The Reaction of CH₂OH Radicals with O₂ Studied by Laser Magnetic Resonance Technique

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The reaction of CH₂OH with O₂ was studied in an isothermal flow system at 296 K. A rate coefficient, \( k_1 \) (296 K) = \( (6.4 \pm 1.5) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \), has been determined for the overall reaction

\[
\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{products} \quad (1)
\]

by monitoring the decay of the LMR signal of the CH₂OH radical. A value of \( (6.3 \pm 2.8) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) has been obtained for the overall rate coefficient by following the formation of the product HO₂ radicals in the specific reaction channel

\[
\text{CH}_2\text{OH} + \text{O} \rightarrow \text{HO}_2 + \text{CH}_2\text{O} \quad (1a)
\]

No dependence on pressure of \( k_1 \) was observed in the pressure range \( 0.69 \leq P/\text{mbar} \leq 6.50 \) studied. A complex mechanism has been proposed for the formation of \( \text{HO}_2 \) and \( \text{CH}_2\text{O} \) in the reaction.

1. Introduction

Hydroxy-methyl radicals (CH₂OH) play an important role in combustion processes and the chemistry of the atmosphere. Under atmospheric conditions the OH-initiated oxidation of ethylene and terminal olefins proceeds through \( \pi \)-hydroxy-alkoxyl radicals which decompose rapidly to CH₂OH radicals [1]. The oxidation of methanol initiated by OH radical attack also leads to CH₂OH [2, 3a, 4, 5]. With the prospect of methanol as an alternative automotive fuel the interest in the mechanism of its oxidation has renewed.

In oxidation systems the fate of CH₂OH is essentially determined by the reaction with O₂. The two most probable reaction routes are hydrogen abstraction (1 a) and addition (1 b):

\[
\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_2\text{O} \quad (1a)
\]

\[
\rightarrow \text{OOCCH}_2\text{OH} \quad (1b)
\]

Both the absolute value of the overall rate constant \( k_1 = k_{1a} + k_{1b} \) and the branching ratio between the two channels, among other reactions, are of importance in modelling the chemistry of the polluted troposphere. They have a significant effect on the predicted ozone level as well as on the organic product yields [1, 6].

While it is generally accepted that reaction (1) is fast, only very few rate measurements have been performed. The primary obstacle to perform direct studies has been the lack of suitable techniques for the detection of CH₂OH. The recent identification of Laser Magnetic Resonance (LMR) spectra of CH₂OH by Radford et al. [4] has provided a sensitive and selective means for studying its reactions. Recently, mass spectrometry at low electron energies [3, 7, 8] and resonance enhanced multiphoton ionisation spectrometry [9] have also proved to be effective. Another possibility to study reaction (1) is the detection of the product \( \text{HO}_2 \) [5, 10].

In the present paper we report a direct investigation of reaction (1) using the discharge flow technique combined with LMR. The consumption of CH₂OH and the formation of \( \text{HO}_2 \) were monitored simultaneously. Overall rate constants were determined from both types of experiments.

2. Experimental

The experimental set up was very similar to that used previously [11]. Here only the special features of the technique are described.

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The vertically positioned flow reactor consisted of a 3.9 cm i.d. Pyrex tube of 70 cm length, coated with teflon (Du Pont FEP 856-200). The flow tube was equipped with an inner moveable quartz probe of 15 mm o.d. with radial perforation (1 mm holes) at the end. It contained a second coaxial inner tube (~ 4 mm o.d.) through which CH$_2$OH was introduced. The distance of the end of the inner tube from the end of the probe was approximately 8 cm.

Hydroxymethyl radicals were generated inside the moveable probe by reacting F atoms with methanol. Fluorine atoms were produced by passing 1% F$_2$ in He through a microwave discharge burning in an Al$_2$O$_3$ insert tube. Methanol in excess was introduced into the coaxial inner tube and was admixed with the F atoms in the lower 8 cm part of the probe. Flow conditions were adjusted to allow for the complete conversion of fluorine atoms into CH$_2$OH (and CH$_3$O). The reactant O$_2$ (or O$_2$/He mixture) was introduced through a side arm at the upper end of the flow tube.

The decay of CH$_2$OH and build-up of HO$_2$ radicals were monitored with a far infrared laser magnetic resonance spectrometer [11]. The following FIR laser lines, lasing gas, CO$_2$ laser lines, laser polarizations, and magnetic field strengths were applied to detect the radicals:

CH$_2$OH: $\lambda = 119$ µm, CH$_3$OH, $9p36$, $\pi$, $H_0 = 0.04$ Tesla [9], HO$_2$: $\lambda = 163$ µm, CH$_3$OH, 10R38, $\pi$, $H_0 = 0.23$ Tesla [12].

Among the different CH$_2$OH transitions reported by Radford et al. [5], the one indicated above proved to be most intense and its symmetric form was of further advantage especially at low signal to noise ratios.

He (Messer Griesheim, 99.999%) served as the main carrier gas. Either pure O$_2$ (99.998%) or 1.98 (r/r) % He/O$_2$ mixture (each Messer Griesheim) were used as reactants. CH$_2$OH (Merck, 99.7%) was carefully degassed by freeze/thaw cycles prior to use. Special care was taken to remove impurities from the F$_2$/He line by using a solid NaF and a series of liquid N$_2$ traps. One of the N$_2$ (1) traps was attached close to the discharge cavity.

The carrier gas and O$_2$ flows were measured and regulated with Tylan mass flow controllers. CH$_3$OH and F$_2$ flows were regulated by needle valves. Their flow rates could be determined by measuring the pressure rise in calibrated volumes. The total pressure was measured with a pressure transducer (MKS Instruments) downstream of the flow tube.

3. Results

Experiments were carried out at $T = (296 \pm 1)$ K in the pressure range of 0.69 $\pm$ P/mbar $\leq$ 6.50. The average linear flow rates were varied between 9 and 28 m/s. The concentration of F$_2$ ranged from 1.8 x 10$^{-13}$ mol/cm$^3$ to 2.0 x 10$^{-12}$ mol/cm$^3$. Methanol concentration was typically about 2 x 10$^{-9}$ mol/cm$^3$ calculated for the conditions in the reactor.

The F + CH$_2$OH reaction used for generating CH$_2$OH radicals is known to produce also CH$_3$O radicals in about equal amount [3, 13]. The absolute radical concentrations have not been measured in this study. Computer simulations were made to estimate the initial radical concentrations (see in 3.3). Accordingly, the average initial hydroxymethyl and methoxy radical concentrations were approximately 4.6 x 10$^{-13}$ mol/cm$^3$ and 1.3 x 10$^{-12}$ mol/cm$^3$, respectively and were varied by about a factor of four.

The O$_2$ concentration was varied between 3.8 x 10$^{-12}$ mol/cm$^3$ and 2.4 x 10$^{-11}$ mol/cm$^3$ in the CH$_2$OH monitoring experiments and was increased up to about 2.5 x 10$^{-10}$ mol/cm$^3$ in the HO$_2$ monitoring runs. At the lowest O$_2$ concentrations minor corrections had to be made to allow for the oxygen consumption during the reaction.

3.1. Determination of the Overall Rate Coefficient by Monitoring CH$_2$OH Consumption

The rate constant for the overall reaction

$$\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{product(s)} \quad (1)$$

has been determined by recording the amplitude of the LMR signal of the CH$_2$OH radical under pseudo first order conditions ([O$_2$] $\gg$ [CH$_2$OH]) as a function of the reaction time (the position of the moveable probe). Some typical experimental CH$_2$OH decay curves are shown in Figure 1 a. In the absence of competitive reactions the decay of [CH$_2$OH] under pseudo first order conditions is given by the expression

$$- \ln \frac{[\text{CH}_2\text{OH}]_{t=0}}{[\text{CH}_2\text{OH}]_{t}} = - \ln \frac{S(\text{CH}_2\text{OH})_{t}}{S(\text{CH}_2\text{OH})_{t=0}} = k_1 [\text{O}_2] t = k_f^* t, \quad (A)$$
where $S_{\text{CH}_2\text{OH}} + \text{O}_2$ and $S_{\text{CH}_2\text{OH}} - \text{O}_2$ are the peak-to-peak amplitudes of the LMR signals of the hydroxymethyl radical in the presence and absence of oxygen, respectively.

In a series of experiments the $\text{O}_2$ concentration was varied between $3.8 \times 10^{-12}$ mol/cm$^3$ and $2.4 \times 10^{-11}$ mol/cm$^3$ at constant, $P = 2.32 \pm 0.11$ mbar pressure. The experimental conditions are summarized in Table 1. Some typical experimental results are plotted in Fig. 2 according to (A) (solid lines). From the slopes of the straight lines the pseudo first order rate coefficient, $k_1^f$ could be obtained. A plot of $k_1^f$ vs. $\text{O}_2$ is shown in Figure 3. The full straight line going through the origin represents a least squares fit to the data points, the slope gives a rate coefficient of $k_1^f = (6.7 \pm 1.0) \times 10^{12}$ cm$^3$/mol s$^{-1}$, with the error limits corresponding to the 95% confidence interval.

The natural logarithm of the amplitudes of the $\text{CH}_2\text{OH}$ LMR signals plotted vs. the reaction time in the absence of $\text{O}_2$ also gave straight lines. The slopes of the straight lines provided the experimentally measured "effective wall rate coefficients".

Table 1. Experimental conditions for the study of the $\text{CH}_2\text{OH} + \text{O}_2$ reaction ($T = 296$ K, $P = 2.32$ mbar).

<table>
<thead>
<tr>
<th>$\text{O}_2$ (mol/cm$^3$)</th>
<th>$\text{F}_2$ (mol/cm$^3$)</th>
<th>$\varepsilon$ (cm/s)</th>
<th>$k_w$ (s$^{-1}$)</th>
<th>$k_1^f$ (s$^{-1}$)</th>
<th>$10^{-12}k_1^f$ (cm$^3$/mol s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.83</td>
<td>12.2</td>
<td>1604</td>
<td>29</td>
<td>23</td>
<td>5.9</td>
</tr>
<tr>
<td>6.37</td>
<td>5.3</td>
<td>1734</td>
<td>22</td>
<td>42</td>
<td>6.6</td>
</tr>
<tr>
<td>8.45</td>
<td>2.6</td>
<td>1716</td>
<td>22</td>
<td>45</td>
<td>6.7</td>
</tr>
<tr>
<td>10.00</td>
<td>1.8</td>
<td>2465</td>
<td>37</td>
<td>62</td>
<td>6.2</td>
</tr>
<tr>
<td>12.10</td>
<td>20.0</td>
<td>2071 (64)</td>
<td>73</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>15.70</td>
<td>1.8</td>
<td>2756</td>
<td>28</td>
<td>94</td>
<td>6.0</td>
</tr>
<tr>
<td>18.10</td>
<td>2.2</td>
<td>2000</td>
<td>30</td>
<td>124</td>
<td>6.9</td>
</tr>
<tr>
<td>23.50</td>
<td>12.2</td>
<td>1612</td>
<td>32</td>
<td>161</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Table 2. The overall rate coefficient measured at different pressures.

<table>
<thead>
<tr>
<th>Pressure (mbar)</th>
<th>$10^{-12}[\text{O}_2]$ (mol/cm$^3$)</th>
<th>$\varepsilon$ (cm/s)</th>
<th>$k_1^f$ (s$^{-1}$)</th>
<th>$10^{-12}k_1^f$ (cm$^3$/mol s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.69</td>
<td>5.95</td>
<td>4.63</td>
<td>5.48 varied</td>
<td>8.45</td>
</tr>
<tr>
<td>0.93</td>
<td>6.1</td>
<td>6.5</td>
<td>7.0</td>
<td>5.9</td>
</tr>
<tr>
<td>1.70</td>
<td>7.0</td>
<td>6.7</td>
<td>5.9</td>
<td>6.7</td>
</tr>
<tr>
<td>2.32$^a$</td>
<td>5.9</td>
<td>6.5</td>
<td>7.0</td>
<td>5.9</td>
</tr>
<tr>
<td>2.95</td>
<td>5.9</td>
<td>6.5</td>
<td>7.0</td>
<td>5.9</td>
</tr>
<tr>
<td>3.99</td>
<td>6.5</td>
<td>7.0</td>
<td>5.9</td>
<td>6.7</td>
</tr>
<tr>
<td>6.50</td>
<td>6.5</td>
<td>7.0</td>
<td>5.9</td>
<td>6.7</td>
</tr>
</tbody>
</table>

$^a$ The average of eight runs.
They have been found to be in the range of $k_f^{O_2} = 29 \pm 5 \text{ s}^{-1}$.

The results of the pressure variation experiments are summarized in Table 2. Only single experiments with one oxygen concentration were carried out at pressures other than 2.32 mbar. The rate coefficients show no systematic variation with pressure in the range studied. It should be mentioned, however, that because of the known difficulties with flow systems [14], only a relatively small pressure range could be covered. Thus, it cannot be precluded that some dependence on pressure of $k_f$ may exist.

A weighted average of the data in Table 2 gave a value of $k_f = (6.4 \pm 1.0) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (the error limits are two standard deviations).

The final results for the overall rate coefficient determined by the decay of the CH$_2$OH radicals, is: $k_f$ (296 K) = $(6.4 \pm 1.5) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (the error limits are the estimated maximum uncertainties).

### 3.2. Determination of the Overall Rate Coefficient by Monitoring the Build-up of HO$_2$

Strong LMR absorption signals of the product hydroperoxyl radicals were observed in the experiments. The formation of HO$_2$ radicals has been studied with a fixed position of the probe (constant reaction time) by varying the O$_2$ concentration. The experimental arrangement and data analysis were similar to those used by Radford [5]. Some representative hydroperoxyl LMR signals as a function of [O$_2$] are given in Figure 1b. (For comparison one of the CH$_2$OH decay curves is also shown.) A characteristic feature of all of the HO$_2$ curves is a limiting HO$_2$ value reached after the complete
conversion of the CH$_2$OH radicals. The amplitudes of these maximal signals remained constant while moving the probe towards larger distances. This behaviour has been observed also by Radford and means that the HO$_2$ radical is a "stable product" with the time-scale employed. (The different $S_{\text{max}}$ boundary values in Fig. 1b reflect the differences in the initial CH$_2$OH concentrations.)

No HO$_2$ signals could be detected in the absence of O$_2$ indicating the vacuum-tightness of the system. The measurability of the HO$_2$ radicals was significantly better than that of the CH$_2$OH radicals because of the greater sensitivity of the LMR spectrometer towards HO$_2$.

A rate coefficient can be derived for the overall reaction from the measured HO$_2$ signals, evaluating the relative intensities ($S_{\text{HO}_2}/S_{\text{max}}$) at different oxygen concentrations. The following expression is obtained from mass-balance considerations, after the integration of the rate equations (see also in [5]):

$$\frac{S_{\text{HO}_2}}{S_{\text{max}}^{\text{HO}_2}} = \frac{1 - \exp \{- (k_1[O_2] + k_w) t\}}{1 + \frac{k_w}{k_1[O_2]}}, \quad \text{(B)}$$

A least squares fitting computer program was used to estimate $k_1$. All of the $S_{\text{HO}_2}/S_{\text{max}}^{\text{HO}_2} - [O_2]$ data pairs from different experiments were taken in one fitting procedure with the average $k_w = 29$ s$^{-1}$ and $t = 10.6$ ms parameters. (Because of the increased uncertainties, the data points with $S_{\text{HO}_2}/S_{\text{max}}^{\text{HO}_2} > 0.80$ have been omitted.) The fitted (solid) curve together with the experimental points are shown in Figure 4. The rate coefficient obtained with the combined statistical and estimated systematic errors is

$$k_1 = (6.3 \pm 2.8) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$
3.3. The Significance of Side Reactions

The linearity of the plots in Figs. 2 and 3 and the zero intercept in Fig. 3 indicate that consecutive and parallel reactions cannot be significant under our experimental conditions. Among the side reactions the radical-radical reactions are thought to play some role. The experimentally measured "effective wall rate constant" presented a slight increase with increasing initial radical concentration, from which a 20 s\(^{-1}\) "true wall rate constant" and a rate coefficient of about \(1 \times 10^{13}\) cm\(^3\) mol\(^{-1}\) s\(^{-1}\) for the self-combination reaction of the CH\(_2\)OH radicals could be estimated. The latter is in good agreement with the value reported by Grotheer et al. [8]. So, the decay of CH\(_2\)OH without O\(_2\) in greater part can be due to heterogeneous processes, in which case the on-off technique directly corrects for the side reactions [15].

In order to further assess the importance of the possible interfering reactions we have carried out computer simulations with the reactions and rate coefficients summarized in Table 3 by using the computer routine of [16]. As a first step, the initial radical concentrations were calculated by modelling the reactions inside of the movable probe (steps (2) – (10)). The dissociation of F\(_2\) in the microwave discharge was taken to be complete and the wall recombination of F atoms was neglected [17]. The other possible reactions of HO\(_2\) in the reactor have been omitted on the basis of the experimental findings that the HO\(_2\) radical behaved as a "stable product" in the system after the complete conversion of CH\(_2\)OH into HO\(_2\).

The modelling of the [CH\(_2\)OH] decays yielded practically identical results with the results of the usual pseudo first order analysis of the experimentally measured CH\(_2\)OH LMR signals when the
Table 3. Reactions used in the model calculations.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k ) (296 K) ( \text{cm}^3 \text{mol}^{-1} \text{s}^{-1} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_3\text{O} )</td>
<td>( k_1 ) varied</td>
<td></td>
</tr>
<tr>
<td>( \text{F} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{HF} )</td>
<td>( k_{2a} = 5 \times 10^{13} )</td>
<td>estim.</td>
</tr>
<tr>
<td>( \rightarrow \text{CH}_3\text{O} + \text{HF} )</td>
<td>( k_{2b} = 0.7 )</td>
<td>[2]</td>
</tr>
<tr>
<td>( \text{F} + \text{CH}_3\text{OH} \rightarrow \text{HF} + \text{CH}_3\text{O} )</td>
<td>( k_3 = 1 \times 10^{14} )</td>
<td>estim.</td>
</tr>
<tr>
<td>( \text{F} + \text{CH}_3\text{O} \rightarrow \text{HF} + \text{CH}_2\text{O} )</td>
<td>( k_4 = 1 \times 10^{14} )</td>
<td>estim.</td>
</tr>
<tr>
<td>( \text{CH}_2\text{OH} \rightarrow \text{prod.} )</td>
<td>( k_5 = 9.0 \times 10^{12} )</td>
<td>[8]</td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} + \text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{O} )</td>
<td>( k_6 = k_4 )</td>
<td>assumed</td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} + \text{CH}_2\text{OH} \rightarrow \text{HO}_2 + \text{CH}_3\text{O} )</td>
<td>( k_7 = 7 \times 10^{4} )</td>
<td>estim. ( ^a )</td>
</tr>
<tr>
<td>( \text{CH}_2\text{OH} \rightarrow \text{wall prod.} )</td>
<td>( k_8 = 2 \times 10^{6} )</td>
<td>estim. ( ^b )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{O} \rightarrow \text{wall prod.} )</td>
<td>( k_9 = k_{10} = 20 )</td>
<td>this work</td>
</tr>
<tr>
<td>( \text{CH}_3\text{O} + \text{HO}_2 \rightarrow \text{prod.} )</td>
<td>( k_{10} = k_9 )</td>
<td>assumed</td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} + \text{HO}_2 \rightarrow \text{prod.} )</td>
<td>( k_{11} = 3.6 \times 10^{13} )</td>
<td>[8]</td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} + \text{HO}_2 \rightarrow \text{CH}_3\text{OH} + \text{O}_2 )</td>
<td>( k_{12} = 1.0 \times 10^{12} )</td>
<td>[8]</td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_3\text{O} )</td>
<td>( k_{13} = 1.1 \times 10^{9} )</td>
<td>[3b]</td>
</tr>
<tr>
<td>( \text{HO}_2 + \text{CH}_3\text{O} \rightarrow \text{prod.} )</td>
<td>( k_{14} = 1 \times 10^{10} )</td>
<td>[25]</td>
</tr>
</tbody>
</table>

\( ^a \) The rate coefficient of the reaction: \( \text{CH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{CH}_3\text{O} \) [29].

\( ^b \) The rate coefficient of the reaction: \( \text{CH}_2\text{O} + \text{C}_3\text{H}_5 \rightarrow \text{CH}_3\text{OH} + \text{C}_3\text{H}_5 \) [29].

\( k_1 = 6.4 \times 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1} \) rate coefficient was used as an input parameter in the simulations (compare the solid and dotted lines in Figs. 2 and 3). Similarly, the best agreement was found between the the experimentally measured and calculated \([\text{HO}_2]/[\text{HO}_2]^{\text{max}}\) ratios when \( k_1 \) was chosen to be in the range of \((6.0-6.7) \times 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}\). In Fig. 4 the dotted curve shows the result of a simulation carried out with \( k_1 = 6.4 \times 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1} \).

The later model calculations have also justified the use of (B) in deriving \( k_1 \) at our low radical concentrations (cf. the dotted and solid curves in Figure 4).

4. Discussion

The rate coefficients determined by monitoring the decay of \( \text{CH}_3\text{OH} \) radicals and the formation of \( \text{HO}_2 \) radicals with the LMR technique in a flow system at 296 K are

\[ k_1 = (6.4 \pm 1.5) \times 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1} \]

and

\[ k_1 = (6.3 \pm 2.8) \times 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1} \]

respectively. They are in excellent agreement with each other.

There are only a few direct studies of reaction (1) known from the literature. Two investigations have been carried out by directly monitoring the hydroxy-methyl radicals. Shortly after the description of \( \text{CH}_3\text{OH} \) by Radford et al. [4], Rohrbeck, Radford, and Fortuno [18] reported a value of \( k_1 = (1.5 \pm 0.2) \times 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1} \) at room temperature. In a very recent study at 300 K in a flow system using mass spectrometric detection of \( \text{CH}_3\text{OH} \) radicals, Grotheer et al. [8] obtained \( k_1 = (5.7 \pm 1.5) \times 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1} \). While the very recent mass spectrometric results are in excellent agreement with our \( k_1 \) value, the value of Rohrbeck et al. disagrees.

In the study of Rohrbeck et al. the experimental arrangement probably was very similar to ours (flow tube technique, LMR detection of the \( \text{CH}_3\text{OH} \) radicals, pseudo first order conditions, etc.). In their study a “clean” \( \text{CH}_3\text{OH} \) source, the reaction of \( \text{Cl} \) atoms with methanol [19] was used. Searching for the cause of discrepancy, we have carried out a few experiments using the \( \text{Cl} + \text{CH}_3\text{OH} \) reaction to generate \( \text{CH}_3\text{OH} \) radicals. The average of rate coefficient derived was \( 5.9 \times 10^{12} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1} \), in good agreement with our value obtained with the \( \text{F} + \text{CH}_3\text{OH} \) radical source. Thus, at the present stage we can not offer any reasonable explanation for the discrepancy.

In another group of investigations reaction (1) was studied by detecting the reaction product \( \text{HO}_2 \). A common feature of these investigations is the use of (B) in evaluating \( k_1 \). The earliest work was made by Radford [5] at room temperature with the LMR-flow tube combination technique. The measurement
of the relative intensities of the LMR signals as a function of \([O_2]\) allowed a rate coefficient of \((1.2\pm0.3)\times10^{12}\, \text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\) to be derived. Recently Wang et al. [10] have studied the \(\text{CH}_2\text{OH} + \text{O}_2\) reaction in a flow system at room temperature by detecting the \(\text{HO}_2\) radicals from photofragment emission. In this way a rate coefficient of \((8.4\pm2.4)\times10^{11}\, \text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\) has been determined. The above two values are five to eight times lower than the rate coefficient obtained by the very similar treatment of the experimental data in the present work. It is to be noted, however, that the derivation of (B) is based on the assumption that the only important reactions are reaction (1) and the wall consumption of \(\text{CH}_2\text{OH}\). Evidently, this can be the case only at low radical concentrations. At higher radical concentrations the use of (B) can lead to underestimation of \(k_1\) as was shown by Grotheer et al. [8] discussing Radford's low rate coefficient. Similar arguments can be advanced in connection with the study of Wang and coworkers. The \(\text{CH}_2\text{OH}\) concentrations in their system seem to have been at least one order of magnitude higher than those in the present work. Under such conditions the radical-radical reactions of \(\text{CH}_2\text{OH}\) and \(\text{HO}_2\) may have played a not negligible role.

In the present study practically the same rate coefficient was found by monitoring either the consumption of \(\text{CH}_2\text{OH}\) or the build up of \(\text{HO}_2\) radicals. In the second case the product of a single reaction channel is monitored, and this may give the impression that the rate coefficient of a specific reaction route is measured. It is to be noted, however, that information can be gained only on the overall rate coefficient with the methods applied here.

The formation of \(\text{HO}_2 + \text{CH}_2\text{O}\) appears to be the only reaction channel from product analysis and Fourier-transform spectroscopic studies. No indications were found for the occurrence of the combination reaction of \(\text{CH}_2\text{OH}\) with \(\text{O}_2\) during the \(\text{OH}\) initiated oxidation of ethylene and in the study of photochemical oxidation of alcohols under simulated atmospheric conditions [1, 20]. On the other hand, there has been conclusive evidence from the studies of the reverse reaction, the addition of \(\text{HO}_2\) to \(\text{CH}_2\text{O}\), for the existence and relative stability of the \(\text{OOC}\text{H}_2\text{OH}\) radical which is the expected combination product in the \(\text{CH}_2\text{OH} + \text{O}_2\) reaction. In the study of the photochemical oxidation of formaldehyde, Su et al. [21] and Niki et al. [22] identified the compound hydroxymethyl-hydroperoxide (\(\text{HOOCH}_2\text{OH}\)) by the FTIR spectroscopy and explained its formation through the hydroxymethyl-peroxy radical. From these studies a general picture has emerged for the photochemical oxidation of \(\text{CH}_2\text{O}\) in the atmosphere. The first steps are the addition and the fast rearrangement of the adduct formed into the more stable \(\text{OOCH}_2\text{OH}\) radical:

\[
\text{HO}_2 + \text{CH}_2\text{O} \rightarrow \text{HOOCH}_2\text{O} \quad (-\text{D})
\]
\[
\text{HOOCH}_2\text{O}(+\text{M}) \rightarrow \text{OOCH}_2\text{OH}(+\text{M})
\]

We suggest a consistent though basically qualitative interpretation for the reaction of \(\text{CH}_2\text{OH}\) with \(\text{O}_2\) which is in accordance with the results of the formaldehyde oxidation studies. The reaction is assumed to proceed via a "complex" mechanism:

\[
\text{CH}_2\text{OH} + \text{O}_2 \rightarrow (\text{OOCH}_2\text{OH})^* \rightarrow \text{OCH}_2\text{OOH}
\]

In the first step the vibrationally excited \((\text{OOCH}_2\text{OH})^*\) radical is formed with about 137 kJ/mol excess energy. (The complex formation has been found to be the dominant pathway in the reaction of \(\text{O}_2\) with \(\text{C}_2\text{H}_5\), which is isoelectronic with the hydroxymethyl radical [23].) In principle, the "chemically activated" \((\text{OOCH}_2\text{OH})^*\) adduct can decay by three different routes: redissociation \((-\text{C})\), stabilization \((-\text{S})\), and isomerization through \(1.4\) hydrogen atom transfer \((-\text{D})\). The energetic of the reactions have been schematically illustrated in Figure 5.

The stabilization route may not play a significant role because no pressure dependence was observed in our experiments. An activation energy for the \(\text{OOCH}_2\text{OH} \rightarrow \text{OCH}_2\text{OOH}\) rearrangement can be estimated by the rate coefficient \(k_{i0} = 1.5\,\text{s}^{-1}\) determined by Su et al. [20] during the study of formaldehyde oxidation. Accepting \(A_{i0}\) to be equal to \(10^{11.2}\,\text{s}^{-1}\), the preexponential factor for a five membered transition-state reaction [24], \(E_{i0} = 63\,\text{kJ/mol}\) activation energy can be calculated. The significant difference in the barrier heights makes the isomerization of the \(\text{OOCH}_2\text{OH}\) radical favourable to the redissociation. The last step in the scheme,
the decomposition of the isomerized HOOCH₂O radical, is practically thermoneutral. Its activation energy must be small according to the high rate coefficients measured for the reverse reaction (see e.g. $k_{-D} = 6.9 \times 10^9$ cm$^3$ mol$^{-1}$ s$^{-1}$ [21] or $k_{-D} = 1.0 \times 10^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ [25]). The HOOCH₂O radical still may have some excess energy and decompose in a fast step to HO₂ and CH₂O.

It follows from the kinetic considerations made above that the measured rate coefficient is equal to the rate coefficient of the combination reaction, i.e.: $k_1 = k_{(C)}$ and the reaction proceeds through fast consecutive steps which are the reverse steps of the HO₂ addition to formaldehyde. The intermediate OOCH₂OH radical has significantly more excess energy when formed in the CH₂OH + O₂ reaction than when it is formed in the HO₂ + CH₂O reaction. This difference in energy can explain why the characteristic HOOCH₂OH product could be observed in the HO₂ + CH₂O investigations whereas no indication was found for it in the CH₂OH + O₂ studies.

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