

Reaction between CH₃ and H₂ at Combustion Temperatures

Hyun Ju Baeck, Kuan Soo Shin*, H. Yang¹, V. Lissianski¹, and W. C. Gardiner, Jr.¹

Department of Chemistry, Soong Sil University, Seoul 156-743, Korea
¹Department of Chemistry and Biochemistry,
The University of Texas at Austin, Austin, Texas 78712, U.S.A.
Received March 14, 1995

The reaction between CH₃ radicals and H₂ was investigated behind incident shock waves at temperatures between 1308 and 1825 K by following the consumption of CH₃ using a time resolved UV absorption method at 2139 nm. The rate coefficient expression $1.10 \times 10^{10} \exp(-7370 \text{ K/T}) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ for the reaction of CH₃ with H₂ was derived.

Introduction

The reaction between CH₃ with H₂,

$$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H} \quad (14)$$

and its reverse reaction play important roles in methane pyrolysis and combustion. Numerous experimental²⁻⁶ and theoretical⁷⁻¹⁰ studies of reaction 14 (see Table 2) and its reverse reaction have been reported, and extensive review articles¹¹⁻¹⁴ have been published. Nearly all of the previous investigations of CH₃ with H₂ and its reverse reaction have been measured by indirect methods. Möller et al.⁵ measured $k_{14}(T)$ more directly in a shock tube over the temperature range from 1066 to 2166 K utilizing the UV absorption of CH₃ at 2165 nm in the pyrolysis of azomethane or tetramethyltin to generate methyl radical. Their data were fit to the Arrhenius expression $k_{14}(T)=2.0 \times 10^{10} \exp(-7200 \text{ K/T}) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Rabinowitz et al.⁶ also measured the rate of the reverse reaction, CH₄ + H → CH₃ + H₂, using a flash photolysis-shock tube technique in the temperature range from 897 to 1729 K. They reported $k_{14}(T)=3.1 \times 10^{12} \exp(-5940 \text{ K/T})$ and $k_{14}(T)=1.1 \times 10^{14} \exp(-6440 \text{ K/T}) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. The agreement of those recent two results is not good. The Möller et al.⁵ expression is about 100% larger than the Rabinowitz et al.⁶ expression at 1200 K and more than 150% larger at 1700 K. The purpose of the present investigation is to measure the rate coefficient of the CH₃ reaction with H₂ at combustion temperatures using spectroscopic determination of CH₃ concentration profiles during the thermal decomposition of azomethane or methyl iodide in the presence of large excess of H₂.

Experiment

The experiments were done utilizing incident shock waves in a Monel shock tube of 7.62 cm inside diameter which was described in detail elsewhere¹⁷. Shock parameters were computed from the measured incident shock velocities by standard methods²⁰ using JANAF²¹ and NASA²² thermochemical data under the assumption of steady flow and no wall boundary layer formation. The concentration of CH₃ radicals was measured using the absorption of 213.9 nm light from a Pen-Ray Zn arc lamp (Ultra-Violet Products) directed through two opposed sapphire windows combined with two slits (width 1 mm) and an interference filter of 9 mm (fwhm) band-pass and 19% peak transmission onto an EMI 9526B photomultiplier tube. The signal-to-noise ratio of the transmitted beam was about 50, resulting in a detection limit of about 200 mol/m³ for CH₃. The transmitted light intensity was recorded with a Nicolet Explorer II storage oscilloscope and stored on floppy disk for later use. Azomethane, synthesized according to the method of Renaud and Leitch¹⁹ and methyl iodide (99.5%, Aldrich) were used as sources of CH₃ radicals. Ar (99.999%, Matheson) and H₂ (99.97%, Matheson) were used without further purification. Test gas mixtures were prepared manometrically and allowed to stand for 48 hours before use.

Results and Discussion

The removal of CH₃ by H₂ was investigated behind incident shock waves at temperatures between 1308 and 1825 K and densities from 2.6 to 5.9 mol/m³. The mixture compositions studied are shown in Table 1. The concentrations of azomethane and methyl iodide were limited to 3000 ppm to suppress the contribution of CH₃ self-reactions and the influence of their reaction products. High H₂ concentrations were selected to enhance the rate of the CH₃ + H₂ reaction.

A typical absorption profile at 213.9 nm is shown in Figure 1. The steep rise in absorption due to production of CH₃ by thermal decomposition of azomethane or methyl iodide is followed by decay due to the reaction of CH₃ with H₂ and the CH₃ self-reactions. The absorption at long times is due to eventual accumulation of products of reaction. Even though the contributions of other species which make absorption at this wavelength were small, they were also included.

<table>
<thead>
<tr>
<th>Table 1. Mixture Compositions in Ar</th>
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<tbody>
<tr>
<td>(CH₃)₂N₂  (%)</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
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<tr>
<td>4</td>
</tr>
</tbody>
</table>
Figure 1. Typical experimental absorption profile of \( \text{CH}_3 \) at 213.9 nm. Shock conditions: 0.0994\% \( \text{C}_2\text{H}_4\text{N}_2 \), 5.32\% \( \text{H}_2 \) in Ar, \( T_1 = 1308 \text{ K} \), \( P_1 = 5.63 \text{ mol/m}^3 \).

**Table 2. Reaction mechanism**

<table>
<thead>
<tr>
<th>Elementary reaction</th>
<th>( \log A )</th>
<th>( n )</th>
<th>( E_a ) (KJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{1a} ) ( \text{C}_2\text{H}_5\text{N}_2 = \text{CH}_3 + \text{CH}_3 + \text{N}_2 )</td>
<td>9.08</td>
<td>−</td>
<td>98.9</td>
</tr>
<tr>
<td>( \text{1b} ) ( \text{CH}_3 + \text{I} = \text{CH}_3 + \text{I} )</td>
<td>14.48</td>
<td>−</td>
<td>133.9</td>
</tr>
<tr>
<td>( \text{2} ) ( \text{C}_2\text{H}_6 = \text{CH}_3 + \text{CH}_3 )</td>
<td>58.26</td>
<td>−10.61</td>
<td>412.4</td>
</tr>
</tbody>
</table>

Falloff parameters:

1.060 \( \times 10^9 \), −2.792, 389.6, 0.310, 518, 445

3. \( \text{CH}_3 + \text{CH}_3 = \text{CH}_3 + \text{H} \) 12.45 − 40.0

4. \( \text{CH}_3 + \text{CH}_3 = \text{CH}_3 + \text{H} \) 12.78 − 69.0

5. \( \text{CH}_3 + \text{C}_2\text{H}_6 = \text{CH}_3 + \text{C}_2\text{H}_5 \) −0.05 4.00 40.5

6. \( \text{CH}_3 + \text{C}_2\text{H}_4 = \text{CH}_3 + \text{C}_2\text{H}_3 \) 11.62 11.62 46.4

7. \( \text{CH}_3 + \text{C}_2\text{H}_4 = \text{CH}_3 + \text{C}_2\text{H}_4 \) −3.36 5.00 34.7

8. \( \text{C}_2\text{H}_6 + \text{H} = \text{C}_2\text{H}_5 + \text{H} \) 14.12 − 39.0

9. \( \text{C}_2\text{H}_6 = \text{C}_2\text{H}_5 + \text{H} \) 40.67 −7.04 182.0

Falloff parameters:

4.97 \( \times 10^9 \), 0.732, 154.2, 0.278, 1.032 \( \times 10^5 \), 754.2

10. \( \text{C}_2\text{H}_5 + \text{H} = \text{C}_2\text{H}_5 + \text{H} \) 12.23 − 0.0

11. \( \text{CH}_3 + \text{M} = \text{CH}_3 + \text{H} + \text{M} \) 16.00 − 377.0

12. \( \text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_4 + \text{H} \) 13.30 − 0.0

13. \( \text{CH}_3 + \text{H} = \text{CH}_3 + \text{H} \) 36.80 − 5.25 451.3

Falloff parameters:

3.71 \( \times 10^7 \), −0.558, 438.8, 0.483, 409.3, 341.3

14. \( \text{CH}_3 + \text{H} = \text{CH}_4 + \text{H} \) 12.76 − 53.0

15. \( \text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_4 + \text{H} + \text{M} \) 17.41 − 332.0

16. \( \text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_4 + \text{H} + \text{M} \) 17.41 − 404.0

17. \( \text{H} + \text{CH}_3 = \text{H} + \text{CH}_3 \) 11.50 0.70 33.5

18. \( \text{CH}_3 + \text{C}_2\text{H}_4 = \text{CH}_3 + \text{C}_2\text{H}_4 \) −3.36 5.00 34.7

19. \( \text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_4 + \text{H} \) 39.08 − 7.17 212.0

20. \( \text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_4 + \text{H} \) 13.30 − 0.0

21. \( \text{H} + \text{M} = \text{H} + \text{M} \) 12.35 0.50 387.0

22. \( \text{CH}_3 + \text{CH}_3 = \text{CH}_4 + \text{CH}_4 \) 9.23 0.56 52.6

Notes: Units are cm\(^3\), mol, s and KJ. The rate coefficients for \( \text{1a} \) and \( \text{1b} \) were taken from Møller et al.\(^a\) and Davidson et al.\(^b\) respectively. For reactions 2, 9 and 13 the tabulated parameters refer to the low pressure limit rate coefficients; the first three of the falloff parameters listed for these reactions are \( \log A \), \( n \) and \( E_a \) for their high pressure limit rate coefficients, and the remaining falloff parameters are the \( a \), \( b \) and \( c \) values that define the temperature dependence of the broadening factor.

Figure 2. Logarithmic response sensitivity spectra\(^2\) for the effective rate coefficient \( k_{eff} \) for 0.0994\% \( \text{C}_2\text{H}_4\text{N}_2 \), 5.32\% \( \text{H}_2 \) in Ar, \( T_2 = 1560 \text{ K} \), \( P_2 = 24.6 \text{ Torr} \). The filled and striped bars were computed by multiplying and dividing the Table 2 rate coefficient value by 1.5. Sensitivities less than 0.01 are not shown.

in the computer simulations described below using the extinction coefficients measured by Gardiner et al.\(^2\) under similar conditions.

The reaction mechanism used to analyze the experimental data is shown in Table 2. It was constructed starting with the Hwang et al.\(^3\) mechanism used to determine the rate coefficients for \( \text{CH}_3 \) self-reactions. These rate coefficient expressions had been optimized to describe \( \text{CH}_3 \) concentration profiles in azomethane argon mixtures shock heated in the same apparatus to conditions (temperatures from 1300 to 1700 K, densities from 2 to 9 mol/m\(^3\)) that were similar to ours. The rate coefficient expressions for \( \text{C}_2\text{H}_4\text{N}_2 \) and \( \text{CH}_3 \) decompositions were taken from Møller et al.\(^a\) and Davidson et al.\(^b\) respectively. In the final data analysis, literature values of all rate coefficient parameters were used without modification except for those of reaction 14. Sensitivity calculations\(^3\) (Fig. 2) showed that reaction 14 and \( \text{CH}_3 \) self-reactions contribute substantially to the \( \text{CH}_3 \) decay profiles.

For conditions where reaction 14 removes the main part of the \( \text{CH}_3 \) radicals and the decomposition of azomethane is fast, the decrease of the \( \text{CH}_3 \) concentration should come close to following first-order kinetics, i.e.,

\[
d[\text{CH}_3]/dt = -k_{eff}[\text{CH}_3]
\]

where \( k_{eff} = k_{11}[\text{H}_2] + k_{12}[\text{CH}_3] \). For small contributions of \( \text{CH}_3 \) self-reactions

\[
\ln ([\text{CH}_3]/[\text{CH}_3]) = k_{eff} t
\]

The absorption at 213.9 nm is almost entirely due to \( \text{CH}_3 \)

\[
\log(I_0/I) = e_{\text{CH}_3}[\text{CH}_3] d
\]

where \( d \) is the absorption path length and \( I \) is the transmitted intensity. Thus, the \( \text{CH}_3 \) concentration is related to the transmitted intensity by

\[
[\text{CH}_3]/[\text{CH}_3] = \log(I_o/I)/e_{\text{CH}_3} d
\]

\[
[\text{CH}_3]/[\text{CH}_3] = \log(I_o/I)/(e_{\text{CH}_3} d)
\]

The decrease of \( \text{CH}_3 \) follows

\[
[\text{CH}_3]/[\text{CH}_3] = \log(I_o/I)/(e_{\text{CH}_3} d)
\]
where $I_{\text{max}}$ is the transmitted intensity at maximum absorption in an experiment. From Eqs. (1) and (2) the effective rate coefficient $k_{\text{eff}}$ of CH$_3$ disappearance is given by

$$k_{\text{eff}} = (d/dt) \ln \left( \frac{I_0/I_{\text{max}}}{I_0/I} \right)$$

This analysis, based on the assumption of instantaneous azomethane decomposition and first-order decay, thus suggests that the right-hand side (rhs) of Eq. 3 should be a suitable measure of the reaction rate for the CH$_3$ loss, even though the actual removal mechanism is known to be complicated.

Figure 3 shows a plot of the rhs of Eq. 2 as a function of time under the conditions of the experiment shown in Figure 1. It shows that the intensity profile follows a first-order rate law closely for the main part of the observed disappearance of CH$_3$. For small contributions of CH$_3$ self-reactions the value of $k_{\text{eff}}$ does not depend on the extinction coefficient of CH$_3$ at all, and $k_{\text{eff}}$ can therefore be used in general for comparisons between experimental and calculated absorption profiles with confidence that the rate coefficient influences can be isolated from the value of the CH$_3$ extinction coefficient. As shown later, it also permits an evaluation of the extinction coefficient of CH$_3$ from measurements of $I_{\text{max}}$. Experimental results were compared with calculations taking into account the self-reactions of CH$_3$ and the finite rate of azomethane decomposition as follows. The CH$_3$ absorption profiles were simulated for the conditions of each run with the help of the mechanism in Table 2 using a predecessor of the LSODE$^{24}$ program for the integration of the differential equations, and the value of $k_{\text{H}_2}$ was adjusted until the experimental and calculated values of $k_{\text{eff}}$ coincided. The results of $k_{\text{H}_2}$ calculations done in this manner are presented in Figure 4 together with the results of Möller et al.$^5$, Rabinowitz et al.$^6$, Clark and Dove$^7$, Schatz et al.$^8$, and Joseph et al.$^9$. A linear least-squares fit to the data results in the expression

$$k_{\text{H}_2} = 1.10 \times 10^{13} \exp(-7370 \text{ K/T}) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$$

for the temperature range from 1308 to 1825 K. The present result is in better agreement with the expression of Rabinowitz et al.$^6$ than that of Möller et al.$^5$. The values of Schatz et al.$^8$ and Clark and Dove$^7$ also agree reasonably well with the present result but have steeper temperature dependence. The present results are in excellent agreement with the values calculated by Joseph et al.$^9$.

The rate coefficient data for reaction 14 were used to compute values of the rate coefficient for the reverse reaction. Equilibrium constant values were determined at each experimental temperature by using a polynomial fit to the JANA$^{27}$ data (1300 K < T < 1900 K):$^{27}$

$$K_d(T) = 0.125 - (1.39 \times 10^{-1} T) + (7.68 \times 10^{-8} T^2) - (1.42 \times 10^{-11} T^3)$$

The results are presented in Figure 5 together with the results of Roth and Just,$^4$ Rabinowitz et al.$^6$, Schatz et al.$^8$, Clark and Dove.$^7$ Joseph et al.$^{10}$ and Allara and Shaw.$^{13}$ Our $k_{\text{H}_2}(T)$ results are described by Arrhenius expression (1308-1825...
\[ k_{-14}(T) = 3.1 \times 10^{14} \exp(-7600 \, \text{K/T}) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \]

The extinction coefficient of CH\textsubscript{3} (\epsilon_{\text{CH}_3}) can be calculated from \( I_{\text{SM}} \) and the known \( k_{14} \), because the value of \( I_{\text{SM}} \) mainly depends on \( k_{14} \) and \( \epsilon_{\text{CH}_3} \). For the temperature range from 1308 K to 1825 K, our value of \( \epsilon_{\text{CH}_3} \) is \( 5.2 \times 10^4 \text{ cm}^2\text{mol}^{-1}\text{s}^{-1} \). Our results are close to those of Hwang \textit{et al.}\textsuperscript{21} and Yang \textit{et al.}\textsuperscript{25} who conducted experiments with the same Zn lamp and do not show any, or at most a very weak, dependence on temperature.

Acknowledgment. This research was supported by KOSEF (941-0300-016-2), the Basic Science Research Institute, Ministry of Education, Korea (BSRI-94-3419), the Gas Research Institute and the Robert A. Welch Foundation.

References