

THE PRESSURE AND TEMPERATURE DEPENDENCE OF THE RATE CONSTANT FOR METHYL RADICAL RECOMBINATION OVER THE TEMPERATURE RANGE 296–577 K

Martyn T. MACPHERSON, Michael J. PILLING and Martin J.C. SMITH

Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, UK

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The rate constant for methyl radical recombination has been measured over the temperature range 296–577 K and at pressures between 5 and 500 Torr using laser flash photolysis, coupled with absorption spectroscopy at 216.36 nm. Analysis of the fall-off curves gives $k_{\infty} = (2.78 \pm 0.18) \times 10^{-11} \exp(154 \pm 22 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_0 = (6.0 \pm 3.3) \times 10^{-29} \exp(1680 \pm 300 \text{ K}/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. The quoted errors (two standard deviations) do not include the present uncertainty in the absorption cross section, which is a major source of error ($\pm 30\%$).

1. Introduction

The recombination of methyl radicals



is of central importance in hydrocarbon pyrolysis [1]. In addition the reaction has been widely employed as a reference in studies of radical/molecule reactions [2] and as a testing ground for unimolecular rate theory [3,4]. A recent evaluation of the available rate data [5] shows that, whilst there is good agreement on the rate constant at room temperature, and the reaction has been studied in shock tubes at temperatures above $\approx 1200 \text{ K}$ [6,7], the reaction is poorly characterised in the important region between 300 and 1000 K and, in particular, there is little information on the fall-off behaviour. We report a study of the reaction by laser flash photolysis over the temperature range 296–577 K and at argon pressures between 5 and 500 Torr.

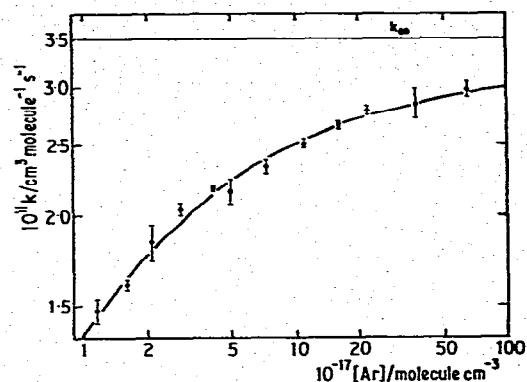
2. Experimental

The experimental technique and methods of data analysis have been reported [8]. CH_3 was produced by laser photolysis of azomethane at 193 nm and was observed via its UV adsorption at 216.36 nm, with a

band pass of 0.6 nm. The data were averaged over 32–64 shots, with a laser pulse intensity variation of $< 5\%$. The argon/azomethane ratio was always greater than 200 : 1, so that flash heating of the reaction mixture was negligible ($< 3 \text{ K}$) even at the lowest pressures used. Some vibrationally excited CH_3 was formed during the flash, but this was fully relaxed before any observations were made; relaxation was complete within 0.2 ms, even at 1 Torr total pressure at 296 K. End-product analysis experiments showed that the photolysis was quite clean; CH_2 and H were formed, but in concentrations $\leq 2\%$ of the methyl radicals. Since any effects of these additional products are within experimental error, they have been ignored in the present analysis.

3. Results and discussion

Analysis of the radical decay profiles provide experimental estimates of k/σ [8], where σ is the effective CH_3 absorption cross section at 216.36 nm, for a 0.6 nm band pass. Glänzer et al. [7] discussed the temperature dependence of σ and this was evaluated for our experimental conditions by Quack [9] based on the values of σ at 300 [10] and 1200 K [7]. As shown in table 2 below, σ decreases with temperature. Fig. 1 shows a fall-off plot for k_1 at 577 K and indicates the precision of the data. The experimental



points correspond to averages over, typically, four measurements and the error bars correspond to \pm two standard deviations, but do not contain any contribution from the uncertainty in σ . Since the spectrum shows strong lifetime broadening, pressure broadening is negligible, and the *shape* of the fall-off curves is independent of σ , although the absolute values of k depend

Fig. 1. Fall-off plot for the rate constant for methyl radical recombination at 577 K. Diluent gas = Ar, argon/azomethane > 200 .

Table 1
Rate constants for methyl radical recombination as a function of temperature, and argon pressure ^{a)}

T (K)	Pressure (Torr)	$10^{11} k$ (cm ³ molecule ⁻¹ s ⁻¹)	T (K)	Pressure (Torr)	$10^{11} k$ (cm ³ molecule ⁻¹ s ⁻¹)
296	5.39	3.79 ± 0.10	539	7.15	1.90 ± 0.24
	14.30	3.90 ± 0.09		9.07	1.95 ± 0.13
	41.10	4.11 ± 0.05		12.80	2.15 ± 0.07
	101.0	4.24 ± 0.03		16.70	2.19 ± 0.10
	244.0	4.33 ± 0.04		20.80	2.40 ± 0.07
	492.6	4.35 ± 0.04		25.42	2.39 ± 0.04
407	6.05	3.01 ± 0.11		30.90	2.42 ± 0.07
	9.61	3.16 ± 0.09		41.30	2.55 ± 0.07
	14.12	3.16 ± 0.07		62.20	2.69 ± 0.09
	25.60	3.43 ± 0.08		90.70	2.88 ± 0.02
	51.15	3.62 ± 0.04		130.0	3.08 ± 0.03
	194.0	3.83 ± 0.08		189.0	3.13 ± 0.04
	411.0	3.74 ± 0.03		272.7	3.16 ± 0.08
474	7.66	2.41 ± 0.11		430.2	3.26 ± 0.04
	7.97	2.34 ± 0.11	577	5.12	1.37 ± 0.06
	8.96	2.59 ± 0.05		6.87	1.47 ± 0.05
	9.97	2.46 ± 0.06		9.48	1.60 ± 0.02
	12.00	2.43 ± 0.13		12.40	1.83 ± 0.11
	17.37	2.49 ± 0.03		17.00	2.04 ± 0.04
	20.30	2.93 ± 0.04		24.60	2.18 ± 0.02
	24.00	2.63 ± 0.03		29.42	2.16 ± 0.08
	31.62	2.89 ± 0.05		43.40	2.33 ± 0.05
	43.87	2.96 ± 0.02		65.60	2.51 ± 0.04
	66.55	3.00 ± 0.04		95.15	2.65 ± 0.03
	91.80	3.19 ± 0.06		130.2	2.78 ± 0.05
	152.2	3.52 ± 0.04		222.0	2.84 ± 0.14
	390.0	3.87 ± 0.06		394.2	2.97 ± 0.07
513	11.30	2.22 ± 0.10			
	18.80	2.33 ± 0.12			
	27.70	2.60 ± 0.06			
	41.00	2.79 ± 0.09			
	58.00	2.77 ± 0.03			
	80.00	2.95 ± 0.01			
	125.5	3.04 ± 0.06			

^{a)} Quoted errors refer to \pm two standard deviations, but do not include any contribution from the uncertainty in σ .

linearly on σ . Table 1 gives the experimental values for the rate constants as a function of temperature and pressure.

The fall-off curves were analysed using the method described by Troe [11,12]:

$$\frac{k}{k_\infty} = \frac{k_0[M]/k_\infty}{1 + k_0[M]/k_\infty} \times F^{SC}(k_0[M]/k_\infty) F^{WC}(\beta_c, k_0[M]/k_\infty), \quad (2)$$

where k is the recombination rate constant at a third-body concentration $[M]$, k_0 and k_∞ are, respectively, the limiting zero-pressure third-order and limiting infinite-pressure second-order rate constants, F^{SC} and F^{WC} are correction factors, discussed by Troe [11,12], and β_c is the collisional efficiency of the stabilising gas, M. The experimental data were fitted to eq. (2) using a non-linear least-squares method. There are three variable parameters, k_0 , k_∞ and β_c , but the curves depend only weakly on β_c and fits in which all three parameters were allowed to float were not reliable. Troe [13] showed that

$$\beta_c/(1 - \beta_c^{1/2}) \approx -(\Delta E)/F_E kT,$$

where $\langle \Delta E \rangle$ is the average energy transferred per collision and F_E describes the energy dependence of the density of states. A value of 300 cm^{-1} , assumed independent of temperature, was chosen for $\langle \Delta E \rangle$, based on an examination of the efficiency of argon in thermal recombination/dissociation reactions. The values of k_0 , k_∞ , β_c and $P_{1/2}$ (the pressure at which $k/k_\infty = 0.5$) are shown in table 2.

Fig. 2 shows an Arrhenius plot for k_∞ and compares the present results with literature values. Most

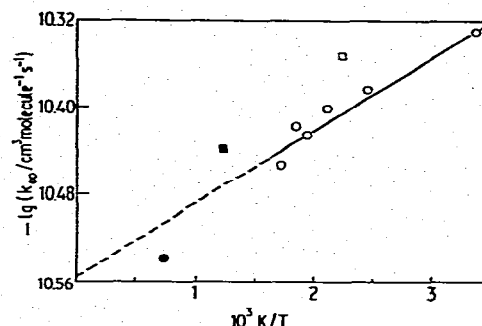


Fig. 2. Arrhenius plot for the limiting high-pressure rate constant (k_∞) for methyl radical recombination. O, this work; ●, ref. [7]; ■, ref. [14]; □, ref. [15].

direct measurements have been made near room temperature and Baulch and Duxbury [5] recommend a temperature-independent value of $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–420 K. A weighted fit to our data gives $k_\infty = (2.78 \pm 0.18) \times 10^{-11} \exp[(154 \pm 22)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (quoted errors: two standard deviations). Extrapolation to high temperatures shows quite good agreement with the values of Glänzer et al. [7] and Pacey and Wimalasena [14].

Fig. 3 shows an Arrhenius plot for k_0 and compares our data with literature values. A weighted least-squares fit to our data gives $k_0 = (6.0 \pm 3.3) \times 10^{-29} \times \exp[(1680 \pm 300)/T] \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ (quoted errors: two standard deviations); rate constants from other determinations are also shown. Allowance was made, where necessary, for the different third bodies (M) employed, by multiplying k_0 by $\beta_c^{\text{Ar}} Z_{\text{LJ}}^{\text{Ar}} / \beta_c^{\text{M}} Z_{\text{LJ}}^{\text{M}}$. (The values used were $\beta_c^{\text{Ar}} / \beta_c^{\text{He}} = 1.94$, $\beta_c^{\text{Ar}} / \beta_c^{\text{BA}} =$

Table 2
Dependence of kinetic data for CH_3 recombination on temperature ^{a)}

T (K)	$10^{11} k_\infty$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$10^{27} k_0$ ($\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$)	$P_{1/2}$ (Torr)	β	$10^{17} \sigma$ (cm^2)
296	4.67 ± 0.04	17.4 ± 7.0	0.4	0.45	3.04
407	4.13 ± 0.11	6.80 ± 3.4	1.2	0.37	2.56
474	3.97 ± 0.32	1.86 ± 0.94	5.5	0.34	2.30
513	3.75 ± 0.10	1.59 ± 0.40	7.0	0.32	2.16
539	3.83 ± 0.09	1.20 ± 0.21	10.5	0.31	2.07
577	3.52 ± 0.09	1.15 ± 0.11	11.7	0.29	1.95

^{a)} Quoted errors refer to \pm two standard deviations but do not include any contribution from the uncertainties in σ and β_c (see text).

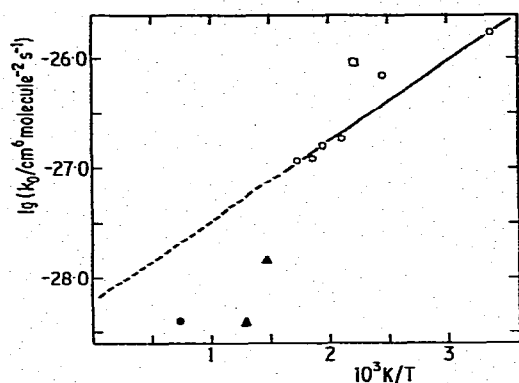


Fig. 3. Arrhenius plot for the limiting low-pressure rate constant (k_0) for methyl radical recombination. O, this work; ●, ref. [7]; □, ref. [15]; ▲, ref. [16].

0.26–0.23, $Z_{LJ}^{Ar}/Z_{LJ}^{He} = 0.75$, $Z_{LJ}^{Ar}/Z_{LJ}^{BA} = 0.68$, where BA = biacetyl [16]. Z_{LJ} is the Lennard-Jones collision frequency.)

4. Errors

The errors quoted in tables 1 and 2 and in the Arrhenius expressions for k_∞ and k_0 refer only to the random errors derived directly from our data analysis. They do not include any error estimates associated with β_c and σ . k_0 and k_∞ are both linearly dependent on σ and the estimated error in this quantity is $\approx 30\%$. The uncertainty in the temperature dependence of σ is likely to be much less than this. Uncertainties in σ have no effect on $P_{1/2}$.

The rate constants were followed almost to their high-pressure limits and so the effects on k_∞ of the large uncertainty in β_c is quite small. Even increasing β_c by a factor of 20 (from 0.05 to 1.0) only decreases k_∞ by 4% at 296 K and by 8% at 577 K. Conversely, since the low-pressure limit was not closely approached, k_0 is much more sensitive to the choice of β_c and the same change decreases k_0 by a factor of 3.1 at 296 K and 1.7 at 577 K.

The intrinsic precision of the decay measurements presented here cannot be fully exploited until σ is

measured to similar precision as a function of temperature. Experiments on this are in progress. Similarly, further kinetic measurements are in progress with a variety of inert gases, aimed at obtaining more reliable estimates of β_c and at permitting a more direct application of the fall-off data in the analysis of pyrolysis systems.

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