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中文摘要： 我們使用衝擊波管-原子共振螢光技術在 1700-2000K 高溫範圍研究亞甲基(CH₂)與氫氣反應動力學，除成功地量得單態亞甲基之速率常數為 $k = (1.27 \pm 0.36) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 。同時也測得二碘甲烷分解之動力學資訊： $\text{CH}_2\text{I}_2 + \text{Ar} \rightarrow \text{CH}_2\text{I} + \text{I} + \text{Ar}$ (1a)及 $\text{CH}_2\text{I} + \text{Ar} \rightarrow 3\text{CH}_2 + \text{I} + \text{Ar}$ (1b)。反應(1a)極快而(1b)為速率決定步驟： $\ln(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -(17.28 \pm 0.79) - (30.17 \pm 1.40) \times 10^3/T$ 。研究成果已投稿至 J. Phys. Chem. A, 也被接受(JPCA, Just Accepted, 01/20/2012)

中文關鍵詞： 亞甲基，氫氣，二碘甲烷，反應動力學，衝擊波管

英文摘要：

英文關鍵詞：

Study on The Reaction of CH₂ with H₂ at High Temperature

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Abstract

Thermal decomposition of CH_2I_2 [sequential C-I bond fission processes, $\text{CH}_2\text{I}_2 + \text{Ar} \rightarrow \text{CH}_2\text{I} + \text{I} + \text{Ar}$ (1a) and $\text{CH}_2\text{I} + \text{Ar} \rightarrow {}^3\text{CH}_2 + \text{I} + \text{Ar}$ (1b)], and the reactions of ${}^3\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ (2) and ${}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ (3) have been studied by using atomic resonance absorption spectrometry (ARAS) of I and H atoms behind reflected shock waves. Highly diluted CH_2I_2 (0.1 - 0.4 ppm) with/without excess H_2 (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 $\text{CH}_2\text{I}_2 + \text{Ar}$ mixture over 1550-2010 K, it is confirmed that two-step sequential C-I bond fission processes of CH_2I_2 , (1a) and (1b) dominate over other product channels. Decomposition step (1b) is confirmed to be the rate determining process to produce ${}^3\text{CH}_2$ and the least-squares analysis of the measured rate gives, $\ln(k_{1b}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) = -(17.28 \pm 0.79) - (30.17 \pm 1.40) \times 10^3/T$. By utilizing this result, reactions (2) and (3) are examined by monitoring evolution of H atoms in the 0.2 - 0.4 ppm $\text{CH}_2\text{I}_2 + 300$ ppm H_2 mixtures over 1850 - 2040 K. By using a theoretical result on k_2 (Lu, K. W.; Matsui, H.; Huang, C.-L.; Raghunath, P.; Wang, N.-S.; Lin, M. C., *J. Phys. Chem. A*, **2010**, 114, 5493), the rate for (3) is determined as $k_3/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1} = (1.27 \pm 0.36) \times 10^{-10}$. The upper limit of k_3 ($k_{3\text{max}}$) is also evaluated by assuming $k_2 = 0$, i.e., $k_{3\text{max}}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1} = (2.26 \pm 0.59) \times 10^{-10}$. The present experimental results on k_3 and $k_{3\text{max}}$ is found to agree very well with the previous frequency modulation spectroscopy study (Friedrichs, G.; Wagner, H. Gg. *Z. Phys. Chem.* **2001**, 215, 1601), i.e., the importance of the contribution of ${}^1\text{CH}_2$ in the reaction of CH_2 with H_2 at elevated temperature range is reconfirmed.

1. Introduction

The methylene radical, CH_2 ($\tilde{X}^3\text{B}_1$ and $\tilde{a}^1\text{A}_1$, represented as $^3\text{CH}_2$ and $^1\text{CH}_2$, respectively) is regarded as an important reaction intermediate in hydrocarbon combustion. In the standard combustion conditions, CH_2 radicals are supplied mostly in the secondary reactions such as $\text{CH}_3 + \text{OH} \rightarrow ^1\text{CH}_2 + \text{H}_2\text{O}$ and sequential collisional quenching $^1\text{CH}_2 + \text{M} \rightarrow ^3\text{CH}_2 + \text{M}$,¹⁻³ therefore, higher the concentration of fuel species, the importance of the role of CH_2 increases. Also, it is indicated that $^1\text{CH}_2$ is a direct product in the thermal decomposition of CH_3OH .^{2,3} In this case, CH_2 radical plays an important role in the initial stage of the chain branching processes even if concentration of CH_3OH is low.

Detection of CH_2 radical has been tried by using various techniques (LMR spectrometers, mass spectrometers, infrared diode laser absorption for $^3\text{CH}_2$, and LIF and others for $^1\text{CH}_2$); a large amount of information about the rate constants and reaction mechanism of CH_2 radical have been accumulated at low temperature range.⁴⁻²¹ Also, shock tube works combined with ARAS (atomic resonance absorption spectrometry) and the frequency modulation spectroscopy have been conducted to explore the CH_2 reactions above 1000 K.^{22-25, 36}

Main issue of this study is to obtain reliable kinetic information by monitoring evolution of H atoms produced in the reaction of $\text{CH}_2 + \text{H}_2$ at high temperature range. Highly sensitive detection of H atoms ($1 \times 10^{11}/\text{cm}^3$) 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 CH_2CO has been used as a source of supplying CH_2 . As CH_2CO is relatively stable below 2000 K, it is also the issue of the present study to search a clean source of producing CH_2 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 178.3nm in the mixture of 0.1 ppm $\text{CH}_2\text{I}_2 + \text{Ar}$ over 1550 – 2010 K to examine the thermal decomposition process (1), i.e.,



and



By using the result of thermal decomposition of CH_2I_2 , the reaction of CH_2 radical with H_2 , the reactions



and

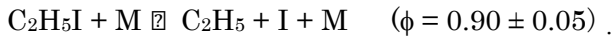


have been examined by monitoring H atoms. Even though ${}^3\text{CH}_2$ is expected to be the main products in (1b), it is important to take into account (3) at elevated temperature condition, as the collisional energy transfer between ${}^1\text{CH}_2$ and ${}^3\text{CH}_2$, (4) is very fast;



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.^{26,27} An atomic resonance absorption spectrometry (ARAS) detection system has been used for the measurements of temporal profiles of [I] and [H], i.e., resonant atomic absorption of I atoms at 178.3nm (corresponding to transition ${}^2\text{P}_{1,3/2} - {}^2\text{P}_{0,3/2}$) and that of H atoms at 121.6nm is monitored by using a microwave-discharge lamp filtered with a vacuum UV (VUV) monochromator and detected by a solar-blind photomultiplier tube (PMT). 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, 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 $\text{C}_2\text{H}_5\text{I}$,



and sequential decomposition of C_2H_5 ,



Attention has been paid in the optical alignment to keep the sensitivity to be optimized; detection limit of 10^{11} atom/cm³ 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 $\text{C}_2\text{H}_5\text{I}$ at 1900 - 2000 K and 2 atm., the response time of the detection system is measured to be about 25 μ s.

However, the reliability of the observed evolutions of the signal intensities can be sufficiently retained (except for the initial 25 μ s) if proper experimental conditions have been chosen; this is confirmed by analyzing evolutions of H atoms in the reaction of $\text{H} + \text{O}_2$ between 1700 - 2000 K in the mixtures of 0.2 - 0.4 ppm $\text{C}_2\text{H}_5\text{I}$ + 300 - 500 ppm O_2 .

Present experiment is conducted at very low concentration of sample mixtures, 0.1 - 0.4 ppm CH_2I_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) and Ar (99.9995%, AGA Specialty Gases), H_2 (99.9995%, AGA Specialty Gases) are used without further purification. CH_2I_2 (99%, Sigma-Aldrich, Reagent Plus grade) and $\text{C}_2\text{H}_5\text{I}$ (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_2I_2

Almost no kinetic information is available in the past literatures for CH_2I_2 decomposition. In the study on thermal decomposition of CH_2I_2 , evolution of I atoms in the 0.1 ppm CH_2I_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 since it is shown at high temperature that $[\text{I}]_\infty/[\text{CH}_2\text{I}_2]_0 = 2$

(where, $[I]_{\infty}$ and $[CH_2I_2]_0$ denote the concentrations of final iodine atoms and initial CH_2I_2 , respectively). Also, the first decomposition step, $CH_2I_2 + Ar \rightarrow CH_2I + I + Ar$ (1a) is found to be very fast, in comparison with the second step, $CH_2I + Ar \rightarrow {}^3CH_2 + I + Ar$ (1b), exhibiting that the reaction intermediate CH_2I is stable even in the relatively high temperature range ($T > 1500$ K).

For the sequential decomposition of CH_2I_2 , the profile of concentration of I atoms is analytically given by,

$$[I]/[CH_2I_2]_0 = [1 - \exp(-R_1t)] + F_1[1 - \exp(-R_1t)] + F_2[1 - \exp(-R_2t)] \quad (I)$$

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

$$[I]/[CH_2I_2]_0 = [1 - \exp(-R_1t)] + [1 - \exp(-R_2t)]. \quad (II)$$

The observed initial rise rate of $[I]$ is found to be too fast to evaluate k_{1a} 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 (1b) was evaluated by using an estimated rate for R_1 into equation (II)²⁸ and the result is summarized in Table 1 as well as in Figure 2. Linear least-squares analysis of the data on k_{1b} gives,

$$\ln(k_{1b}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) = -(17.28 \pm 0.79) - (30.17 \pm 1.40) \times 10^3/T \quad (III).$$

over the temperature range of $T = 1500 - 2000$ K.

The heat of reaction is estimated as $\Delta H^0_{298} = 51.5$ kcal mol⁻¹ and $\Delta H^0_{298} = 64.4$ kcal mol⁻¹ for (1a) and (1b), respectively, based on the recent experimental data on the heat of formation of CH_2I and the C - H bond fission energy.²⁹ The heat of reaction for other possible 3-centered reactions such as, $CH_2I_2 + M \rightarrow CHI + HI + M$, $CH_2I_2 + M \rightarrow {}^1,3CH_2 + I_2 + M$, and $CH_2I + M \rightarrow CH + HI + M$, is estimated as $\Delta H^0_{298} = 72.5$ kcal mol⁻¹, 79.1 kcal mol⁻¹ (for the spin - forbidden ${}^3CH_2$ formation), and 93.9 kcal mol⁻¹, respectively.³⁰⁻³³ Therefore, dominance of (1) over other channels, as well as two-steps production behavior of I atoms observed in this study can be justified thermodynamically. The observed activation energy of 60 kcal/mol for (1b) seems to be consistent with the endothermicity of the reaction.

CH_2I_2 is confirmed to be a clean and better source for supplying ${}^3CH_2$ than CH_2CO for the shock tube study below 2000 K, however, about 1800 K is indicated to be the

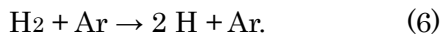
lower limit for the purpose of quick supply. As (1b) is the rate determining step to produce $^3\text{CH}_2$, the result (III) is used as the production rate for $^3\text{CH}_2$ in the analysis in the $\text{CH}_2 + \text{H}_2$ reaction in the following section. More detailed study on thermal decomposition of CH_2I_2 is now under way and will be presented elsewhere.³⁴

3.2 Reaction of CH_2 with H_2

Evolution of $[\text{H}]$ in the mixtures of 0.2 - 0.4 ppm CH_2I_2 + 300 ppm H_2 in Ar is monitored over 1850 - 2040 K. In conducting an experiment with very low concentration of sample gas such as employed in this study, it is especially important to examine the validity of the prepared concentration of minor component, as well as to confirm that the reaction system is free from the effect of impurities: these requirements may not be generally so easy to achieve when the concentration of sample gas is extremely low. As described above, validity of the nominal concentration of CH_2I_2 prepared by pressure measurement has been confirmed here (since the measured yield of I atoms is equal to 2 times of the nominal concentration of CH_2I_2 for $T > 1800$ K). In addition, measurement of $[\text{H}]$ in the $\text{CH}_2\text{I}_2 + (\text{excess } \text{H}_2)$, as described below is useful to confirm this. These evidences ensure that the loss of CH_2I_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 are 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 ± 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 $\text{H}_2 + \text{Ar}$ (both sample mixtures are prepared in the same condition with the mixture of 0.2 - 0.4 ppm $\text{CH}_2\text{I}_2 + 300$ ppm $\text{H}_2 + \text{Ar}$) to confirm that H atom is not supplied by impurities in Ar, H_2 nor the shock tube wall. Background H atom produced in the pure Ar sample was confirmed to be below the detection limit (1×10^{11} atom/cm³) in all the experimental conditions, but small amount of H atom production is observed (up to 5×10^{11} atom/cm³) in the 300 ppm $\text{H}_2 + \text{Ar}$ mixture at the highest temperature of this study: this is not from the impurities but it can be attributed to thermal decomposition of H_2 .^{1,35}



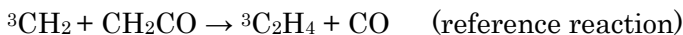
An example of the observed profile of H atom produced in the mixtures of 0.2 ppm CH₂I₂ + 300 ppm H₂ is shown in Figure 3-A.

Numerical simulations has been conducted to analyze the reaction rates of (2) and (3): however, it is practically impossible to evaluate k_2 and k_3 independently, since the collisional energy transfer from ³CH₂ to ¹CH₂ (-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 as,²⁷

$$k_2 / \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1} = 7.32 \times 10^{-19} T^{2.3} \exp(-3,699/T), T = 200 - 3000 \text{ K} \quad (\text{IV}).$$

Using (IV) may be justified by the fact that (IV) agrees very well with the semi-empirical data on k_2 based on the measurement of Gesser and Steacie¹² for the relative rate constant for the reaction of ³CH₂ with H₂ (2) against,



combined with computed rate constant for ³CH₂ + CH₂CO²⁷ for the temperature range of 230 - 370 K.

By using a reaction scheme shown in Table 3, fitting the numerical simulation to the observed profile was conducted for the evolution of H atoms in the range of initial fast rise for $t = 25 - 150 \mu\text{s}$, where, profile of H atoms is sensitive to the reactions ³CH₂ + H₂ → CH₃ + H (2) and ¹CH₂ + H₂ → CH₃ + H (3). The optimized solutions for k_3 which give the best fit to the experimental profiles are summarized in Table 3, and an example is shown by the red solid curve in Figure 3-A.

The second approach of the present analysis is the limiting case evaluating the upper limit of k_3 , i.e., $k_{3\text{max}}$, with an assumption $k_2 = 0$. As shown by the black circle in Figure 3-A, 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 $k_{3\text{max}}$ are summarized also in Table 3.

An example of the computed sensitivity coefficients (non-dimensional) are shown in Figure 3-B. Contributions of the reactions in Table 3 other than (1) - (6) are in fact negligibly small, as the concentration of CH₂I₂ used in this study is very low. Contribution for the delay of producing ³CH₂ in the thermal decomposition of CH₂I₂ (1)

is significant at the initial stage of the reaction, $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2$ (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_2I_2 for all the experimental data; computation to estimate the accuracy for $[\text{CH}_2\text{I}_2]_0$ 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_2 can be expressed as,

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

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

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

for the temperature range of $T = 1850 - 2050$ K, here, the error limit is given by 2σ .

The result of the present study on k_3 is compared with previous works on k_2 and k_3 in Figure 4-A (summary of the data for a wide temperature range), and in Figure 4-B (high temperature data including $k_{3\text{max}}$).

As shown in Figure 4-A and 4-B, the rate for (3) evaluated in this study is found to agree very well with that of previous shock tube work¹⁵, 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 K¹⁷ implies that k_3 shows almost no temperature dependence. Although the result by Friedrichs and Wagner²⁵ was indicated to be $k_2 + k_3$, it should be approximately equal to k_3 , since the contribution of k_2 is indicated to be minor. Their estimated upper limit for $k_2 + k_3$ also agrees very well with $k_{3\text{max}}$ 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_2 evaluated by Friedrichs and Wagner²⁵ are also shown in Figure 4, but it seems difficult to extract 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 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, since they confirmed that 2/3 of the products of this reaction was H atom. For the molecules other than H_2 , insertion reaction can still be a part of the main channels for the thermal reactions of 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.

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Table 1. Summary of the experimental condition for thermal decomposition of CH_2I_2 and the rate constant k_{1b}

T/K	P/atm.	$[\text{CH}_2\text{I}_2]_0^a$	$[\text{Ar}]^b$	k_{1b}^c
1556	2.16	1.02	10.2	8.64×10^{-17}
1648	1.36	0.607	6.07	3.93×10^{-16}
1648	1.36	0.607	6.07	3.28×10^{-16}
1761	2.12	0.882	8.82	1.23×10^{-15}
1763	2.12	0.883	8.83	1.46×10^{-15}
1843	2.07	0.825	8.25	2.52×10^{-15}
1849	2.08	0.826	8.26	3.33×10^{-15}
1852	2.09	0.827	8.27	2.84×10^{-15}
1848	2.08	0.826	8.26	2.66×10^{-15}
2012	1.92	0.701	7.01	7.86×10^{-15}
2012	1.92	0.701	7.01	7.33×10^{-15}

a: in 10^{12} molecule/ cm^3 , b: in 10^{18} atom/ cm^3 , c: in the unit of $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

Table 2 Summary of The experimental Conditions for CH₂ + H₂ reaction and The Measured Rate Constants k_2 and k_5

T/K	P/atm.	[Ar] ^a	[CH ₂ I ₂] ₀ ^b	k_3^c	$k_{3\max}^c$
0.4ppmCH ₂ I ₂ +300ppmH ₂ +Ar					
2044	1.75	6.29	0.252	(1.03±0.33)×10 ⁻¹⁰	(2.14±0.83)×10 ⁻¹⁰
1958	1.99	7.45	0.298	(1.44±0.20)×10 ⁻¹⁰	(2.31±0.73)×10 ⁻¹⁰
1852	2.09	8.27	0.313	(1.15±0.31)×10 ⁻¹⁰	(2.16±0.18)×10 ⁻¹⁰
0.2ppmCH ₂ I ₂ +300ppmH ₂ +Ar					
2041	1.86	6.69	0.134	(1.40±0.15)×10 ⁻¹⁰	(2.66±0.47)×10 ⁻¹⁰
2002	1.88	6.9	0.138	(1.36±0.47)×10 ⁻¹⁰	(2.39±0.93)×10 ⁻¹⁰
1938	2.01	7.62	0.152	(1.17±0.64)×10 ⁻¹⁰	(2.16±0.30)×10 ⁻¹⁰
1902	2.01	7.77	0.155	(1.40±0.19)×10 ⁻¹⁰	(2.21±0.45)×10 ⁻¹⁰
1855	2.08	8.23	0.165	(1.21±0.55)×10 ⁻¹⁰	(2.06±0.83)×10 ⁻¹⁰

a: in 10¹⁸ atom cm⁻³, b: in 10¹³ molecule cm⁻³, c: in the unit of cm³molecule⁻¹s⁻¹

Table 3 Reaction mechanism for analyzing the observed profile of H atom.

Reaction ^a	A ^b	n ^b	E ^b	Reference
1. CH ₂ I ₂ +M → ³ CH ₂ +2I+M	3.12x10 ⁻⁸	0	30170	this study
2. ³ CH ₂ +H ₂ = CH ₃ +H	7.32x10 ⁻¹⁹	2.3	3699	26
3. ¹ CH ₂ +H ₂ = CH ₃ +H	1.26x10 ⁻¹⁰	0	0	this study
4. ¹ CH ₂ +M = ³ CH ₂ +M	4.0x10 ⁻¹⁴	0.9	0	15
5. CH ₃ +H ₂ = CH ₄ +H	1.47x10 ⁻²⁰	2.74	4740	26
6. 2H+M = H ₂ +M ^c	1.66x10 ⁻⁶	-1	0	1
7. ³ CH ₂ +CH ₃ = H+C ₂ H ₄	1.89x10 ⁻¹⁰	-0.1317	8.2	1
8. ³ CH ₂ +CH ₄ = 2CH ₃	4.09x10 ⁻¹⁸	2	4164	1
9. ¹ CH ₂ +CH ₃ = H+C ₂ H ₄	2.0x10 ⁻⁶	0	-287	1
10. ¹ CH ₂ +CH ₄ = 2CH ₃	2.66x10 ⁻¹¹	0	-287	1
11. 2CH ₃ +M = C ₂ H ₆ +M ^d	1.12x10 ⁻⁷	-1.18	329.3	1
12. CH ₃ +CH ₃ = C ₂ H ₅ +H	1.14x10 ⁻¹¹	0	5337	1
13. ³ CH ₂ + ³ CH ₂ = C ₂ H ₃ +H	2.39x10 ⁻¹⁰	0.0254	17.1	1
14. ³ CH ₂ + ³ CH ₂ = C ₂ H ₂ +H ₂	1.66x10 ⁻¹¹	0	0	1
15. C ₂ H ₅ +M → C ₂ H ₄ +H+M ^d	1.66x10 ⁻⁷	0	15609	1
16. C ₂ H ₃ +M → C ₂ H ₂ +H+M ^d	4.98x10 ⁻⁹	0	16113	1
17. ³ CH ₂ +C ₂ H ₆ = CH ₃ +C ₂ H ₅	1.88x10 ⁻¹⁰	0	3950	1
18. CH ₃ +C ₂ H ₆ = CH ₄ +C ₂ H ₅	1.02x10 ⁻¹⁷	1.7	5262	1
19. H+C ₂ H ₆ = H ₂ +C ₂ H ₅	1.91x10 ⁻¹⁶	1.9	3792	1
20. H+CH ₃ +M = CH ₄ +M ^d	2.31x10 ⁻⁹	-0.534	270	1

a: forward and reverse reactions are considered when connected by " = "

b: $k = A T^n \exp(-E_a/RT)$ [molecule, cm³, K, cal]

c: third-body collision efficiency for M (= Ar) is taken from Ref. 1.

d: only parameters for high pressure limit are shown but the rate for fall-off region is evaluated by using parameters given in Ref.1

Figure Captions

Figure 1. Examples of the observed evolution of I atoms in the 0.1 ppm $\text{CH}_2\text{I}_2 + \text{Ar}$
A: $T = 1556 \text{ K}$, $P = 2.16 \text{ atm.}$, $[\text{Ar}] = 1.02 \times 10^{19}/\text{cm}^3$; B: $T = 1761 \text{ K}$, $P = 2.12 \text{ atm.}$; $[\text{Ar}] = 8.82 \times 10^{18}/\text{cm}^3$; C: $T = 1848 \text{ K}$, $P = 2.08 \text{ atm.}$, $[\text{Ar}] = 8.26 \times 10^{18}/\text{cm}^3$
Calculated profiles of I atoms by using equation (III) is shown by the dotted curve. where, initial rise is given for Figure 1-A, by using $k_{1a} = 4.36 \times 10^{-9} \exp(-19858/T)/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$, (the rate for thermal decomposition of CH_3I 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 Figures 1B and 1C.

Figure 2. Arrhenius plot of the reaction rate for $\text{CH}_2\text{I} + \text{Ar} \rightarrow {}^3\text{CH}_2 + \text{I} + \text{Ar}$ (1b)
Linear least squares-analysis of the data is given by $k_{1b} / \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} = 3.12 \times 10^{-8} \exp(-30170/T)$ and expressed by the straight solid line.

Figure 3. An example of the observed evolution of H atoms in the highly diluted $\text{CH}_2\text{I}_2 + 300 \text{ ppm H}_2$ in Ar and comparisons with simulations.
A: experimental result is shown by the black solid line; sample gas: 0.2 ppm $\text{CH}_2\text{I}_2 + 300 \text{ ppm H}_2$ in Ar, $T = 2002 \text{ K}$, $P = 1.83 \text{ atm.}$, $[\text{Ar}] = 6.69 \times 10^{18}/\text{cm}^3$, $[\text{CH}_2\text{I}_2]_0 = 1.34 \times 10^{12}/\text{cm}^3$. Kinetic simulations using the mechanism of Table 2 is shown by the red solid curve and the values for $\pm 30\%$ of k_3 are shown by the red broken curves, respectively. The solution with the best fit of $k_3^*_{\text{max}}$ (maximum value for k_3 assuming $k_2 = 0$) is shown by the black open circle,
B: The sensitivity coefficient (non-dimension) for H atoms; S_{H_j} , 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 ${}^3\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ (2) and ${}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ (3).
A: **k_2 (expressed by the black symbols):** black solid line and black dashed line: TST calculation without Eckert correction and TST calculation with Eckert correction, respectively (Reference26), Δ connected by the black broken line; semi-empirical result obtained by the relative measurement of k_2 combined with TST/quantum chemical calculation (Reference 12 and Reference 26), $\blacksquare$: Reference 13, $\blacklozenge$: Reference 14, dotted line: Reference 16, $\times$ and $+$; Reference 25.

k_3 (expressed by the red symbols): red circle; present study, red solid line and red dashed line; Reference 25 (k_2+k_3), red dash-dotted line; Reference 17, red dash line; Reference 18, red square; Reference 20, red triangle; Reference 21.

B: k_2 (expressed by the black symbols): black solid line and black dash line: TST calculation without Eckert Correction, and with Eckert Correction, respectively (Reference21), $\times$ and $+$ with dotted line; Reference 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., $k_3^*_{\max}$ (see text), red solid line; Reference 25 (k_2+k_3) , where, the upper and lower limit of Reference 25 are shown by the red dash lines, red dotted line; extrapolation of the low temperature study of Reference 17,

Figure 1

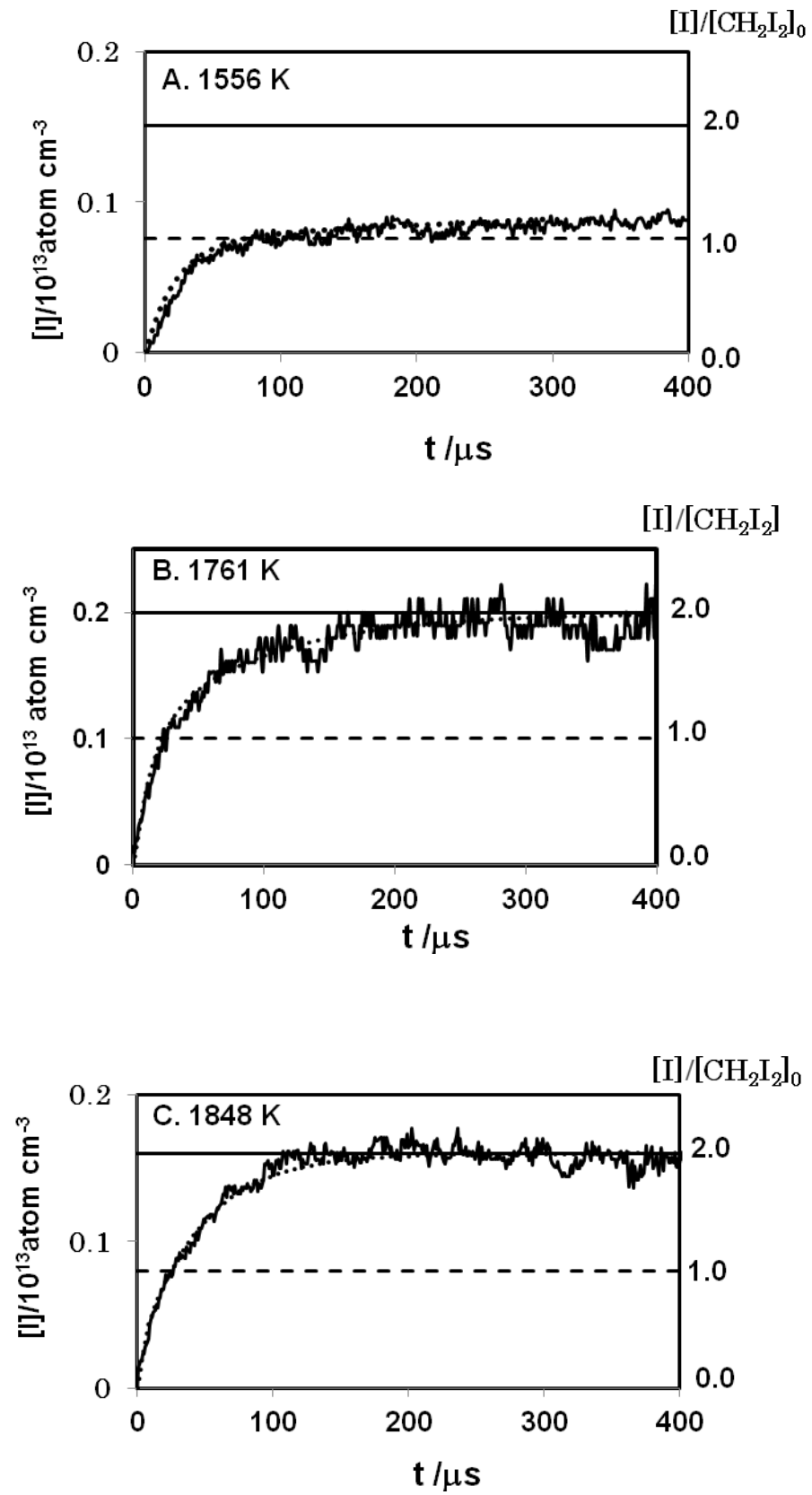


Figure 2

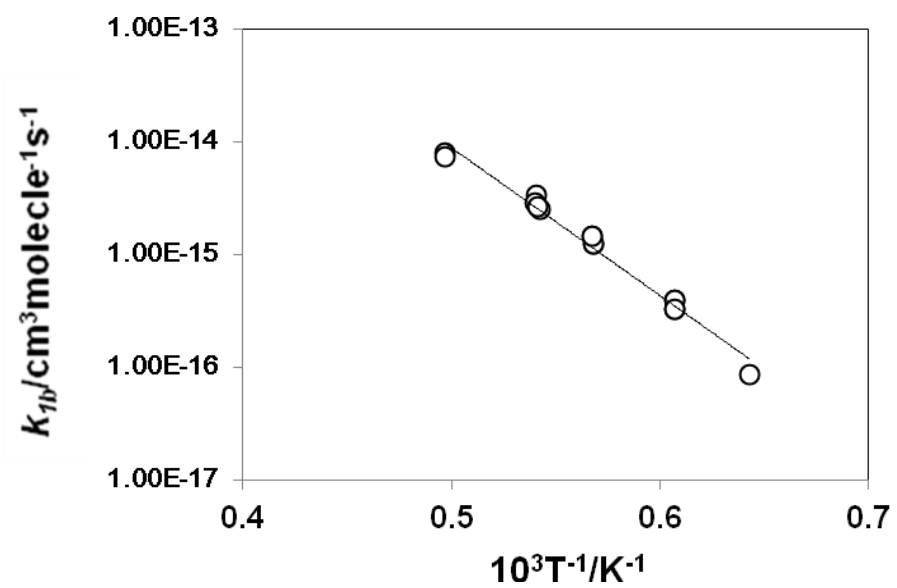


Figure 3

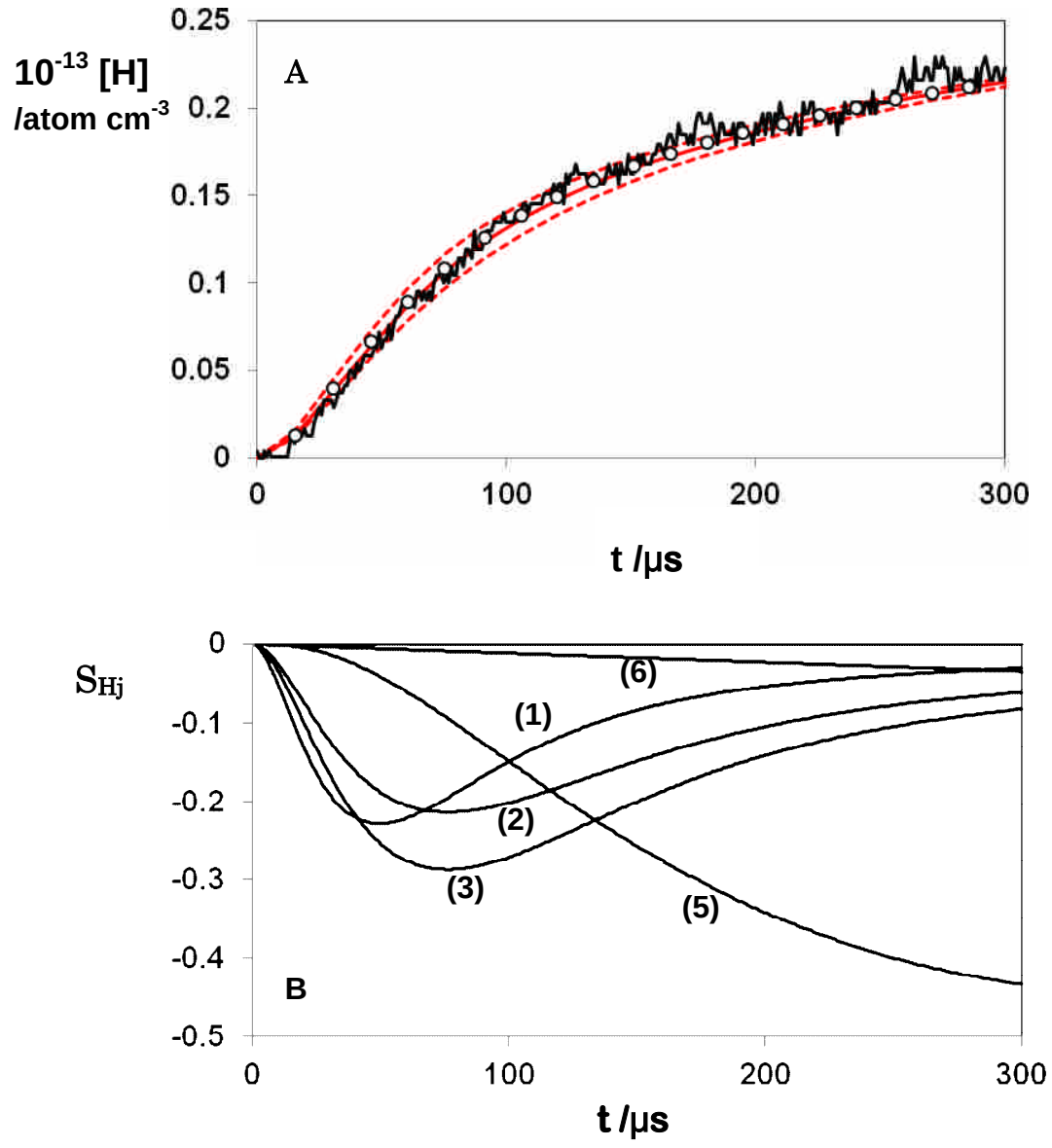


Figure 4-A

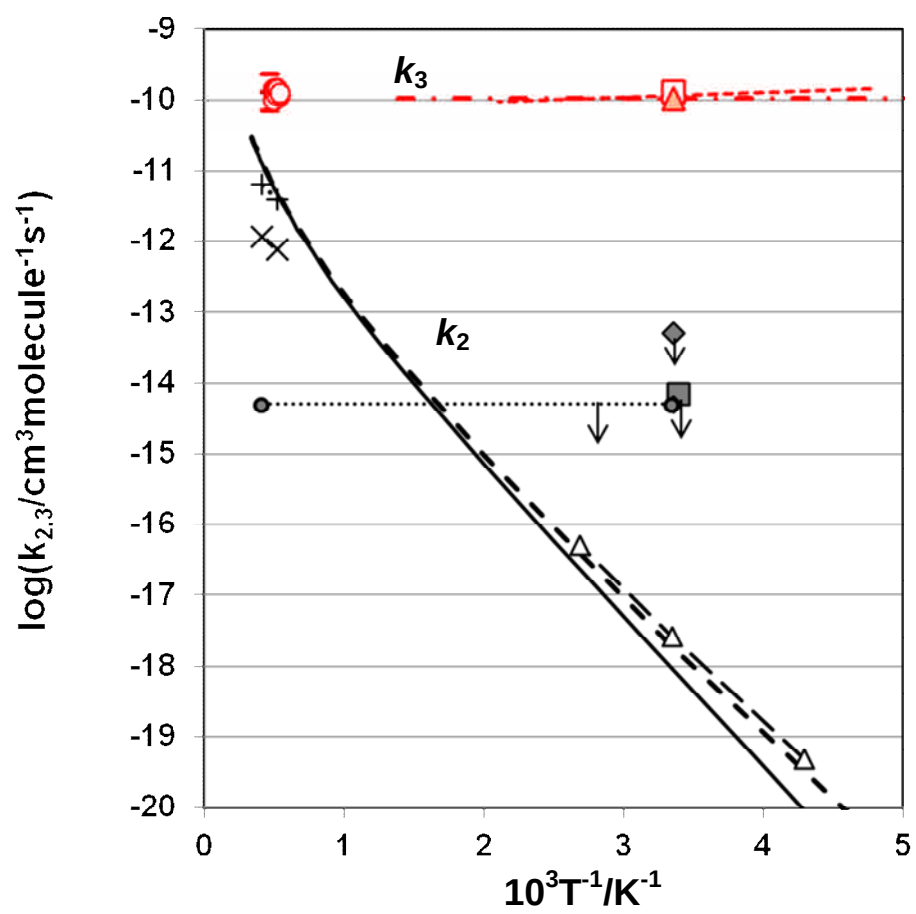


Figure 4-B

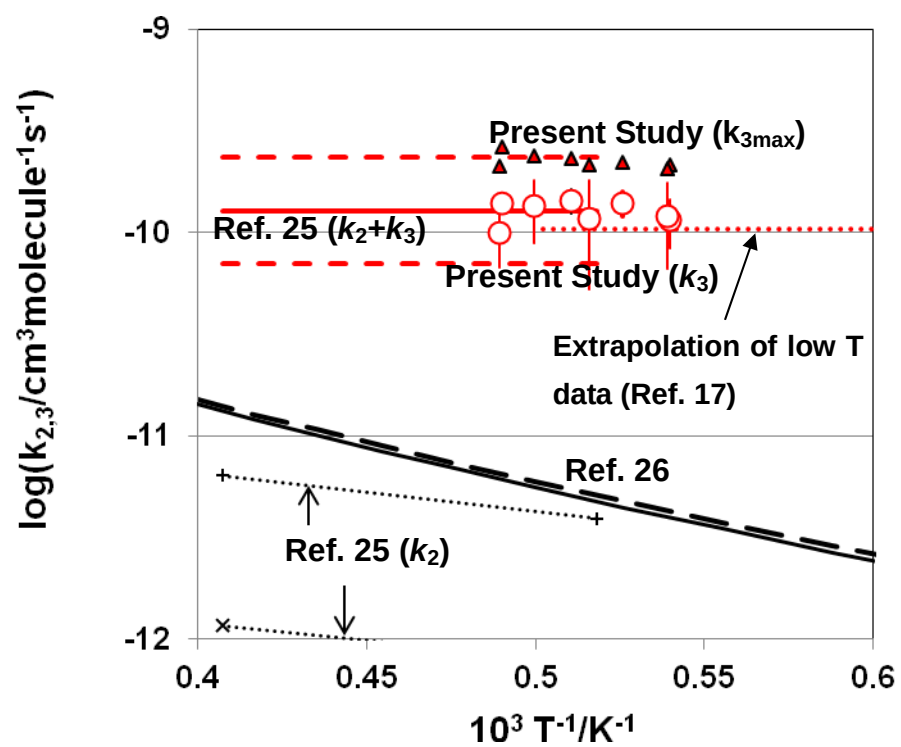
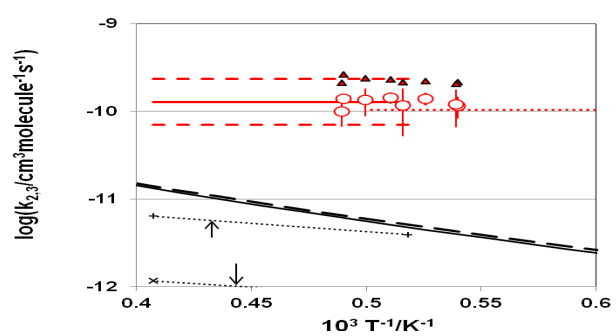


Table of Contents



國科會補助計畫衍生研發成果推廣資料表

日期:2012/01/31

國科會補助計畫	計畫名稱: 燃燒化學中重要自由基之反應動力學研究(II)
	計畫主持人: 王念夏
	計畫編號: 99-2113-M-009-014-學門領域: 物理化學

無研發成果推廣資料

99 年度專題研究計畫研究成果彙整表

計畫主持人：王念夏			計畫編號：99-2113-M-009-014-				
計畫名稱：燃燒化學中重要自由基之反應動力學研究(II)							
成果項目			量化			單位	備註（質化說明：如數個計畫共同成果、成果列為該期刊之封面故事...等）
			實際已達成數（被接受或已發表）	預期總達成數(含實際已達成數)	本計畫實際貢獻百分比		
國內	論文著作	期刊論文	0	0	100%	篇	
		研究報告/技術報告	0	0	100%		
		研討會論文	1	1	100%		
		專書	0	0	100%		
	專利	申請中件數	0	0	100%	件	
		已獲得件數	0	0	100%		
	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
	參與計畫人力（本國籍）	碩士生	1	2	75%	人次	
		博士生	0	0	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		
國外	論文著作	期刊論文	1	1	100%	篇	
		研究報告/技術報告	0	0	100%		
		研討會論文	0	0	100%		
		專書	0	0	100%	章/本	
	專利	申請中件數	0	0	100%	件	
		已獲得件數	0	0	100%		
	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
	參與計畫人力（外國籍）	碩士生	0	0	100%	人次	
		博士生	0	0	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		

其他成果 (無法以量化表達之成果如辦理學術活動、獲得獎項、重要國際合作、研究成果國際影響力及其他協助產業技術發展之具體效益事項等，請以文字敘述填列。)	無
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	成果項目	量化	名稱或內容性質簡述
科 教 處 計 畫 加 填 項 目	測驗工具(含質性與量性)	0	
	課程/模組	0	
	電腦及網路系統或工具	0	
	教材	0	
	舉辦之活動/競賽	0	
	研討會/工作坊	0	
	電子報、網站	0	
	計畫成果推廣之參與（閱聽）人數	0	

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

☒達成目標

☐未達成目標（請說明，以 100 字為限）

☐實驗失敗

☐因故實驗中斷

☐其他原因

說明：

2. 研究成果在學術期刊發表或申請專利等情形：

論文：☒已發表 ☐未發表之文稿 ☐撰寫中 ☐無

專利：☐已獲得 ☐申請中 ☒無

技轉：☐已技轉 ☐洽談中 ☒無

其他：（以 100 字為限）

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

成功地以二碘甲烷為前驅物在 1700-2050K 高溫範圍製造亞甲基(CH₂)，並以此研究其與 H₂ 之反應動力學，提供重要碳氫化合物燃燒之動力學資訊，即將發表於 J. Phys. Chem. A。並繼續研究與 O₂, C₂H₄ 等分子之反應動力學。