RATE CONSTANTS FOR THE REACTIONS OF OH WITH CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, and CH$_3$Br

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Abstract. Rate constants for the reactions of OH with CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, and CH$_3$Br have been measured by a relative rate technique in which the reaction rate of each compound was compared to that of HFC-152a (CH$_3$CHF$_2$) and, for CH$_2$Cl$_2$, HFC-161 (CH$_3$CH$_2$F). Using absolute rate constants for HFC-152a which we have determined relative to those for CH$_4$ and CH$_3$CCl$_3$, and for HFC-161 as determined relative to C$_2$H$_6$ [Hsu and DeMore, 1994], temperature dependent rate constants of both compounds were derived. The derived rate constant for CH$_3$Br is in good agreement with recent absolute measurements [Mellouki et al, 1992; Zhang et al., 1992]. However, for the chloromethanes all the rate constants are lower at atmospheric temperatures than previous estimates [JPL 92-20], especially for CH$_2$Cl$_2$ where the present rate constant is about a factor of 1.6 below the JPL 92-20 value. The new rate constant appears to resolve contradictions between observed atmospheric concentrations and estimated release rates for that compound [Koppmann et al., 1993].

Introduction

The compounds CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, and CH$_3$Br are significant atmospheric species which are present at concentrations of about 600 ppt for CH$_3$Cl and about an order of magnitude less for the other three compounds. [See WMO, 1985; Koppmann et al., 1993; and previous references quoted therein]. Methyl chloride, which is mainly of natural origin, is a significant source of stratospheric chlorine. Methylene chloride has largely industrial sources in the Northern hemisphere, and has a latitudinal gradient which makes it useful as an atmospheric tracer. Sources of CHCl$_3$ are not well understood, but are probably both industrial and

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natural. CH$_3$Br has both man made and natural sources, and is especially significant as a source of atmospheric bromine. The principal fate of all three compounds is destruction by OH attack. To determine the atmospheric lifetimes, it is necessary to have accurate temperature dependent rate constants for the OH abstraction reactions. Measurements of rate constants relative to that for CH$_3$CCl$_3$ are especially useful because global distributions of that compound are used to calculate average tropospheric OH concentrations. [Singh, 1977; Prinn et al., 1992]. Global distributions of CH$_3$CCl$_3$, combined with the known emission rates [Midgely, 1989], have been used to calculate the CH$_3$CCl$_3$ lifetime in the atmosphere. Therefore, atmospheric lifetimes relative to that of methyl chloroform may be calculated from the inverse dependence on the ratio of rate constants [Prather and Spivakovsky, 1990]. The derived lifetimes are thus independent of the absolute CH$_3$CCl$_3$ rate constant.

Experimental Method

The experimental method was similar to that previously described [DeMore, 1992 and 1993]. The major advantage of this method is that it is not sensitive to reactant impurities, secondary reactions of OH, or wall loss of OH. The OH radicals are produced by UV photolysis of O$_3$ in the presence of water vapor in a slow-flow, temperature-controlled photochemical reactor. All experiments were at atmospheric pressure. Each reactant is depleted by the OH reaction in a manner similar to that of the atmosphere. The rate constant ratio is obtained from the relation:

$$\frac{k_{\text{reactant}}}{k_{\text{reference}}} = \frac{\ln(DF)_{\text{reactant}}}{\ln(DF)_{\text{reference}}} \quad (I)$$

The quantity DF (depletion factor) is given by:

$$DF = \frac{\text{Initial Conc.}}{\text{Final Conc.}} \quad (II)$$

HFCs 152a and 161 were used as reference compounds because their infrared spectra are resolved from those of the chloromethanes, and they have strong, well-defined C-F bands which are suitable for the relative concentration measurements. We have separately measured the rate constant for HFC-152a with reference to both CH$_4$ and
CH₃CCl₃ [Hsu and DeMore, 1994], using the currently recommended rate constants for those compounds [JPL 92-20]. Although 152a was the principal reference compound used for all four compounds in the present work, CH₂Cl₂ was also measured against HFC-161 as a check on the HFC-152a results. This was considered necessary in view of the fact that our derived rate constant for CH₂Cl₂ is much lower than previous measurements have indicated. The reference rate constants used were k(CH₂Cl₂) = 2.3E-12 exp(-1275/T) and k(CH₄) = 1.0E-12 exp(-1228/T), in units of cm³/molec-s. The 152a rate constant is an average of calibrations versus CH₄ and CH₃CCl₃: k(152a)CH₄ = 1.87E-12 exp(-1221/T) and k(152a)CH₃CCl₃ = 2.76E-12 exp(-1330/T). These two results are in excellent agreement and give k(298 K) for 152a = 3.1E-14 and 3.2E-14 cm³/molec-s, respectively. This result is similar to our previous experience with HFC-134a [DeMore,1993], in which similarly identical results for the 134a rate constant were obtained from CH₄ and CH₃CCl₃ as references. The implication is that the JPL 92-20 rate constants for CH₄ and CH₃CCl₃ are accurate, at least on a relative basis.

Initial reactant concentrations were in the range 10¹⁴ to 10¹⁵ cm⁻³, and depletion factors were normally about 1.1 to 1.5. Concentrations were monitored with a Nicolet 20SX FTIR operated at 0.5 cm⁻¹ resolution in the absorbance mode using a White cell with a three-meter path length. The photolysis cell was quartz with a water jacket for temperature control. The light source was a low pressure Hg lamp.

Results

Table 1 summarizes the ratios measured, and Figures 1(a)-(e) are graphs of the ratio data in Arrhenius form. The Arrhenius expressions as derived from linear least squares fits of these data are listed in Table 2. Table 3 gives the calculated rate constants, based on the reference rate constants as indicated in the footnotes. Figures 2-4 show a graphical comparison of the present results compared to other recent work.

Discussion

The rate constants reported in this work are based on those of CH₄, CH₃CCl₃, and (to a lesser extent) C₂H₆. CH₄ and CH₃CCl₃ are useful as references because their OH rate
constants appear to be very accurately known, and CH₃CCl₃ is used to calibrate OH concentrations in the troposphere, as previously mentioned. When compared to a common reference such as HCFC-141b, HFC-134a, or HFC-152a. [DeMore, 1993; Huder and DeMore, 1993; and Hsu and DeMore, 1994], the CH₄ and CH₃CCl₃ rate constants as recommended in JPL 92-20 are mutually consistent within 3% or better at 298 K. This consistency also shows that little propagation of error is introduced through the use of a transfer standard such as HFC-152a. The C₂H₆ rate constant, which we used to obtain the HFC-161 rate constant, also appears to be accurate on an absolute basis, although a direct comparison with CH₄ and CH₃CCl₃ is difficult because of the large difference in magnitude of the rate constants.

The three chloromethane rate constants derived in this work are substantially lower than those of the JPL 92-20 evaluation. This is in keeping with the general trend of recently measured OH abstraction rate constants to be lower than those of earlier work.

Our CH₃Cl rate constant is 40% lower at 298 K than the JPL 92-20 recommendation (see Table 3). Agreement with the Taylor et al. [1993] results is good at higher temperatures (around 370 K), but less satisfactory at 298 K (see Figure 2).

The results for CH₂Cl₂ are the most surprising, being about a factor of 1.6 lower than previous absolute measurements, which are in good agreement with each other. Because of this discrepancy, we tested our results by additional experiments relative to HFC-161, which in turn was referenced to C₂H₆. The resulting consistency (within 12%) argues against any large error in our ratio measurements or in our rate constant for the reference compound HFC-152a. We thus believe that the CH₂Cl₂ rate constant is indeed much lower than previously reported. This conclusion is consistent with atmospheric measurements of CH₂Cl₂ [Koppmann et al., 1993], which showed higher concentrations of that compound (by about the same factor) than expected on the basis of estimated release rates and the previous rate constant.

Our result for CHCl₃ is in reasonable agreement with earlier measurements (Table 3 and Figure 4), although again somewhat lower. Previous problems with the reported Arrhenius parameters for this compound [Cohen and Westberg, 1991], which were revealed by transition state
theory (TST) calculations, appear to have been resolved both by our work and by the recent data of Taylor et al. (1993). The new results yield much lower rate constants at high temperature than previous measurements from that laboratory, and are now consistent with the TST predictions. Our rate constant for CH$_3$Br is in good agreement with the JPL 92-20 recommendation, both in terms of the absolute value (6% lower at 298 K) and the Arrhenius parameters. A recent absolute measurement by Chichinin et al. (1993) is also in good agreement at 298 K with the previous results, although the Arrhenius parameters are slightly lower.

Acknowledgements

The author is grateful to colleagues at the Jet Propulsion Laboratory for helpful discussions. Dr. Norm Cohen pointed out to us the need for additional experimental work on CHCl$_3$. Dr. Pauline Midgely called to our attention the situation regarding atmospheric measurements of CH$_2$Cl$_2$. DuPont Chemicals generously provided the chemical samples used in this work. This work was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References

DeMore, W. B., Rates of Hydroxyl Reactions with some HFCs, Optical Methods in Atmospheric Chemistry, 1715, 72-76, 1992a.
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.


Fig. 1. Arrhenius plots of the rate constant ratio data from Table 1.

Fig. 2. Arrhenius plot of the data for CH₃Cl and comparison with previous results.

Fig. 3. Arrhenius plot of the data for CH₂Cl₂ and comparison with previous results.

Fig. 4. Arrhenius plot of the data for CHCl₃ and comparison with previous results.

Fig. 5. Arrhenius plot of the data for CH₃Br and comparison with previous results.
Table 1. Experimental Data for Ratios Measured vs. HFC-152a and HFC-161

<table>
<thead>
<tr>
<th>CH₃Cl</th>
<th>CH₂Cl₂</th>
<th>CHCl₃</th>
<th>CH₃Br</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T(K)</td>
<td>Ratio/152a</td>
<td>T(K)</td>
</tr>
<tr>
<td>293</td>
<td>0.958</td>
<td>2.562</td>
<td>298</td>
</tr>
<tr>
<td>298</td>
<td>0.934</td>
<td>2.652</td>
<td>298</td>
</tr>
<tr>
<td>298</td>
<td>1.028</td>
<td>2.594</td>
<td>298</td>
</tr>
<tr>
<td>301</td>
<td>0.998</td>
<td>2.535</td>
<td>310</td>
</tr>
<tr>
<td>308</td>
<td>1.072</td>
<td>2.472</td>
<td>319</td>
</tr>
<tr>
<td>308</td>
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<td>2.453</td>
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<td>313</td>
<td>1.059</td>
<td>2.239</td>
<td>341</td>
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<td>323</td>
<td>1.104</td>
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<td>353</td>
</tr>
<tr>
<td>333</td>
<td>1.118</td>
<td>2.158</td>
<td>368</td>
</tr>
<tr>
<td>345</td>
<td>1.025</td>
<td>2.241</td>
<td>360</td>
</tr>
<tr>
<td>358</td>
<td>1.090</td>
<td>2.162</td>
<td>360</td>
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Table 2. Ratios Measured and Their Temperature Dependences

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Arrhenius Expression(^{(a)})</th>
<th>Ratio at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k(\text{CH}_3\text{Cl})/k(152a))</td>
<td>((1.91 \pm 0.45) \exp \left((-195 \pm 74)/T\right))</td>
<td>0.99</td>
</tr>
<tr>
<td>(k(\text{CH}_2\text{Cl}_2)/k(152a))</td>
<td>((0.97 \pm 0.09) \exp \left((294 \pm 29)/T\right))</td>
<td>2.60</td>
</tr>
<tr>
<td>(k(\text{CH}_2\text{Cl}_2)/k(161))</td>
<td>((0.32 \pm 0.02) \exp \left((171 \pm 20)/T\right))</td>
<td>0.57</td>
</tr>
<tr>
<td>(k(\text{CHCl}_3)/k(152a))</td>
<td>((0.52 \pm 0.11) \exp \left((495 \pm 64)/T\right))</td>
<td>2.74</td>
</tr>
<tr>
<td>(k(\text{CH}_3\text{Br})/k(152a))</td>
<td>((1.94 \pm 0.28) \exp \left((-232 \pm 46)/T\right))</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Units of \(A\) and \(k\) are \(\text{cm}^3/\text{molec-s}\).

\(^{(a)}\) Errors shown are standard deviations. Actual uncertainties are approximately a factor of 1.3 in the \(A\)-factor ratios and 75-125 K in the \(E/R\) values.
Table 3. Derived Rate Constants and Comparisons with Other Work.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>A-Factor</th>
<th>E/R (K)</th>
<th>k(298 K)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃Cl</td>
<td>4.4E-12</td>
<td>1470</td>
<td>3.1E-14</td>
<td>This work(a)</td>
</tr>
<tr>
<td></td>
<td>2.1E-12</td>
<td>1150</td>
<td>4.4E-14</td>
<td>JPL 92-20</td>
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<tr>
<td></td>
<td>1.1E-11</td>
<td>1712</td>
<td>3.5E-14</td>
<td>Taylor et al. (1993)</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>2.2E-12</td>
<td>981</td>
<td>8.2E-14</td>
<td>This work(a)</td>
</tr>
<tr>
<td></td>
<td>3.2E-12</td>
<td>1057</td>
<td>9.2E-14</td>
<td>This work(b)</td>
</tr>
<tr>
<td></td>
<td>5.8E-12</td>
<td>1100</td>
<td>1.4E-13</td>
<td>JPL 92-20</td>
</tr>
<tr>
<td></td>
<td>6.0E-12</td>
<td>1096</td>
<td>1.5E-13</td>
<td>Taylor et al. (1993)</td>
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<tr>
<td>CHCl₃</td>
<td>1.2E-12</td>
<td>780</td>
<td>8.8E-14</td>
<td>This work(a)</td>
</tr>
<tr>
<td></td>
<td>4.3E-12</td>
<td>1100</td>
<td>1.1E-13</td>
<td>JPL 92-20</td>
</tr>
<tr>
<td></td>
<td>1.2E-12</td>
<td>714</td>
<td>1.1E-13</td>
<td>Taylor et al. (1993)</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>4.4E-12</td>
<td>1507</td>
<td>2.8E-14</td>
<td>This work(a)</td>
</tr>
<tr>
<td></td>
<td>1.9E-12</td>
<td>1230</td>
<td>3.0E-14</td>
<td>Chichinin et al. (1993)</td>
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<tr>
<td></td>
<td>2.4E-12</td>
<td>1300</td>
<td>3.0E-14</td>
<td>Mellouki et al. (1992)</td>
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<tr>
<td></td>
<td>5.8E-12</td>
<td>1560</td>
<td>3.1E-14</td>
<td>Zhang et al. (1992)</td>
</tr>
</tbody>
</table>

Units of A and k are cm³/molec-s.
(a) Using k(HFC-152a) = 2.3E-12exp(-1275/T). See text.
(b) Using k(HFC-161) = 1.0E-11exp(-1228/T). See text.
Figure 1a

(a) CH$_3$Cl vs. 152a
Figure 1b

(b) CH2Cl2 vs. 152a

Log \( k(\text{CH2Cl2})/k(152a) \)

\[
\begin{align*}
1000/T (K) & \quad 0.1 & \quad 0.2 & \quad 0.3 & \quad 0.4 & \quad 0.5 & \quad 0.6 & \quad 0.7 \\
2.7 & \quad 2.9 & \quad 3.1 & \quad 3.3 & \quad 3.5 & \quad 3.7
\end{align*}
\]
Figure 1c

(d) CH2Cl2 vs. HFC-161

![Graph showing the logarithm of the ratio of CH2Cl2 to HFC-161 versus the reciprocal of temperature (1000/T in K).](image)
Figure 1d

(c) CHCl₃ vs. 152a

Log $k(\text{CHCl}_3)/k(152\text{a})$ vs. $1000/T$ (K)
Figure 1e

(d) CH3Br vs. 152a
Figure 3

![Graph showing the dependence of logarithm of reaction rate constant (Log k/cm^3 molec s^-1) on inverse temperature (1000/T K) for CH2Cl2.](image)

- ■ Taylor et al. (1993)
- □ Davis et al. (1976)
- JPL 92-20
- ◊ Howard and Evenson (1976)
- ● This work/152a
- △ This work/161
Figure 5

Log k/cm³/mole·s.

CH₃Br

-14.2
-13.7
-13.2
-12.7
-12.2

1000/T (K)


- Mellouki et al. (1992).
- Zhang et al. (1992)
- JPL 92-20
- Chichinin et al.
- This work/152a