Study on the Reaction of CH2 with H2 at High Temperature

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ABSTRACT: Thermal decomposition of CH2I2 [sequential C–I bond fission processes, CH2I2 + Ar → CH2I + I + Ar (1a) and CH2I + Ar → 3CH2 + I + Ar (1b)], and the reactions of 3CH2 + H2 → CH2 + H (2) and 3CH2 + H2 → CH3 + H (3) have been studied by using atomic resonance absorption spectrometry (ARAS) of I and H atoms behind reflected shock waves. Highly diluted CH2I2 (0.1–0.4 ppm) with/without excess H2 (300 ppm) in Ar has been used so that the effect of the secondary reactions can be minimized. From the quantitative measurement of I atoms in the 0.1 ppm CH2I2 + Ar mixture over 1550–2010 K, it is confirmed that the reaction of CH2 with H2 proceeds via the two-step sequential C–I bond fission processes of CH2I2, 1a and 1b, dominate over other product channels. The decomposition step (1b) is confirmed to be the rate determining process to produce 3CH2 and the least-squares analysis of the measured rate gives, ln(k30/k1, cm3 molecule−1 s−1) = −(17.28 ± 0.79) − (30.17 ± 1.40) × 103/T. By utilizing this result, we examine reactions 2 and 3 by monitoring evolution of H atoms in the 0.2–0.4 ppm CH2I2 + 300 ppm H2 mixtures over 1850–2040 K. By using a theoretical result on k1 (Lu, K. W.; Matsui, H.; Huang, C.-L.; Raghunath, P.; Wang, N.-S.; Lin, M. C. J. Phys. Chem. A 2010, 114, 5493), we determine the rate for (3) as k3/cm3 molecule−1 s−1 = (1.27 ± 0.36) × 10−10. The upper limit of k1 (k30) is also evaluated by assuming k1 = 0, i.e., k3/cm3 molecule−1 s−1 = (2.26 ± 0.59) × 10−10. The present experimental results on k1 and k30 is found to agree very well with the previous frequency modulation spectroscopy study (Friedrichs, G.; Wagner, H. G. Z. Phys. Chem. 2001, 215, 1601); i.e., the importance of the contribution of 3CH2 in the reaction of CH2 with H2 at elevated temperature range is reconfirmed.

1. INTRODUCTION

The methylene radical, CH2 (3XB1 and 1A1, represented as 3CH2 and 1CH2, respectively), is regarded as an important reaction intermediate in hydrocarbon combustion. In the standard combustion conditions, CH2 radicals are supplied mostly in the secondary reactions such as CH3 + OH → 1CH2 + H2O and sequential collisional quenching 1CH2 + M → 3CH2 + M, therefore, the higher the concentration of fuel species, the more the importance of the role of CH2. Also, it is indicated that 1CH2 is a direct product in the thermal decomposition of CH2OH.1,2 In this case, CH2 radical plays an important role in the initial stage of the chain branching processes even if the concentration of CH2OH is low.

Detection of CH2 radical has been tried by using various techniques (LMR spectrometers, mass spectrometers, infrared diode laser absorption for 3CH2, and LIF and others for 1CH2); a large amount of information about the rate constants and reaction mechanism of CH2 radical have been accumulated at low temperature range.3–21 Also, shock tube works combined with ARAS (atomic resonance absorption spectrometry) and the frequency modulation spectroscopy have been conducted to explore the CH2 reactions above 1000 K.22–25,36

The main issue of this study is to obtain reliable kinetic information by monitoring evolution of H atoms produced in the reaction of CH2 + H2 at high temperature range. Highly sensitive detection of H atoms (1 × 1011/cm3) of this study would be efficient to reduce the effects of the side reactions. In addition, excellent reproducibility of the experimental condition in this shock tube system enables comparative measurement to confirm the concentration of the minor component in the sample mixture, as well as to examine the contributions of the background H atoms.

In most of the previous experimental studies, photolysis or thermal decomposition of CH2CO has been used as a source of supplying CH2. As CH2CO is relatively stable below 2000 K, it is also the issue of the present study to search a clean source of producing CH2 radical at lower temperature range. Therefore, this study is divided into two main experimental parts. In the first part, evolution of I atoms has been monitored by using VUV absorption at 178.3 nm in the mixture of 0.1 ppm CH2I2 + Ar over 1550–2010 K to examine the thermal decomposition process (1), i.e.,

\[ \text{CH2I2} + \text{Ar} \rightarrow \text{CH2I} + \text{I} + \text{Ar} \]  (1a)

and

\[ \text{CH2I} + \text{Ar} \rightarrow 3\text{CH2} + \text{I} + \text{Ar} \]  (1b)

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2. EXPERIMENTAL SYSTEM

Experimental study has been conducted behind reflected shock waves in a diaphragmless shock tube apparatus (length 5.9 m and i.d. 7.6 cm). Details of experiments were described in previous studies. An atomic resonance absorption spectrometry (ARAS) detection system has been used for the measurements of temporal profiles of [I] and [H]; i.e., the resonant atomic absorption of I atoms at 178.3 nm (corresponding to transition $^{2S}_{1/2} \rightarrow ^{2P}_{3/2}$) and that of H atoms at 121.6 nm are monitored by a microwave-discharge lamp filtered with a vacuum UV (VUV) monochromator and detected by a solar-blind photomultiplier tube (PMT). A gas mixture of about 1% I$_2$ and H$_2$ diluted in He of 10 Torr is supplied in the microwave-discharge lamp. VUV light passes perpendicularly through the MgF$_2$ windows at 4 cm upstream of the end plate of the shock tube. In the measurement of I atoms, a solid iodine pellet cooled at 281 K is used to supply I$_2$.

Calibration curves for H and I atoms have been constructed by using decomposition of C$_2$H$_5$I,

$$C_2H_5I + M \rightarrow C_2H_5 + I + M \quad (\phi = 0.90 \pm 0.05)$$

and sequential decomposition of C$_2$H$_5$I,

$$C_2H_5 \rightarrow C_2H_4 + H$$

Attention has been paid in the optical alignment to keep the sensitivity to be optimized; detection limit of 10$^{15}$ atom/cm$^3$ for I and H atoms has been attained. In compensation for the achievement of high sensitivity, the resolution time of the detection is not sufficiently short for the measurements of very rapid reaction phenomena. By monitoring evolutions of I and H atoms in the thermal decomposition of C$_2$H$_5$I at 1900–2000 K and 2 atm, we measured the response time of the detection system to be about 25 $\mu$s.

However, the reliability of the observed evolutions of the signal intensities can be sufficiently retained (except for the initial 25 $\mu$s) if proper experimental conditions have been chosen; this is confirmed by analyzing evolutions of H atoms in the reaction of H + O$_2$ between 1700–2000 K in the mixtures of 0.2–0.4 ppm C$_2$H$_5$I + 300–500 ppm O$_2$.

The present experiment is conducted at very low concentration of sample mixtures, 0.1–0.4 ppm CH$_3$I$_2$ (and + 300 ppm H$_2$) diluted in Ar so as to reduce the influence of the side reactions; however, the sample mixtures are prepared simply by the measurement of pressure by using combination of Baratron pressure gauges.

He (99.9995%, AGA Specialty Gases), Ar (99.9995%, AGA Specialty Gases), and H$_2$ (99.9995%, AGA Specialty Gases) are used without further purification. CH$_3$I$_2$ (99%, Sigma-Aldrich, Reagent Plus grade) and C$_2$H$_5$I (99%, Sigma-Aldrich, Reagent Plus grade) are purified by repeating degassing by successive freezing and pumping cycles.

3. RESULTS AND DISCUSSIONS

3.1. Thermal Decomposition of CH$_3$I$_2$. Almost no kinetic information is available in the past literatures for CH$_3$I$_2$ decomposition. In the study on thermal decomposition of CH$_3$I$_2$, evolution of I atoms in the 0.1 ppm CH$_3$I$_2$ in Ar is monitored behind reflected shock waves over 1550–2010 K. Examples of the observed profile of [I] are demonstrated in Figure 1. As clearly shown, it is indicated that sequential two decomposition steps of C–I bond fission dominate over other product channels because it is shown at high temperature that [I]$_{\infty}$/[CH$_3$I$_2$]$_0$ = 2 (where [I]$_{\infty}$ and [CH$_3$I$_2$]$_0$ denote the concentrations of final iodine atoms and initial CH$_3$I$_2$, respectively). Also, the first decomposition step, CH$_3$I$_2$ + Ar $\rightarrow$ CH$_3$I + I + Ar (1a) is found to be very fast, in comparison with the second step, CH$_3$I + Ar $\rightarrow$ C$_2$H$_5$ + I + Ar (1b), exhibiting that the reaction intermediate CH$_3$I is stable even in the relatively high temperature range (T > 1500 K).

Figure 1. Examples of the observed evolution of I atoms in 0.1 ppm CH$_3$I$_2$ + Ar: (A) $T = 1556$ K, $P = 2.16$ atm, [Ar] = 1.02 x 10$^{19}$/cm$^3$; (B) $T = 1761$ K, $P = 2.12$ atm, [Ar] = 8.82 x 10$^{19}$/cm$^3$; (C) $T = 1848$ K, $P = 2.08$ atm, [Ar] = 8.26 x 10$^{19}$/cm$^3$. Calculated profiles of I atoms by using eq III is shown by the dotted curve, where the initial rise is given for (A) by using $k_{1a} = 4.36 \times 10^{-9}$ exp($-19858/T$)/cm$^3$ mol$^{-1}$ s$^{-1}$ (the rate for thermal decomposition of CH$_3$I$_2$, which has nearly equal dissociation energy with reaction 1a), and the rise rate given by the response time of the detection system was used for (B) and (C).
For the sequential decomposition of CH$_2$I$_2$, the profile of concentration of I atoms is analytically given by

$$\frac{[I]}{[CH_2I_2]_0} = [1 - \exp(-R_1t)] + F_1[1 - \exp(-R_2t)] + F_2[1 - \exp(-R_2t)]$$  

where $R_1 = k_1(Ar)$, $R_2 = k_{1b}(Ar)$, $F_1 = R_2/(R_2 - R_1)$, and $F_2 = R_1/(R_1 - R_2)$. Because $R_1 \gg R_2$, the simple eq II is available in the analysis of the present experimental result,

$$\frac{[I]}{[CH_2I_2]_0} = [1 - \exp(-R_1t)] + [1 - \exp(-R_2t)]$$

(II)

The observed initial rise rate of [I] is found to be too fast to evaluate $k_{1b}$ in the temperature range above 1500 K. From the profile of I atoms in the range $1 < [I]/[CH_2I_2]_0 < 2$, the rate of the linear least-squares analysis of the data is given by $k_{1b} = 3.12 \pm 0.4$ in 10$^{15}$ molecule/cm$^3$. molecule$^{-1}$ s$^{-1}$. In the unit of cm$^3$ molecule$^{-1}$ s$^{-1}$.

The heat of reaction is estimated as

$$\Delta H^R_{298} = 72.5 \text{ kcal mol}^{-1}$$

The observed initial rise rate of [H] in the CH$_2$I$_2$+(excessH$_2$), as described below is useful to determine the validity of the nominal concentration of CH$_2$I$_2$ prepared by the procedure in the following section.

$$k_{1a} = \frac{1}{P_{CH_2I_2}} \frac{[Ar]_{a}}{[CH_2I_2]_{a}}$$

because the measured yield of I atoms is equal to 2 times of the nominal concentration of CH$_2$I$_2$ prepared by pressure measurement has been confirmed here (because the measured yield of I atoms is equal to 2 times of the nominal concentration of CH$_2$I$_2$ for $T > 1800$ K). In addition, measurement of [H] in the CH$_2$I$_2$+(excess H$_2$), as described below is useful to confirm this. These evidence ensure that the loss of CH$_2$I$_2$ should be negligible even for such low concentration samples.

The experimental condition of the present study is summarized in Table 2. All the data shown in the table is the averages of 2 data points conducted at the same shock wave condition; shot-by-shot fluctuation of the temperature shown in this table is less than $\pm 5$ K. Averaged values are shown for $T$ and $P$. Repetition of the measurement at the same condition is useful to improve the S/N ratio (by signal averaging), as well as to confirm that reasonable reproducibility of the profiles of H atoms has been attained.
Also all the data shown in Table 2 are associated with blank tests using pure Ar and 300 ppm H₂ + Ar (both sample mixtures are prepared in the same condition with the mixture of 0.2−0.4 ppm CH₂I₂ + 300 ppm H₂ + Ar) to confirm that H atom is not supplied by impurities in Ar, H₂, nor the shock tube wall. Background H atom produced in the pure Ar sample was confirmed to be below the detection limit (1 × 10¹¹ atom/cm³) in all the experimental conditions, but a small amount of H atom production is observed (up to 5 × 10¹¹ atom/cm³) in the 300 ppm H₂ + Ar mixture at the highest temperature of this study: this is not from the impurities but it can be attributed to thermal decomposition of H₂.¹³⁻¹⁵

\[ \text{H}_2 + \text{Ar} \rightarrow 2\text{H} + \text{Ar} \]  

(6)

An example of the observed profile of H atom produced in the mixtures of 0.2 ppm CH₂I₂ + 300 ppm H₂ is shown in Figure 3A.

Numerical simulations have been conducted to analyze the reaction rates of (2) and (3), however, it is practically impossible to evaluate \( k_2 \) and \( k_3 \) independently, because the collisional energy transfer from "CH₂ to "CH₂ (−4) is very fast and quasi-equilibrium between the two electronic states of CH₂ is maintained; two kinds of analyses have been tried in this study to estimate \( k_3 \) by assuming the magnitude of \( k_2 \), as described below.

The first approach of the analysis on \( k_3 \) here is to employ the result of theoretical calculation (ab initio molecular orbital and transition state theory, including Eckert correction) for the reaction (2) expressed as²⁷

\[ k_3/\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1} = 7.32 \times 10^{-19}T^{2.3}\exp(-3699/T) \]  

(IV)

Using (IV) may be justified by the fact that (IV) agrees very well with the semiempirical data on \( k_2 \) based on the measurement of Gesser and Steacie¹² for the relative rate constant

\[ \text{H}_2 + \text{Ar} \rightarrow 2\text{H} + \text{Ar} \]  

(6)

Figure 3. Example of the observed evolution of H atoms in the highly diluted CH₂I₂ + 300 ppm H₂ in Ar and comparisons with simulations. (A) Experimental result shown by the black solid line. Sample gas: 0.2 ppm CH₂I₂ + 300 ppm H₂ in Ar, \( T = 2002 \text{ K}, P = 1.88 \text{ atm}, [\text{Ar}] = 6.90 \times 10^{18}/\text{cm}^3, [\text{CH₂I₂}]_0 = 1.38 \times 10^{12}/\text{cm}^3. \) Kinetic simulations using the mechanism of Table 2 are shown by the red solid curve and the values for ±30% of \( k_3 \) are shown by the red broken curves, respectively. The solution with the best fit of \( k_{\text{max}} \) (maximum value for \( k_3 \) assuming \( k_2 = 0 \)) is shown by the black open circle. (B) Sensitivity coefficient (nondimension) for H atoms; \( S_{\text{Hj}} \) evaluated for the experimental condition of (A). The number indicated in this figure corresponds to the reaction number in the text and Table 3. The reactions in Table 3 not shown in this figure do not show any sensitivity.

Figure 4. Summary of the reaction rates for "CH₂ + H₂ → CH₃ + H (2) and "CH₂ + H₂ → CH₃ + H (3). (A) \( k_2 \) (expressed by the red symbols): red circle, present study; red solid line and red dashed line, ref 25 (\( k_2 + k_3 \)); red dashed-dotted line, ref 17; red dotted line, ref 16; × and +, ref 25, \( k_3 \) (expressed by the red symbols): red circle, present study for \( k_3 \); red triangle, present study for the maximum value for \( k_3 \), i.e., \( k_{\text{max}} \) (see text); red solid line, ref 25 (\( k_3 + k_2 \)), where the upper and lower limits of ref 25 are shown by the red dashed lines; red dotted line, extrapolation of the low temperature study of ref 17.

Numerical simulations have been conducted to analyze the reaction rates of (2) and (3), however, it is practically impossible to evaluate \( k_2 \) and \( k_3 \) independently, because the collisional energy transfer from "CH₂ to "CH₂ (−4) is very fast and quasi-equilibrium between the two electronic states of CH₂ is maintained; two kinds of analyses have been tried in this study to estimate \( k_3 \) by assuming the magnitude of \( k_2 \), as described below.

The first approach of the analysis on \( k_3 \) here is to employ the result of theoretical calculation (ab initio molecular orbital and transition state theory, including Eckert correction) for the reaction (2) expressed as²⁷
Table 3. Reaction Mechanism for Analyzing the Observed Profile of the H Atom

<table>
<thead>
<tr>
<th>reaction</th>
<th>$A^b$</th>
<th>$n^b$</th>
<th>$E^b$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH$_2$I$_2$ + M → ³CH$_2$ + 2I + M</td>
<td>$3.12 \times 10^{-4}$</td>
<td>0</td>
<td>30170</td>
<td>this study</td>
</tr>
<tr>
<td>2. ³CH$_2$ + H$_2$ = CH$_3$ + H</td>
<td>$7.32 \times 10^{-19}$</td>
<td>2.3</td>
<td>3699</td>
<td>26</td>
</tr>
<tr>
<td>3. ¹CH$_2$ + H$_2$ = CH$_3$ + H</td>
<td>$1.26 \times 10^{-2}$</td>
<td>0</td>
<td>0</td>
<td>this study</td>
</tr>
<tr>
<td>4. ¹CH$_2$ + M = ³CH$_2$ + M</td>
<td>$4.0 \times 10^{-14}$</td>
<td>0.9</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>5. CH$_3$ + H$_2$ = CH$_4$ + H</td>
<td>$1.47 \times 10^{-20}$</td>
<td>2.74</td>
<td>4740</td>
<td>26</td>
</tr>
<tr>
<td>6. 2H + M = H$_2$ + M</td>
<td>$1.66 \times 10^{-6}$</td>
<td>-1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>7. ³CH$_2$ + CH$_3$ = H + C$_2$H$_4$</td>
<td>$1.89 \times 10^{-10}$</td>
<td>-0.1317</td>
<td>8.2</td>
<td>1</td>
</tr>
<tr>
<td>8. ³CH$_2$ + C$_2$H$_4$ = 2CH$_3$</td>
<td>$4.09 \times 10^{-18}$</td>
<td>2</td>
<td>4164</td>
<td>1</td>
</tr>
<tr>
<td>9. ¹CH$_3$ + CH$_4$ = H + C$_2$H$_4$</td>
<td>$2.0 \times 10^{-6}$</td>
<td>0</td>
<td>-287</td>
<td>1</td>
</tr>
<tr>
<td>10. ¹CH$_3$ + CH$_4$ = 2CH$_3$</td>
<td>$2.66 \times 10^{-11}$</td>
<td>0</td>
<td>-287</td>
<td>1</td>
</tr>
<tr>
<td>11. 2CH$_3$ + M = C$_2$H$_6$ + M</td>
<td>$1.12 \times 10^{-7}$</td>
<td>-1.18</td>
<td>329.3</td>
<td>1</td>
</tr>
<tr>
<td>12. CH$_3$ + CH$_3$ = C$_2$H$_6$ + H</td>
<td>$1.14 \times 10^{-11}$</td>
<td>0</td>
<td>5337</td>
<td>1</td>
</tr>
<tr>
<td>13. ³CH$_2$ + ³CH$_2$ = C$_2$H$_4$ + H</td>
<td>$2.39 \times 10^{-10}$</td>
<td>0.0254</td>
<td>17.1</td>
<td>1</td>
</tr>
<tr>
<td>14. ¹CH$_3$ + ³CH$_2$ = C$_2$H$_4$ + H</td>
<td>$1.66 \times 10^{-11}$</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>15. C$_2$H$_5$ + M → C$_2$H$_4$ + H + M</td>
<td>$1.66 \times 10^{-7}$</td>
<td>0</td>
<td>15609</td>
<td>1</td>
</tr>
<tr>
<td>16. C$_2$H$_5$ + M → C$_2$H$_4$ + H + M</td>
<td>$4.98 \times 10^{-9}$</td>
<td>0</td>
<td>16113</td>
<td>1</td>
</tr>
<tr>
<td>17. ³CH$_2$ + C$_2$H$_6$ = CH$_3$ + C$_2$H$_3$</td>
<td>$1.88 \times 10^{-10}$</td>
<td>0</td>
<td>3950</td>
<td>1</td>
</tr>
<tr>
<td>18. CH$_3$ + C$_2$H$_6$ = CH$_4$ + C$_2$H$_3$</td>
<td>$1.02 \times 10^{-17}$</td>
<td>1.7</td>
<td>5262</td>
<td>1</td>
</tr>
<tr>
<td>19. H + C$_2$H$_4$ = H$_2$ + C$_2$H$_3$</td>
<td>$1.91 \times 10^{-16}$</td>
<td>1.9</td>
<td>3792</td>
<td>1</td>
</tr>
<tr>
<td>20. H + CH$_3$ + M = CH$_4$ + M</td>
<td>$2.31 \times 10^{-10}$</td>
<td>-0.534</td>
<td>270</td>
<td>1</td>
</tr>
</tbody>
</table>

"Forward and reverse reactions are considered when connected by ‘+→’.

"Only parameters for the high pressure limit are shown but the rate for the falloff region is evaluated by using parameters given in ref 1.

for the reaction of ³CH$_2$ with H$_2$ (2) against

³CH$_2$ + CH$_2$CO → ³C$_2$H$_4$ + CO (reference reaction)

combined with computed rate constant for ³CH$_2$ + CH$_2$CO$^{27}$ for the temperature range 230–370 K.

By using a reaction scheme shown in Table 3, we conducted fitting the numerical simulation to the observed profile for the evolution of H atoms in the range of initial fast rise for $t = 25$–$150$ μs, where the profile of H atoms is sensitive to the reactions ³CH$_2$ + H$_2$→ CH$_3$ + H (2) and ¹CH$_3$ + H$_2$→ CH$_4$ + H (3). The optimized solutions for $k_a$ which give the best fit to the experimental profiles, are summarized in Table 2, and an example is shown by the red solid curve in Figure 3A.

The second approach of the present analysis is the limiting case evaluating the upper limit of $k_a$, i.e., $k_{a_{max}}$, with an assumption $k_2 = 0$. As shown by the black circle in Figure 3A, it is possible to achieve good agreement of the numerical simulation to the experimental profile of H atoms even for neglecting the contribution of (2). The results of the analyses on $k_{a_{max}}$ are summarized also in Table 2.

An example of the computed sensitivity coefficients (non-dimensional) are shown in Figure 3B. Contributions of the reactions in Table 3 other than (1)–(6) are in fact negligibly small, as the concentration of CH$_2$I$_2$ used in this study is very low. Contribution for the delay of producing ³CH$_2$ in the thermal decomposition of CH$_2$I$_2$ (1) is significant at the initial stage of the reaction, CH$_3$ + H$_2$→ CH$_4$ + H (5) dominates for large $t$, and the reaction (6) has some sensitivity at high temperature range, $T > 2000$ K, nevertheless, it is demonstrated that (2) and (3) are sufficiently sensitive to evaluate kinetic rate constant. It is also worthwhile to mention that the numerical simulation can reproduce very well the observed profile of H atoms with using the nominal value of the initial concentration of CH$_2$I$_2$ for all the experimental data; computation to estimate the accuracy for $[CH_2I_2]_0$ has been also performed and the nominal value is concluded to be reliable with ±10% error limit.

The present experimental result for (3) by employing theoretical result for $k_3$ can be expressed as

$$k_3/cm^3\text{ molecule}^{-1}\text{ s}^{-1} = (1.27 \pm 0.36) \times 10^{-10}$$  \hspace{1cm} (V)

and the upper limit of $k_3$ ($k_{3_{max}}$) by assuming $k_2 = 0$ can be expressed as

$$k_{3_{max}}/cm^3\text{ molecule}^{-1}\text{ s}^{-1} = (2.26 \pm 0.59) \times 10^{-10}$$  \hspace{1cm} (VI)

for the temperature range of $T = 1850–2050$ K, here, the error limit is given by ±10%.

The result of the present study on $k_3$ is compared with previous works on $k_3$ and $k_5$ in Figure 4A (summary of the data for a wide temperature range), and in Figure 4B (high temperature data including $k_{3_{max}}$).

As shown in Figure 4A,B, the rate for (3) evaluated in this study is found to agree very well with that of previous shock tube work$^{15}$ as well as with the experimental works below 1000 K.$^{17 – 20}$ Agreement of the high temperature data on $k_3$ with the experimental result by Gannon et al. conducted between 195–798 K$^{17}$ implies that $k_3$ shows almost no temperature dependence. Although the result by Friedrichs and Wagner$^{27}$ was indicated to be $k_2 + k_9$, it should be approximately equal to $k_a$, because the contribution of $k_2$ is indicated to be
minor. Their estimated upper limit for \( k_2 + k_3 \) also agrees very well with the upper limit of this study.

As for reaction (2), it is difficult to examine \( k_2 \) precisely only from the present experimental information. The results on \( k_3 \) evaluated by Friedrichs and Wagner\(^{25} \) are also shown in Figure 4, but it seems difficult to extract a reliable estimate because it should be very sensitive to the uncertainty of the magnitude of measured \( k_3 \).

The main conclusion of this study, in agreement with Friedrichs and Wagner\(^{25} \), is that the importance of \( ^1\text{CH}_2 \) in the reaction of \( \text{CH}_2 + \text{H}_2 \) has been confirmed; i.e., the reaction at elevated temperature can proceed through collisional excitation from \( ^3\text{CH}_2 \) to \( ^1\text{CH}_2 \) if the reaction rate of \( ^3\text{CH}_2 \) is not extremely large. The same scenario may hold for the reactions of \( \text{CH}_2 \) with other molecules. Gannon et al.\(^{17} \) demonstrated in the study of \( ^1\text{CH}_2 + \text{D}_2 \) reaction that an insertion reaction can be competitive to the direct abstraction reaction, because they confirmed that two-thirds of the products of this reaction was \( \text{H}_2 \) atom. For the molecules other than \( \text{H}_2 \), insertion reaction can still be a part of the main channels for the thermal reactions of \( \text{CH}_2 \) at elevated temperature. Examination of the relative contributions of \( ^3\text{CH}_2 \) and \( ^1\text{CH}_2 \) in many of the key reactions in combustion system seems to be still a challenging task.

**REFERENCES**