A Shock Tube Study of Methyl–Methyl Reactions between 1200 and 2400 K

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Abstract

The methyl-methyl reaction was studied in a shock tube using uv narrowline laser absorption to measure time-varying concentration profiles of CH_3 . Methyl radicals were rapidly formed initially by pyrolysis of various precursors, azomethane, ethane, or methyl iodide, dilute in argon. The contributions of the various product channels, C_2H_6 , C_2H_5 + H, C_2H_4 + H₂, and CH_2 + CH_4 , were examined by varying reactant mixtures and temperature.

The measured rate coefficients for recombination to C_2H_6 between 1200 and 1800 K are accurately fit using the unimolecular rate coefficients reported by Wagner and Wardlaw (1988). The rate coefficient for the C_2H_5 + H channel was found to be 2.4 (± 0.5) × 10¹³ exp(-6480/T) [cm³/mol-s] between 1570 and 1780 K, and is in agreement with the value reported by Frank and Braun–Unkhoff (1988). No evidence of a contribution by the C_2H_4 + H₂ channel was found in ethane/methane/argon mixtures, although methyl profiles in these mixtures should be particularly sensitive to this channel. An upper limit of approximately 10^{11} [cm³/mol-s] over the range 1700 to 2200 K was inferred for the rate coefficient of the C_2H_4 + H₂ channel. Between 1800 and 2200 K, methyl radicals are also rapidly removed by CH₃ + H \Rightarrow ¹CH₂ + H₂. In this temperature range, the reverse reaction was found to have a rate coefficient of 1.3 (\pm 0.3) × 10¹⁴ [cm³/mol-s], which is 1.8 times the room-temperature value. © 1995 John Wiley & Sons, Inc.

Introduction

The methyl-methyl reaction is important in flame propagation and the ignition of simple alkanes. Many product channels of this reaction have been discussed in the literature.

(1)
$$CH_3 + CH_3 \implies C_2H_6$$

(2) $CH_3 + CH_3 \implies C_2H_5 + H \implies C_2H_4 + H + H$

$$(3a) CH_3 + CH_3 \implies CHCH_3 + H_2 \implies C_2H_4 + H_2$$

$$(3b) CH_3 + CH_3 \implies C_2H_4 + H_2$$

$$(4a) CH_3 + CH_3 \implies {}^{3}CH_2 + CH_4$$

(4b)
$$CH_3 + CH_3 \implies {}^{1}CH_2 + CH_4 \implies {}^{3}CH_2 + CH_4$$

High-temperature rate data for the individual channels, however, are scarce or conflicting in some cases. The present state of knowledge concerning the high-

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Figure 1. Arrhenius plot for $CH_3 + CH_3 \Rightarrow$ Products. Solid line, summation of four channels; dashed line, contribution by reaction 1 at 1.2 atm from Wagner and Wardlaw [1]; patterned line, reaction 2 from Frank and Braun–Unkhoff [8]; dotdashed line, reaction 4a from Frenklach et al. [26]; and dotted line, reaction 4b [26].

temperature rates of each product channel is summarized below. Representative rate coefficients are shown in Figure 1.

 $CH_3 + CH_3 \Rightarrow C_2H_6$: A consensus on the high-temperature methyl recombination/ethane decomposition rate has existed since the mid-nineteen-eighties; this consensus value is typified by the unimolecular rate expressions reported by Wagner and Wardlaw [1], Stewart, Larson, and Golden [2], Baulch et al. [3], and Walter et al [4]. Although slightly different expressions for temperature dependences for k_x , k_0 , or F_{cent} of this reaction are reported by each group, the computed values of the rate coefficient at combustion temperatures are generally in close agreement (within $\pm 30\%$) near 1 atm. In particular, the rates from Wagner and Wardlaw which are based on the lower temperature work of Slagle et al., and the review values from Baulch et al. agree within 10% in the range from 1500 K to above 2000 K. The rate coefficient values given by Walter et al., which are more heavily weighed by very low temperature measurements, begin to deviate from this concensus above 1400 K. Some recently reported higher temperature measurements of k_1 , however, diverge from this concensus. Hwang, Wagner, and Wolff [5] measured recombination rates of methyl radicals between 1200 to 1600 K and 10 to 240 atm in a shock tube using uv absorption at 216.5 nm. Their values are approximately 33% lower than those given by the expression of Wagner and Wardlaw. Du, Hessler, and Ogren [6] measured methyl radical recombination between 1180 and 1540 K and 1.1 and 2.3 atm using a tunable-laser flash-absorption technique and found rates that were approximately 100% greater than those of Wagner and Wardlaw. Hwang, Rabinowitz, and Gardiner [7] using methyl absorption at 213.9 nm reported rate measurements between 1300 and 1700 K and 0.25 and 1.25 atm that were 10-25% lower than the expression proposed by Wagner and Wardlaw (contrary to the statement in their own article).

 $CH_3 + CH_3 \Rightarrow C_2H_5 + H$: Two direct studies of this H-atom product channel exist at high temperatures: Frank and Braun–Unkhoff [8] and Lim and Michael [9]. Both studies were done in shock tubes using the H-ARAS technique. In their overlapping temperature ranges, the reported rates agree within 20% of each other. This relatively fast high-temperature rate of reaction 2 is supported by several measurements of near-collisional rates in the reverse direction near room temperature [3].

 $CH_3 + CH_3 \Rightarrow C_2H_4 + H_2$: The rapid rearrangement of the CHCH₃ product of the 1,1-abstraction to form C_2H_4 makes the product channel 3a kinetically indistinguishable from the 1,2-abstraction, reaction 3b. There are no direct high-temperature measurements of the rate coefficient of either channel, but there have been several inferences. An estimate of the contribution of this reaction to CH₃ removal was made to Roth and Just [10] using H-ARAS in shock tube experiments: k_3 = 1.0 imes $10^{16} \exp{(-16100/T)}$ [cm³/mol-s]. The contribution was inferred using a reaction mechanism which did not include singlet methylene chemistry, and which also produced a slightly higher value for k_2 than that of refs. [7] and [8]. The Roth and Just value for k_3 has entered into many hydrocarbon oxidation and pyrolysis mechanisms. The fast rate of this reaction is not entirely unsupported. Recently, Su and Teitelbaum [11], using shock tube laser schlieren measurements of azomethane decomposition, also reported a large value for k_3 . However, in another laser schlieren shock tube study by Keifer and Budach [12], high-temperature ethane decomposition profiles could only be fit by setting k_3 equal to zero and using a value for k_2 that is substantially smaller than that reported by Frank and Braun–Unkhoff [8]. Similarly, in methane pyrolysis experiments, Hidaka et al. [13] found that $3.48 \mu m$ IR emission traces were best fit using the k_2 value of Frank and Braun–Unkhoff, and a value for k_3 at least 100 times smaller than that reported by Roth and Just. Theoretical discussions in Lim and Michael [9] and Gordon et al. [14] support the view that k_3 is not expected to be large.

 $CH_3 + CH_3 \Rightarrow CH_2 + CH_4$: At lower temperatures, the triplet channel, reaction 4a, is expected to be slower than the singlet channel, reaction 4b. Measurements of the reverse reaction rate coefficient k_{-4a} have been reported by Böhland et al. [15], although these required a substantial correction for interference by the singlet channel. The authors show agreement between their results and the BEBO calculations of Carr et al. [16]. The rate expression used in the present study is the Böhland et al. rate modified to include a T^2 dependence [17]. The overall rate coefficient of the reverse reaction of the singlet channel, k_{-4b} , has been measured by several workers near room temperature [18–20]. The measured k_{-4b} are near-collisional and should be viewed as an upper limit for this channel as these reverse reaction measurements could be influenced by singlet deexcitation kinetics. The forward rates of both reactions 4a and 4b are small enough at high temperatures compared to reaction 2, that they have an insignificant effect on the CH₃ concentration profiles in the present study.

In this article, we report methyl-methyl reaction studies between 1200 and 2400 K which attempt to resolve some of the rate coefficient uncertainties described above. Reaction 1 was investigated in the temperature range 1200 to 1800 K, where it is expected to dominate the methyl removal profiles. Between 1550 and 1800 K, the effect of reaction 2 can be kinetically isolated and was investigated. A separate set of experiments was performed in the temperature range 1550 to 2200 K to determine

the magnitude of the rate of reaction 3. Finally, the effect of other methyl radical reactions on the methyl profiles was studied at temperatures above 1800 K.

Experimental Method

The shock tube and laser system used in these experiments have been described previously [21-23]; hence only a brief description will be given here. A 14.3 cm diameter high-purity pressure-driven shock tube was used to produce reflected shock waves; the uniform stationary region behind these shocks provided a constant temperature and pressure bath for the experiments. Vibrationally-equilibrated reflected shock temperatures and pressures were determined from ideal frozen-chemistry shock calculations using measured incident shock velocity measurements.

The following gases and precursors were used: argon, 99.9995% (Linde Gases); ethane, 99.0% (Liquid Carbonic); methane, 99.997% (Liquid Carbonic); methyl iodide, 99.5% (Aldrich) degassed before use; and azomethane, produced by the method of Jahn [21,24].

Methyl radical concentrations were measured at a location 20 mm for the end wall by absorption of narrow-linewidth 216.615 nm laser radiation. Light of this wavelength was generated in a CoherentTM Ar⁺-pumped ring dye laser system by intra-cavity doubling of 433.230 nm radiation with a BBO crystal. The measured fractional absorption, $(I_0 - I)/I_0$, was converted to CH₃ mole fraction using Beer's law:

(1)
$$I/I_0 = \exp\left(-k_\lambda P \chi_{\rm CH3} L\right)$$

where k_{λ} is the temperature-dependent CH₃ absorption coefficient at wavelength λ [atm⁻¹ cm⁻¹], *P* is the total pressure [atm], χ_{CH3} is the mole fraction of CH₃, and *L* is the absorption path length [cm]. k_{λ} , has been determined previously at $\lambda = 216.615$ nm in the temperature range T = 1300 to 2400 K with an uncertainty of $\pm 12\%$ [21,22], and is given by the following expression

(2)
$$k_{216.615 \text{nm}} = 147300/T \exp(-T/1675) [\text{atm}^{-1} \text{cm}^{-1}]$$

which is independent of pressure. This expression for the absorption coefficient is the corrected value given in ref. [22]. Minimum detectivities of approximately 10^{13} molecules/cm³ (equivalent to 2 ppm CH₃ at 1500 K, 1 atm) can be achieved in a 10 cm pathlength using this method. Example absorption data are shown in Figures 2, 8, and 12.

Results and Discussion

Several series of reflected shock experiments were performed using mixtures of azomethane/Ar, ethane/methane/Ar, methyl iodide/Ar, and ethane/Ar. All modeling was done using the Sandia Senkin/Chemkin II kinetics package [25]. The mechanism and thermodynamic database were taken directly from that reported by Frenklach et al. [26] with only few exceptions. These exceptions are reactions 1, 2, 3, 6, and 7, and the precursor reactions 30-37 (which were not included in ref. [26]). The full mechanism is shown in Table I. Consistent with ref. [26], the following heats of formation ΔH_f^{298} in [kcal/mol] were used: CH₃, 35.11; ³CH₂, 93.77; ¹CH₂, 102.75; and C₂H₅, 28.36. The results and discussion are presented below.



Figure 2. Methyl absorption data. The reflected shock conditions were 1407 K, 1.19 atm, with an initial mixture of 233 ppm azomethane/argon. Dashed line, model fit using the rate coefficient from Wagner and Wardlaw for $k_1 = 4.55 \times 10^{12} \text{ [s}^{-1]}$ and dotted lines, variation of k_1 by $\pm 20\%$. Reflected shock arrival time at 0 μ s. Mole fraction data converted from absorbance data using $k_{\lambda} = 45.2 \text{ atm}^{-1} \text{ cm}^{-1}$.

 $CH_3 + CH_3 \Rightarrow C_2H_6$: For mixtures of azomethane in argon at temperatures below 1800 K, the overall removal rate of methyl radicals was determined assuming simple second-order kinetic behavior of the methyl concentration, [CH₃].

(3)
$$d[CH_3]/dt = -2k_{sum}[CH_3][CH_3]$$

The rate coefficient, k_{sum} , was derived from the early-time slope, $S_{1/abs}$ [s⁻¹], of 1/absorbance vs. time plots

(4)
$$k_{\rm sum} = S_{\rm 1/abs} RT \ k_{\lambda} L/2 \ [\rm cm^3/mol-s]$$

where R = 82.06 [atm-cm³/mol-K], L = 14.3 [cm], and the absorbance is defined as the product $(k_{\lambda} P_{\chi CH3}L)$. An example of this fitting method using the data of Figure 2 is shown in Figure 3. The second-order kinetic behavior in this system is confirmed by the sensitivity analysis shown in Figure 4. This plot shows the dominance of reactions 1 and 2 at times longer than 10 μ s. Later-time departure from second-order behavior in Figure 3 is partly caused by interference absorption from the production of acetylene and ethylene [21]. Modeling of data traces was corrected for this interference using absorption coefficients found in ref. [21] and calculated concentration-histories of C₂H₂ and C₂H₄.

As has been shown by both Du et al. [6] and Hwang et al. [7], it is possible to determine both the absorption coefficient for methyl radicals and the rate coefficient for methyl recombination from data such as found in Figure 2. The strongest sensitivity to the absorption coefficient is found in the peak absorption. In cases of rapid decomposition of low concentration azomethane, the determination of the value of the absorption coefficient is effectively decoupled from the rest of the kinetic analysis. The value of the absorption coefficient given in ref. [22] was confirmed in each of the azomethane traces used in this study.

TABLE I. Methyl reaction mechanism.

No.	Reaction	A	n	$\overline{E_A}$	Ref.
1	$2CH3(+M) \Rightarrow C2H6(+M)$		-		[1]
	k_{∞}	9.03E16	-1.18	653.	
	k_0	3.17E41	-7.03	2762.	
	Troe parameters: 0.619, 73.2, 1180				
2	$CH3 + CH3 \Rightarrow H + C2H5$	2.80E13	0.0	13591.	[8]
3	$CH3 + CH3 \Rightarrow H2 + C2H4$	0.0	0.0	0.	this study
4a	$CH2 + CH4 \Rightarrow CH3 + CH3$	2.46E06	2.0	8270.	
4b	$CH2(S) + CH4 \Rightarrow CH3 + CH3$	1.60E13	0.0	570.	
5	$ m H+CH4\Rightarrow CH3+H2$	6.60E08	1.62	10840.	
6	$CH2(S) + H2 \Rightarrow H + CH3$	1.30E14	0.0	0.	this study
7	$CH4 + M \Rightarrow H + CH3 + M$	1.04E18	0.0	96389.	[27]
8a	$H + H + M \Rightarrow H2 + M$	1.00E18	-1.0	0.	
8b	$\mathrm{H}+\mathrm{H}+\mathrm{H2}\Rightarrow\mathrm{H2}+\mathrm{H2}$	9.00E16	-0.6	0.	
9	$H + CH \Rightarrow C + H2$	1.10E14	0.0	0.	
10	$H + C2H3 \Rightarrow H2 + C2H2$	3.00E13	0.0	0.	
11	$H + C2H4 \Rightarrow C2H3 + H2$	1.33E06	2.53	12240.	
12	$H + C2H5 \Rightarrow H2 + C2H4$	2.00E12	0.0	0.	
13	$H + C2H6 \Rightarrow C2H5 + H2$	1.15E08	1.9	7530.	
14	$C + CH2 \Rightarrow H + C2H$	5.00E13	0.0	0.	
15	$C + CH3 \Rightarrow H + C2H2$	5.00E13	0.0	0.	
16	$CH + H2 \Rightarrow H + CH2$	3.32E08	1.79	1670.	
17	$CH + CH2 \Rightarrow H + C2H2$	4.00E13	0.0	0.	
18	$CH + CH3 \Rightarrow H + C2H3$	3.00E13	0.0	0.	
19	$\rm CH$ + $\rm CH4$ \Rightarrow H + $\rm C2H4$	6.00E13	0.0	0.	
20	$CH2 + H2 \Rightarrow H + CH3$	5.00E05	2.0	7230.	
21	$CH2 + CH2 \Rightarrow H2 + C2H2$	3.20E13	0.0	0.	
22	$CH2 + CH3 \Rightarrow H + C2H4$	4.00E13	0.0	0.	
23	$CH3 + C2H4 \Rightarrow C2H3 + CH4$	2.27 E05	2.0	9200.	
24	$CH3 + C2H6 \Rightarrow C2H5 + CH4$	6.14 ± 06	1.74	10450.	
25	$C2H + H2 \Rightarrow H + C2H2$	4.07E05	2.4	200.	
26	$CH2(S) + AR \Rightarrow CH2 + AR$	9.00E12	0.0	600.	
27	$CH2(S) + H \Rightarrow CH + H2$	3.00E13	0.0	0.	
28	$CH2(S) + CH3 \Rightarrow H + C2H4$	1.20E13	0.0	-570.	
29	$CH2(S) + C2H6 \Rightarrow CH3 + C2H5$	4.00E13	0.0	-550.	
30	$C2H6N2 \Rightarrow N2 + 2CH3$	2.00E11	0.0	33500.	[34]
31	$CH3I + M \Rightarrow I + CH3 + M$	7.53 E15	0.0	42560.	[33]
32	$I + H + M \Rightarrow HI + M$	2.05 E10	0.5	43712.	[33]
33	$I + I + M \Rightarrow 12 + M$	2.36E14	0.0	-1498.	[33]
34	$I + H2 \Rightarrow H + HI$	1.69E14	0.0	33640.	[33]
35	$I + HI \Rightarrow H + I2$	8.02E14	0.0	37131.	[33]
36	$I + CH4 \Rightarrow HI + CH3$	1.48E14	0.0	32895.	[33]
37	$I + C2H6 \Rightarrow HI + C2H5$	1.66E14	0.0	27900.	[33]
38	$H + CH2 (+M) \Rightarrow CH3 (+M)$				
	k_{∞}	2.50E16	-0.8	0.	
	k_0	3.20E27	-3.14	1230.	
	Troe parameters: 0.68, 78, 1995, 5590				
39	$H + C2H(+M) \Rightarrow C2H2(+M)$				
	k_{∞}	1.00E17	-1.0	0.	
	k_0	3.75E33	-4.8	1900.	
	Troe parameters: 0.6464, 132, 1315, 5566				

Table 1. (Continued)

No.	Reaction	A	n	E_A	Ref.
40	$H + C2H2(+M) \Rightarrow C2H3(+M)$				
	k_{∞}	5.60E12	0.0	2400.	
	k_0	3.8E40	-7.27	7220.	
	Troe parameters: 0.7507, 98.5, 1302, 4167				
41	$H + C2H3 (+M) \Rightarrow C2H4(+M)$				
	k_{∞}	6.08E12	0.27	280.	
	k_0	1.40E30	-3.860	3320.0	
	Troe parameters: 0.782, 207.5, 2663, 6095				
42	$H + C2H4 (+M) \Rightarrow C2H5 (+M)$				
	k_{∞}	1.08E12	0.454	1820.	
	k_0	1.20E42	-7.62	6970.	
	Troe parameters: 0.9753, 210, 984, 4374				
43	$H + C2H5 (+M) \Rightarrow C2H6 (+M)$				
	k_{∞}	5.21E17	-0.99	1580.	
	k_0	1.99E41	-7.08	6685.	
	Troe parameters: 0.8422, 125, 2219, 6882				
44	$C2H4(+M) \Rightarrow H2 + C2H2(+M)$				
	k_{∞}	8.00E12	0.44	88770.	
	k_0	7.00E50	-9.31	99860.	
	Troe parameters: 0.7345, 180, 1035, 5417				

TABLE I. (Continued)

All values in this table are from ref. [26] except where noted. Rate coefficients are expressed in the form $k = A T^n \exp(-E_A/RT)$, with units of cm³/mol-s or s⁻¹ and T in K. The collision efficiency factors for reaction 8a are: CH₄, 2.0; C₂H₆, 3.0; and Ar, 0.63.

For reactions 32 to 37, representative rates from the NIST Kinetic Database [33], were used.

The collision efficiency factors for reactions 38 to 44 are as follows: H₂, 2.0; CH₄, 2.0; C₂H₆, 3.0; and Ar, 0.7. The Troe parameters are listed in the order: a, T^*, T^{***}, T^{***} .

Data for several pressure regimes, 0.50, 1.20, and 1.45 atm, are summarized in Table II and in Figure 5. The recombination rate data taken at temperatures between 1200 and 1600 K are accurately modeled using only the unimolecular rate coefficient expression reported by Wagner and Wardlaw [1]. The scatter here is typically ± 10 -15%. These results can be compared to the values reported in several other recent studies. Both Du et al. [6] and Hwang, Wagner, and Wolff [5] are at variance with the present work, the former by greater than their published error limits, and the later within their error limits. Hwang, Rabinowitz, and Gardiner [7] are also in agreement. One possible reason for differences in the measured rate coefficients is the variation in the methyl absorption coefficients used in each of these studies. In second-order analyses, the calculated rate coefficients vary linearly with the absorption coefficient, as can be seen from eq. (4).

Davidson et al. [27] have recently reported rate coefficients measurements for the reverse reaction, ethane decomposition, in the range 1450 to 2100 K using the same expression for the absorption coefficient, k_{λ} , as in this study. When these reverse rates are converted to forward rates using the thermodynamic data of ref. [26], good agreement is found with the calculated expression of Wagner and Wardlaw, particularly in the temperature range 1500 to 2000 K. This agreement has significance beyond that of the rate coefficient.



Figure 3. Second-order analysis of data from Figure 2. Dashed line, least-squares fit to slope of early time data = 97320 [s⁻¹]. k_{sum} = 3.63 × 10¹² [cm³/mol-s].

In the analysis of the methyl profiles in the ethane decomposition experiments, the calculated rate coefficient varies inversely with the absorption coefficient, and as described above, in the methyl recombination experiments the calculated rate coefficient varies directly with the absorption coefficient. Only one value of the methyl



Figure 4. Sensitivity analysis for CH₃. Calculations are for the conditions of Figure 2. The sensitivity coefficient is normalized as $S = (k_i/\chi_{max}) d\chi/dk_i$, where χ_{max} is the maximum value of χ_{CH3} achieved during the calculation.



Figure 5. Arrhenius plot for $CH_3 + CH_3 \Rightarrow All$ Products. Date derived from second-order analysis; model curves derived using Table I. Hollow diamonds on dotdashed line, 0.5 atm data; dotted diamonds on dashed line, 1.2 atm data; filled diamonds on solid line, 1.45 atm data; and $\pm 15\%$ error bars in $k, \pm 1\%$ error bars in T_5 . Dotted line contribution by reaction (2).

absorption coefficient at each temperature is consistent with this thermodynamic relationship of the forward and reverse reaction rate coefficients. If a different value of the absorption coefficient is used in this analysis, then the forward and reverse rates of reaction 1 would not be simply related by Kp. The agreement between forward and reverse reaction rates, therefore, is confirmation of the methyl absorption coefficient used in this pair of studies.

 $CH_3 + CH_3 \Rightarrow C_2H_5 + H$: In the azomethane decomposition data above 1500 K, where the contribution by other channels is significant, tight constraints on the sum of the second-order methyl removal rates are set by the data in Table II. Figure 6 shows the rate coefficients from Table II with the Wagner and Wardlaw value of the contribution from reaction 1 subtracted. Here, the entire difference can be accounted for by the $C_2H_5 + H$ channel, using rate coefficients similar to that reported by Frank and Braun–Unkhoff [8]. Because of the small temperature range of the present data and the near-collisional rate of the reverse reaction, we can assume that the reverse reaction rate coefficient is constant in this temperature range. The forward rate data can be fit with an Arrhenius form by varying only the preexponential factor using the activation energy derived from the thermodynamic data, yielding $k_2 = 2.4(\pm 0.5) \times 10^{13} \exp(-6480/T, [K])$ [cm³/mol-s]. This result is within 9% of the Frank and Braun–Unkhoff values.

Figure 7 includes methyl-methyl reaction data from higher temperature methyl iodide/argon and ethane/argon mixtures. The scatter in these data from the simple second-order reduction is substantially greater because of the very short time (less than 20 μ s) where linear fitting is possible. Under these conditions the data are more

T ₅ [K}	P_5 [atm]	Xinitial [ppm]	$k_{ m sum}/10^{12}$ [cm ³ /mol-s]
1772	0.465	208	1.20
1778	0.465	215	1.20
1570	0.513	215	1.75
1686	0.477	215	1.31
1693	0.456	233	1.16
1558	0.505	233	1.76
1474	0.552	233	2.31
1577	0.521	213	1.58
1218	0.688	213	4.65
1407	1.19	233	3.63
1700	1.29	233	1.75
1385	1.06	233	3.87
1467	1.46	208	3.66
1349	1.47	208	4.84
1228	1.42	208	6.26
1311	1.51	208	5.33
1398	1.49	104	4.70
1215	1.39	104	6.68

TABLE II. Overall second-order methyl removal rates: azomethane decomposition data.

accurately modeled using the full mechanism. This modeling is described in the last section.

 $CH_3 + CH_3 \Rightarrow C_2H_4 + H_2$: Independent of the above results for reactions 1 and 2, it is difficult to place constraints on the rate of reaction 3 from simple methyl removal-



Figure 6. Arrhenius plot for $CH_3 + CH_3 \Rightarrow C_2H_5 + H$. Solid circles on solid line, data of Table II above 1500 K with contribution by k_1 subtracted out; dashed line, Frank and Braun-Unkhoff [8]; and dotdashed line, Lim and Michael [9]. $\pm 25\%$ error bars in $k, \pm 1\%$ error bars in T.



Figure 7. Arrhenius plot for $CH_3 + CH_3 \Rightarrow$ Products. Similar to Figure 5 with the following data added: crosses, 1.9 atm methyl iodide data; crossed squares, 1.7 atm ethane data; and $\pm 25\%$ error bars.

rate experiments. This is because the second-order methyl decay due to reaction 3 would be practically indistinguishable from that resulting from reaction 2. We can, however, determine the magnitude of k_3 by taking advantage of the difference in products between the atomic and molecular channels using a scheme suggested by W. Tsang [28].

(2)
$$CH_3 + CH_3 \implies C_2H_5 + H \implies C_2H_4 + H + H$$

(5)
$$CH_4 + H \implies CH_3 + H_2$$

$$(3) CH_3 + CH_3 \implies C_2H_4 + H_2$$

The addition of methane to ethane/argon mixtures results in scavenging of the available H-atoms if the methane concentration and the temperature are sufficiently high. Under these conditions, every methyl radical removed by reaction 2 is replaced by reaction 5. This replacement of methyl radicals does not occur when the methyl products are $C_2H_4 + H_2$, as no H-atoms are formed by this channel. Thus, in the limiting cases, if the dominant CH_3 removal channel is reaction 2, methyl concentration plateaus will form, or if the dominant CH_3 removal channel is reaction 3, the methyl profiles will decay according to second-order kinetics.

Sensitivity plots for this scheme are shown in Figure 8. If reaction 3 is significant, for example if k_3 were as large as 3×10^{11} [cm³/mol-s], then the methyl concentration would show a strong sensitivity to this reaction. If k_3 is much less than this, then the methyl profile would be dominated by the reactions 1, 2, and 7. Because of the appearance of the endothermic methane decomposition reaction in this plot, there also is a sensitivity to temperature in this scheme. For example, a decrease in T_5 of 10 K



Figure 8. Sensitivity analysis for CH₃. Calculations are for the conditions of Figure 9 and using $k_3 = 3 \times 10^{11}$ [cm³/mol-s].

at 1800 K, is approximately equivalent to an increase in k_3 by 7×10^{10} [cm³/mols]. Accurate temperatures are needed to constrain the contribution of methane decomposition to the methyl concentration profile, and the lower detectivity limit of k_3 for this scheme is set by the uncertainty in T_5 . The k_3 rate determination analysis is not sensitive, however, to the value of the absorption coefficient. The shape of the methyl profile, a plateau or a decay, is independent of the value of the k_{λ} .

Three mixtures were studied in the temperature and pressure range 1550 to 2200 K and 1.0 to 1.25 atm: 185 ppm ethane and 1.77% methane in argon, 204 ppm ethane and 0.46% methane in argon, 141 ppm ethane and 1790 ppm methane in argon. In the ethane/methane mixtures, k_3 was varied in an attempt to bring the calculated methyl concentrations into coincidence with the data traces. The upper limit of k_3 was defined as the smallest value of that rate coefficient which still produced a poor fit to the long time behavior of the data. An example of this fitting procedure is shown in Figure 9 where k_3 was varied from zero to 10^{12} [cm³/mol-s]. Calculations which use values of k_3 of 10^{11} or higher show significant decay in the long time absorption, behavior not found in the data. The experimental upper limits for k_3 are shown in Figure 10. The upper limits for k_3 are approximately an order of magnitude lower than the values reported by Su and Teitelbaum [11] and Roth and Just [10]. Contrary to the modeling in these two studies and consistent with the study of Hidaka et al. [13], all the methyl pro-files in the present study can be modeled successfully by setting k_3 equal to zero.

 $CH_3 + H \Rightarrow CH_2(S) + H_2$: The present studies set strong constraints on the rate coefficients of all of the primary methyl-methyl reaction channels. How successfully then do these rates describe methyl radical behavior at higher temperatures? We have noted above that the removal rate of methyl radicals exhibits nonsecond-order decay at temperatures above approximately 1800 K. Thus, some other removal path must



Figure 9. Methyl radical time-histories. The reflected shock conditions were 1835 K, 1.20 atm, with an initial mixture of 187 ppm ethane/0.46% methane/argon. Dashed line, model fit using $k_3 = 0$; dotdashed line, $k_3 = 10^{11}$ [cm³/mol-s]; and dotted line, $k_3 = 10^{12}$ [cm³/mol-s]. Mole fraction data converted from absorbance data using $k_{\lambda} = 26.8$ atm⁻¹ cm⁻¹.



Figure 10. Arrhenius plot for $CH_3 + CH_3 \Rightarrow C_2H_4 + H_2$. Long dashed line, Roth and Just [10]; dashed line, Su and Teitelbaum [11]; dotdashed line, k_2 from Frank and Braun–Unkhoff [8]; and circles on solid line, experimentally determined upper limits for k_3 and fit.



Figure 11. Sensitivity analysis for CH_3 . Calculations are for the conditions of Figure 12.

be contributing to CH₃ decay. Careful examination of the results of the simple secondorder data analysis shown in Figure 7 indicates that even though there is large scatter in the derived rate coefficients, the values approach, but almost never exceed twice the value of k_2 reported by Frank and Braun–Unkhoff. This is the behavior that would be expected if each H-atom generated from reaction 2 also removed another methyl radical, possibly by the reaction (-6), H + CH₃ \Rightarrow ¹CH₂ + H₂. Figure 11 confirms that, at high temperatures, the methyl concentrations show significant sensitivity to only two reactions: 2 and -6.

To measure this rate, the following mixtures were studied: CH₃I mixtures of 187 to 212 ppm CH₃I in argon, 1860 to 2275 K, and 1.7 to 2.2 atm; and 98 and 198 ppm ethane in argon, 2188 to 2360 K, and 1.6 to 1.8 atm. Chemical thermodynamic data for CH₃I was found in ref. [29]. An example data record from one of these mixtures is shown in Figure 12. The methyl profiles for these high-temperature pyrolysis experiments were fit with the full mechanism of Table I. Only the rate coefficient for reaction 6 was varied to bring the modeled methyl profiles into coincidence with the data records. The results of fitting the model to the data are shown in Figure 13 and Table III. At temperatures from 1850 to 2100 K, a value of the rate coefficient $k_6 = 1.3(\pm 0.3) \times 10^{14}$ [cm³/mol-s] was found to give the best fits to the methyl profiles. Note here and below that we give the rate coefficient values for the reaction direction CH₂(S) + H₂ \Rightarrow CH₃ + H₂ which is effectively temperature-independent. Above 2100 K, the CH₃ removal rate begins to increase again, probably as the result of another, but as of yet undetermined, removal path.

The few reported values are shown in Figure 13. The k_{-6} values reported by Bhaskaran et al. [30] are from studies of methane decomposition, those from Olson and Gardiner [31] are from an estimate based on analogy with the CH₄ + H reaction, and the k_6 from Tsang and Hampson [32] are based on a review of



Figure 12. Methyl absorption data. The reflected shock conditions are 1991 K, 1.83 atm, with an initial mixture of 208 ppm CH₃I/argon. Dashed line, model it using $k_6 = 1.4 \times 10^{14}$ [cm/mol-s] and dotted lines, $k_6 \times 2$ and $k_6 \times 0.5$. Mole fraction data converted from absorbance data using $k_{\lambda} = 22.5$ atm⁻¹ cm⁻¹.



Figure 13. Arrhenius plot for ${}^{1}\text{CH}_{2} + \text{H}_{2} \Rightarrow \text{CH}_{3} + \text{H}$. Dotted diamonds on dashed line, methyl iodide/argon data from present study, $k_{6} = 1.3 \times 10^{14} \text{ [cm}^{3}\text{/mol-s]}$; filled circles, ethane/argon data; dotted line, Olson and Gardiner [31]; double-dotted line, Bhaskaran et al. [30]; and dotdashed line, Tsang and Hampson [32]. $\pm 25\%$ error bars.

T ₅ [K]	P_5 [atm]	Xinitial [ppm]	$k_{6}/10^{14}$ $[{ m cm}^{3}/{ m mol-s}]$
Methyl Iodide/Ar	<u></u>		
2329	1.79	190	4.0
2133	1.90	190	2.0
2086	1.91	190	1.4
1868	1.79	208	1.2
1991	1.83	208	1.4
2192	1.82	208	2.0
1948	1.81	210	1.0
2202	1.82	210	2.5
2077	1.80	210	1.0
2102	1.82	188	2.5
1941	2.00	188	1.4
1900	2.06	188	1.4
2116	1.85	200	2.0
2057	2.00	200	1.4
1932	1.99	200	1.7
1864	2.20	200	1.0
Ethane/Ar			
2188	1.80	99	3.0
2307	1.70	198	4.0
2343	1.65	198	4.0
2250	1.79	198	3.0
2271	1.81	198	3.0

TABLE III. Results of fitting methyl iodide/Ar and ethane/Ar data by variation of k_6 .

the reaction at room temperature and assume no temperature dependence. The present measurement is 80% faster than this room temperature value. If we force the Arrhenius fit of the data below 2100 K from the present study to go through the Tsang and Hampson review value of 7.2×10^{13} at 298 K, we recover a rate coefficient $k_6 = 1.5 \times 10^{14} \exp{(-220/T, [K])}$ [cm³/mol/s]. This differs only slightly at combustion temperatures from the temperature-independent value suggested above. Reaction 6, the singlet channel, was not included in the mechanisms used by Frank and Braun–Unkhoff [8] and Lim and Michael [9], but it is found in the mechanism in Du et al. [6].

Conclusion

In this study, we obtained a consistent set of rate coefficients which describe methyl-methyl reactions in shock tube experiments from 1200 K to 2100 K. The measured rate coefficients for recombination to C_2H_6 between 1200 and 1800 K are accurately fit using the unimolecular rate coefficients reported by Wagner and Wardlaw (1988), and are in agreement with ethane decomposition data reported by Davidson et al. [27]. The agreement between forward and reverse rates of the same reaction also confirms the value of the methyl 216.615 nm absorption coefficient used in both these studies. At higher temperatures, the inferred C_2H_5 + H channel rate coefficients agree with those reported by Frank and Braun–Unkhoff [8] and Lim and Michael [9]. No evidence of the C_2H_4 + H_2 channel was found. At temperatures above 1800 K, there is evidence that the enhanced removal rate of methyl radicals is the

result of the reaction $H + CH_3 \Rightarrow {}^1CH_2 + H_2$. This consistent set of rate coefficients should be applicable to simple hydrocarbon combustion modeling and in studies of other methyl reactions.

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