\text{fast}}\)

\[
\begin{align*}
\text{CHBr}_2\text{O} & \quad \overset{k_{3a}}{\rightarrow} \quad \text{CHBrO} + \text{Br} \\
\text{Br} & \quad \overset{k_{3c}}{\rightarrow} \quad \text{diffusional loss}
\end{align*}
\]

\[K_3 = k_{3c} \quad \text{(only loss process)}\]

\[
d[\text{Br}]/dt = k_{2a}[\text{NO}][\text{RO}_2] - K_3[\text{Br}]
\]

Solving this differential equation using the previous expression for \([\text{RO}_2]\), and the boundary condition that \([\text{Br}] = S_0\) at time = 0, yields:

\[
[\text{Br}] = S_0 \exp(-K_3 t) + K_1 K_2 F_1 F_2 S_0 \{M_2/(K_2 - K_3) - M_1/(K_1 - K_3)\}/(K_1 - K_2)
\]

where

\[
F_1 = k_{1a}[\text{O}_2]/K_1 = \text{fraction of R that forms RO}_2
\]

\[
F_2 = k_{2a}[\text{NO}]/K_2 = \text{fraction of RO}_2 \text{ that forms RO}_1 \text{, and thus gives a second Br atom}
\]

\[
M_1 = \{\exp(-K_3 t) - \exp(-K_1 t)\}
\]

\[
M_2 = \{\exp(-K_3 t) - \exp(-K_2 t)\}
\]
For fitting the experimental data, three modifications were made to this theoretical expression:

1. A constant, $B_k$, was added to account for the background count observed as $t \rightarrow $; 

2. A fitted constant, $S_1$, is used in place of the term $(F_1 F_2 S_0)$ so that the assumption that every RO decomposes to give a Br atom can be tested by comparing $S_1/(F_1 F_2)$ with $S_0$;

3. At long times the Br signal displays a double exponential decay, whether NO is present or not; so an additional term was added of the form $S_2 M_3$, where $S_2$ is a fitted constant, typically 45% as large as $(S_0 + S_1)$, and $M_3 = \{\exp(-K_4 t) - \exp(-K_3 t)\}$.

The resulting equation used in the weighted least squares fits was:

$$\text{Signal} = S_0 \exp(-K_3 t) + K_1 K_2 S_1 \{M_2/(K_2-K_3) - M_1/(K_1-K_3)\}/(K_1-K_2) + S_2 M_3 + B_k$$
Rise time constant $K_2$ vs. [NO]

CHBr$_3$/air/NO at 10 Torr total pressure
266 nm (17 and 19 June 2002)
303 nm (8 May 2002)

$[\text{NO}] / 10^{14}$ molecules cm$^{-3}$

$k_2a = (1.93 \pm 0.04) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
Time constant $K_1$ vs. $[O_2]$

CHBr$_3$/O$_2$/NO at 2 Torr total pressure

266 nm (22 May 2002)

$[O_1] = 10^{15}$ molecules cm$^{-3}$

Slope = $k_1a = 1.078 \times 10^{-13}$ cm$^3$ molecules$^{-1}$ s$^{-1}$

using $k_1b = 5.87 \times 10^{-13}$ and imposing intercept = $k_1c = 0.18$ ms$^{-1}$
Slope = $k_{1a} = (2.96 \pm 0.57) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Intercept = $k_{1c} = 0.062 \text{ ms}^{-1}$

Use $k_{1b} = 1.06 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Time constant $K_1$ vs. $[O_2]$

$CHBr_3/O_2/NO$ at 2 Torr total pressure

266 nm (22 May 2002)

\[ \text{Slope} = k_{1a} = 1.078 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \]

\[ \text{using } k_{1b} = 5.87 \times 10^{-13} \text{ and imposing intercept } = k_{1c} = 0.18 \text{ ms}^{-1} \]
<table>
<thead>
<tr>
<th>P / Torr</th>
<th>k1a / $10^{-13}$</th>
<th>k1b / $10^{-13}$</th>
<th>k2a / $10^{-11}$</th>
<th>S1 / (S0 F1 F2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.96</td>
<td>$\sim$10.6</td>
<td>1.93</td>
<td>1.00 +/- 0.015 (266 nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.97 +/- 0.12 (303 nm)</td>
</tr>
<tr>
<td>2</td>
<td>1.08</td>
<td>$\sim$5.9</td>
<td>$\sim$2.0</td>
<td>0.95 +/- 0.06 (266 nm)</td>
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