Reaction between CH_3 and H_2 at Combustion Temperatures

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The reaction between CH_3 radicals and H_2 was investigated behind incident shock waves at temperatures between 1308 and 1825 K by following the consumption of CH_3 using a time resolved UV absorption method at 213.9 nm. The rate coefficient expression 1.10×10^{13} exp(-7370 K/T) $cm^3mol^{-1}s^{-1}$ for the reaction of CH_3 with H_2 was derived.

Introduction

The reaction between CH_3 with H_2,

$$CH_3+H_2\rightarrow CH_4+H \qquad (14)$$

and its reverse reaction play important roles in methane pyrolysis and combustion. Numerous experimental[1~6] and theoretical[7~10] studies of reaction 14 (see Table 2) and its reverse reaction have been reported, and extensive review articles[11~14] have been published. Nearly all of the previous investigations of CH_3 with H_2 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 CH_3 at 216.5 nm in the pyrolysis of azomethane or tetramethyltin to generate methyl radical. Their data were fit to the Arrhenius expression $k_{14}(T)=2.0\times10^{13}$ exp(-7200 K/T) $cm^3mol^{-1}s^{-1}$. Rabinowitz *et al.*[6] also directly measured the rate of the reverse reaction, $CH_4+H\rightarrow CH_3+H_2$, using a flash photolysis-shock tube technique in the temperature range from 897 to 1729 K. They reported $k_{14}(T)=3.1\times10^{12}$ exp(-5940 K/T) and $k_{\ 14}(T)=1.1\times10^{14}$ exp(-6440 K/T) $cm^3 mol^{-1}s^{-1}$. 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 CH_3 reaction with H_2 at combustion temperatures using spectroscopic determination of CH_3 concentration profiles during the thermal decomposition of azomethane or methyl iodide in the presence of large excess of H_2.

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 elsewhere[15]. Shock parameters were computed from measured incident shock velocities by standard methods[16] using JANAF[17] and NASA[18] thermochemical data under the assumption of steady flow and no wall boundary layer formation. The concentration of CH_3 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/m^3 for CH_3. The transmitted light intensity was recorded with a Nicolet Explorer II storage oscilloscope and stored on floppy disks for later use. Azomethane, synthesized according to the method of Renaud and Leitch,[19] and methyl iodide (99.5%, Aldrich) were used as sources of CH_3 radicals. Ar (99.999%, Matheson) and H_2 (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 CH_3 by H_2 was investigated behind incident shock waves at temperatures between 1308 and 1825 K and densities from 2.6 to 5.9 mol/m^3. 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 CH_3 self-reactions and the influence of their reaction products. High H_2 concentrations were selected to enhance the rate of the CH_3+H_2 reaction.

A typical absorption profile at 213.9 nm is shown in Figure 1. The steep rise in absorption due to production of CH_3 by thermal decomposition of azomethane or methyl iodide is followed by decay due to the reaction of CH_3 with H_2 and the CH_3 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 1. Mixture Compositions in Ar

	$(CH_3)_2N_2$ (%)	H_2 (%)	T (K)	ρ (mol/m^3)
1	0.0994	5.32	1308-1825	2.8-5.9
2	0.0986	10.2	1323-1693	2.7-5.3
	CH_3I (%)	H_2 (%)	T (K)	ρ (mol/m^3)
3	0.202	5.31	1439-1793	2.6-5.1
4	0.302	10.0	1498-1671	2.8-3.7

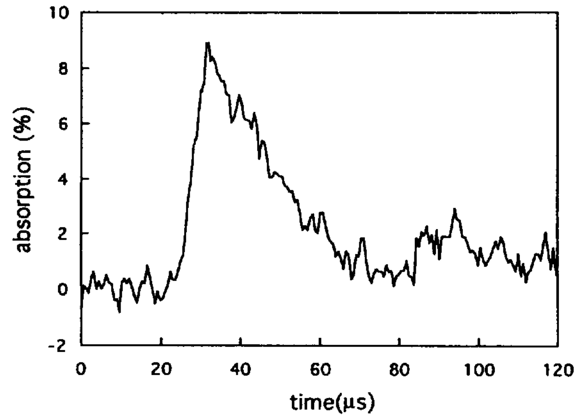

Figure 1. Typical experimental absorption profile of CH_3 at 213.9 nm. Shock conditions: 0.0994% $C_2H_6N_2$, 5.32% H_2 in Ar, $T_2=1308$ K, $\rho_2=5.63$ mol/m^3.

Table 2. Reaction mechanism

	Elementary reaction	log *A*	*n*	*Ea* (KJ)
1a	$C_2H_6N_2=CH_3+CH_3+N_2$	9.08	–	98.9
1b	$CH_3I=CH_3+I$	14.48	–	133.9
2	$C_2H_6=CH_3+CH_3$	58.26	−10.61	412.4
	Falloff parameters:			
	1.060×10^{26}, −2.792, 389.6, 0.310, 518, 445			
3	$CH_3+CH_3=C_2H_5+H$	12.45	–	40.0
4	$CH_3+CH_3=C_2H_4+H_2$	12.78	–	69.0
5	$CH_3+C_2H_6=CH_4+C_2H_5$	−0.05	4.00	40.5
6	$CH_3+C_2H_4=CH_4+C_2H_3$	11.62	11.62	46.4
7	$CH_3+C_2H_5=CH_4+C_2H_4$	−3.36	5.00	34.7
8	$C_2H_6+H=C_2H_5+H_2$	14.12	–	39.0
9	$C_2H_5=C_2H_4+H$	40.67	−7.04	182.0
	Falloff parameters:			
	4.97×10^{10}, 0.732, 154.2, 0.278, 1.032×10^5, 754.2			
10	$C_2H_5+H=C_2H_4+H_2$	12.23	–	0.0
11	$CH_3+M=CH_2+H+M$	16.00	–	377.0
12	$CH_2+CH_3=C_2H_4+H$	13.30	–	0.0
13	$CH_4=CH_3+H$	36.80	−5.25	451.3
	Falloff parameters:			
	3.71×10^{17}, −0.558, 438.8, 0.483, 409.3, 341.3			
14	$CH_3+H_2=CH_4+H$	12.76	–	53.0
15	$C_2H_4+M=C_2H_2+H_2+M$	17.41	–	332.0
16	$C_2H_4+M=C_2H_3+H+M$	17.41	–	404.0
17	$H+C_2H_4=H_2+C_2H_3$	11.50	0.70	33.5
18	$CH_3+C_2H_3=C_2H_2+CH_4$	−3.36	5.00	34.7
19	$C_2H_3+M=C_2H_2+H+M$	39.08	−7.17	212.0
20	$C_2H_3+H=C_2H_2+H_2$	13.30	–	0.0
21	$H_2+M=H+H+M$	12.35	0.50	387.0
22	$CH_3+CH_3=CH_4+CH_2$	9.23	0.56	52.6

Notes: Units are cm^3, mol, s and kJ. The rate coefficients for **1a** and **1b** were taken from Möller *et al.*[5] and Davidson *et al.*,[22] 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 *Ea* 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.

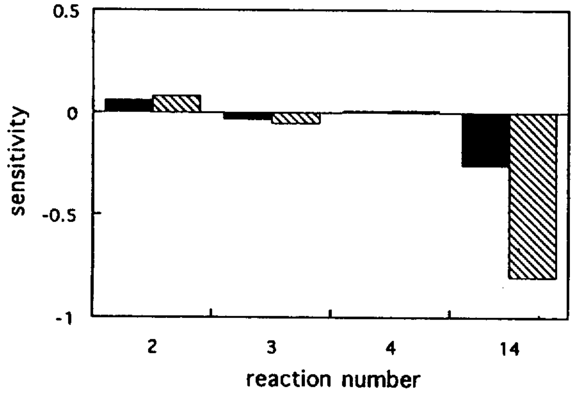

Figure 2. Logarithmic response sensitivity spectra[23] for the effective rate coefficient (k_{eff}) for 0.0994% $C_2H_6N_2$, 5.32% H_2 in Ar, $T_2=1560$ K, $P_1=24.6$ Torr. The filled and striped bars were computed by multiplying and dividing the Table 2 rate coefficient value by 1.5. Sensitivities less than 0.01 are not shown.

in the computer simulations described below using the extinction coefficients measured by Gardiner *et al.*[20] 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.*[21] mechanism used to determine the rate coefficients for CH_3 self-reactions. These rate coefficient expressions had been optimized to describe 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 $C_2H_6N_2$ and CH_3I decompositions were taken from Möller *et al.*[5] and Davidson *et al.*,[22] 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[23] (Fig. 2) showed that reaction 14 and CH_3 self-reactions contribute substantially to the CH_3 decay profiles.

For conditions where reaction 14 removes the main part of the CH_3 radicals and the decomposition of azomethane is fast, the decrease of the CH_3 concentration should come close to following first-order kinetics, *i.e.*,

$$d[CH_3]/dt=-k_{eff}\,[CH_3]$$

where $k_{eff}=k_{14}\,[H_2]+k_{self}\,[CH_3]$. For small contributions of CH_3 self-reactions

$$\ln\,([CH_3]_0/[CH_3])=k_{eff}\,t \tag{1}$$

The absorption at 213.9 nm is almost entirely due to CH_3

$$\log(I_0/I)=\varepsilon_{CH_3}\,[CH_3]\,d$$

where *d* is the absorption path length and *I* is the transmitted intensity. Thus, the CH_3 concentration is related to the transmitted intensity by

$$[CH_3]=\log(I_0/I)/(\varepsilon_{CH_3}\,d)$$
$$[CH_3]_0=\log(I_0/I_{max})/(\varepsilon_{CH_3}\,d)$$

The decrease of CH_3 follows

$$[CH_3]_0/[CH_3]=\log(I_0/I_{max})/\log(I_0/I) \tag{2}$$

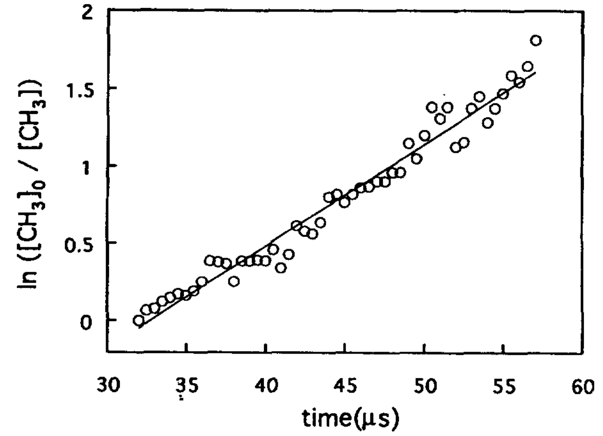

Figure 3. Pseudo-first-order plot of CH_3 concentration for the experiment in Figure 1. See Eq. 2 and the discussion in the text.

where I_{max} is the transmitted intensity at maximum absorption in an experiment. From Eqs. (1) and (2) the effective rate coefficient k_{eff} of CH_3 disappearance is given by

$$k_{eff} = (d/dt)\ [\ln\ \{\log(I_0/I_{max})/\log(I_0/I)\}] \qquad (3)$$

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_{eff} does not depend on the extinction coefficient of CH_3 at all, and k_{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_{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_{14} was adjusted until the experimental and calculated values of k_{eff} coincided. The results of k_{14} 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.*[10] A linear least-squares fit to the data results in the expression

$$k_{14} = 1.10 \times 10^{13}\ \exp(-7370\ \text{K/T})\ \text{cm}^3\text{mol}^{-1}\text{s}^{-1}$$

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.*.[10]

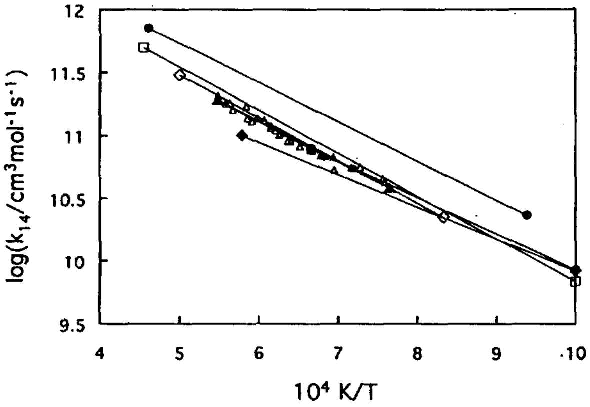

Figure 4. Dependence of k_{14} on temperature: open triangles represent our experimental results, and solid triangle line is a least-square fit of them; filled circle line, Möller *et al.*[5]; filled diamond line, Rabinowitz *et al.*[6]; open diamond line, Clark and Dove[7]; open square line, Schatz *et al.*[8]; open circle line, Joseph *et al.*.[10]

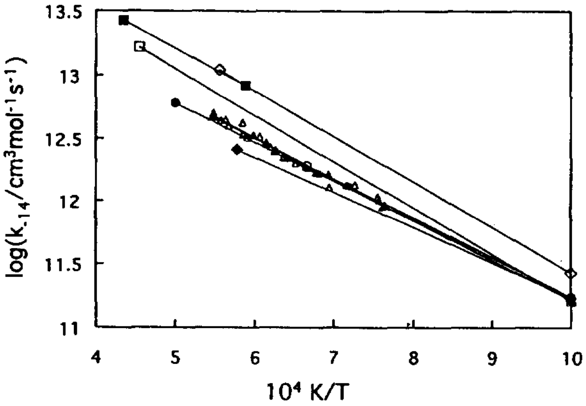

Figure 5. Dependence of k_{-14} on temperature: open triangles represent our experimental results, and solid triangle line is a least-square fit of them; filled square line, Roth and Just[4]; filled diamond line, Ravinowitz *et al.*[6]; open diamond line, Clark and Dove[7]; open square line, Schatz *et al.*[8]; open circle line, Joseph *et al.*[10]; filled circle line, Allara and Show[13].

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 JANAF[17] data (1300 K<T<1900 K):

$$K_{eq}(T) = 0.125 - (1.39 \times 10^{-4}\ T) + (7.68 \times 10^{-8}\ T^2) - (1.42 \times 10^{-11}\ T^3)$$

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 $k_{-14}(T)$ results are described by Arrhenius expression (1308-1825

K):

$$k_{-14}(T)=3.1\times10^{14}\ \exp(-7600\ \mathrm{K/T})\ \mathrm{cm^3mol^{-1}s^{-1}}$$

The extinction coefficient of CH_3 (ε_{CH_3}) can be calculated from I_{max} and the known k_{14}, because the value of I_{max} mainly depends on k_{14} and ε_{CH_3}. For the temperature range from 1308 K to 1825 K, our value of ε_{CH_3} is 5.2×10^5 cm^2/mol. Our results are close to those of Hwang *et al.*[21] and Yang *et al.*,[25] who conducted experiments with the same Zn lamp and do not show any, or at most a very weak, dependence on temperature.

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