Reaction of CH_3 Radicals with Methanol in the Range $525 \le T/K \le 603$

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We have used molecular modulation spectrometry and a simple kinetic analysis, to make the first direct measurements on the reaction of methyl radicals with methanol. Product studies using gas chromatography were also carried out to complement the kinetic measurements. The rate constants derived in the temperature range $525 \le T/K \le 603$ are described by $k_5 = 1.3 \ (+1.3/-0.6) \times 10^{-11} \ \exp(-55.1 \pm 3.3 \ \text{kJ mol}^{-1}/RT) \ \text{cm}^3$ molecule⁻¹ s⁻¹.

1. Introduction

Detailed chemical schemes have been proposed to explain the pyrolysis and oxidation of methanol.^{1,2} The reaction of methyl radicals with methanol is very important in such mechanisms yet there are very few studies of this reaction reported in the literature. Kerr and Parsonage³ have evaluated the relative rate constants from five early product studies carried out at $T \leq 523$ K. More recently, Spindler and Wagner⁴ have studied the pyrolysis of methanol in a shock tube, extracting a rate constant for the reaction of methyl radicals with methanol by computer modelling the observations.

We have used a molecular modulation spectrometer (MMS) to make the first direct study of this reaction. The experiments, carried out in the range $525 \le T/K \le 603$, were complemented by product studies using gas chromatography (g.c.), and were analysed using simple first-order kinetics

2. Experimental

2.1 Method

The experimental apparatus, the procedure and method of analysis have been described in detail before.⁵ Briefly, three low-pressure mercury lamps whose output is essentially at 254 nm periodically photolyse acetone to produce methyl radicals. The radical concentration is modulated and detected by the absorption of light at 216 nm. The signal is digitised and fed into two up-down counters. One of these (in-phase) counts up when the lamps are on and down when they are off. The second (in-quadrature) conducts the same exercise but lags the in-phase counter by 90°. For pseudo-first-order removal of the radicals it can be shown that⁵

$$\frac{6}{\tau_0} = k_1$$

where τ_0 is the photolysis period when the in-phase and inquadrature signals are equal and k_1 is the first-order rate constant. First-order behaviour was confirmed using g.c. to analyse the products at the end of each MMS experiment.

2.2 Materials

Methane, ethane and dimethyl ether were taken directly from cylinders while acetone, methyl ethyl ketone, methanol and ethanol were thoroughly outgassed before use (all materials used were of research grade quality from B.D.H. Chemicals Ltd).

3. Results and Analysis

The behaviour of methyl radicals, generated by the photolysis of acetone $(1.1-2.2 \times 10^{11} \text{ molecule cm}^{-3})$, in the presence of methanol (4.2-21.4 × 10¹⁷ molecule cm}^{-3}) is governed by the following set of reactions at elevated temperatures:

$$CH_3COCH_3 + (hv \approx 254 \text{ nm}) \rightarrow 2CH_3 + CO$$
 (1)

$$CH_3 + CH_3 (+M) \rightarrow C_2H_6 (+M)$$
 (2)

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2$$
 (3)

$$CH_3 + CH_3COCH_2 (+M) \rightarrow CH_3COCH_2CH_3 (+M)$$

$$CH_3 + CH_3OH \rightarrow CH_4 + CH_3O$$
(5a)

$$\rightarrow CH_4 + CH_2OH \tag{5b}$$

$$CH_3 + CH_3O(+M) \rightarrow CH_3OCH_3 + (+M)$$
 (6a)

$$\rightarrow CH_4 + CH_2O$$
 (6b)

$$CH_3 + CH_2OH (+M) \rightarrow CH_3CH_2OH (+M)$$
 (7a)

$$\rightarrow CH_1 + CH_2O$$
 (7b)

where M is a diluent molecule. If square brackets denote concentration, t the time and B the photolysis rate for reaction (1), then

$$\frac{d[CH_3]}{dt} = 2B - 2k_2[CH_3]^2 - k_3[CH_3][CH_3COCH_3] -k_4[CH_3][CH_3COCH_2] - k_5[CH_3][CH_3OH] -k_{6a}[CH_3][CH_3O] - k_{6b}[CH_3][CH_3O] -k_{7a}[CH_3][CH_2OH] - k_{7b}[CH_3][CH_2OH]$$
(I)

where $k_5 = (k_{5a} + k_{5b})$. As expected, the methanol and acetone concentrations were such that the dominant product observed using gas chromatography was methane, mainly from reaction (5) and to a much lesser extent from reaction (3) (q.v.). Smaller quantities of ethane, ethanol and methyl ethyl ketone were also observed but no measurable quantities of dimethyl ether due to reaction (6*a*) were produced. This is not surprising since the production of CH₂OH dominates the production of CH₃O in the CH₃-methanol reaction; for example, reaction (5*b*) is *ca.* 32 kJ mol⁻¹ more exothermic than reaction (5*a*), assuming that ΔH_f of CH₃, CH₂OH and CH₃O are 143.5, ⁶ -17.0⁶ and 14.6⁷ kJ mol⁻¹, respectively. Also, studies involving the reaction of methyl radicals with methanol which has been deuterated at different sites, have shown that reaction (5*b*) dominates.³

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Table 1. Rate information for the reaction of CH₃ radicals with methanol

T/K	[CH ₄]/products	k_{1st} (total)/s ⁻¹	k ₃ [CH ₃ COCH ₃]/s ⁻¹	$k_5/10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
525	14.2	100.0	8.1	4.4
525	4.4	95.0	17.5	4.1
546	4.4	131.0	16.4	7.2
573	4.2	120.0	29.9	10.4
575	4.3	137.0	30.5	13.1
603	4.2	134.0	45.0	23.0

The contribution of reaction (7b) to the methane observed is likely to be small since reaction (7a) is ca. 51 kJ mol⁻¹ more exothermic than reaction (7b). Table 1 gives the ratio of methane to the sum of products containing methyl groups, as ca. 4.3 in the temperature range $525 \le T/K \le 603$. It is worth noting that the results obtained at 525 K were essentially unchanged within experimental error, when the ratio was increased from 4.4 to 14.2 by increasing the CH₃OH concentration and decreasing the CH₃COCH₃ concentration. Eqn



Fig. 1. In-phase (\bigcirc) and in-quadrature (\times) signals as a function of photolysis period for the reaction of CH₃ radicals with CH₃OH ([CH₃COCH₃] = 2.8 × 10¹⁷, [CH₃OH] = 2.0 × 10¹⁸ and total gas density = 1.9 × 10¹⁹ molecule cm⁻³; T = 525 K).



Fig. 2. Arrhenius plot for the reaction of CH₃ radicals with CH₃OH.

(I) reduces to:

$$\frac{d[CH_3]}{dt} \approx 2B - (k_3[CH_3COCH_3] + k_5[CH_3OH])[CH_3]$$
(II)

i.e. pseudo-first-order removal of methyl radicals. As before,⁷ first-order kinetics in the MMS are satisfied by the expression:

$$\frac{6}{\tau_0} = k_{1\text{st}} = k_3[\text{CH}_3\text{COCH}_3] + k_5[\text{CH}_3\text{OH}] \qquad \text{(III)}$$

where τ_0 is the photolysis period when the in-phase and inquadrature signals are equal, and k_{1st} is the first-order rate constant associated with the pseudo-first-order removal of methyl radicals by acetone and methanol. The value for k_3 is taken from the evaluation work of Kerr and Parsonage who quote an uncertainty of 25%. However, the absolute rate constants were derived relative to the rate constant for the selfreaction of methyl radicals which was assumed to be 3.6×10^{-11} cm³ molecule⁻¹ s⁻¹; the value of the latter is now thought to be higher and temperature dependent.⁸ We have corrected the original evaluation work to accommodate this more recent methyl work.

The concentrations of acetone and methanol were measured directly into the reaction vessel via a mixing vessel; since k_3 is known, a measurement of τ_0 gives k_5 using expression (III). Fig. 1 shows a typical absorption signal/log₁₀ τ plot from which the cross-over point, τ_0 , is determined. Table 1 summarises the parameters involved, with the contribution to the first-order component due to reaction (3) ranging from 8 to 34%. An Arrhenius plot for k_5 is shown in fig. 2 and a least-squares analysis of the data leads to the expression $k_5 = 1.3 \ (+1.3/-0.6) \times 10^{-11} \ \exp(-55.3 \pm 3.3 \ \text{kJ mol}^{-1}/RT) \ \text{cm}^3$ molecule⁻¹ s⁻¹. The large error associated with the A factor is due to the long extrapolation from a relatively small temperature range.

4. Discussion

There have been very few studies of this reaction as shown in fig. 3. Kerr and Parsonage³ have evaluated the early product studies, suggesting an Arrhenius expression $k_{11} = 4.0 \times 10^{-13} \exp(-40.5 \text{ kJ mol}^{-1}/RT) \text{ cm}^3$ molecule⁻¹ s⁻¹ for the range $373 \leq T/K \leq 523$, with 40% error limits; as above, we have corrected their original evaluation results using the presently accepted value for the combination of methyl radicals. There is good agreement between their rate constant and that measured in this work at the cross-over temperature of *ca.* 525 K. However, this is fortuitous since both the activation energy and A factor values are different.

More recently, the decomposition of CH₃OH has been studied in a shock tube by Spindler and Wagner.⁴ These authors extracted an A factor value of 1.5×10^{-11} cm³ molecule⁻¹ s⁻¹ and an activation energy of 41.1 kJ mol⁻¹ for the reaction of CH₃ with methanol in the range $1600 \le T/K \le 2100$. The A factor is in very good agreement

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Fig. 3. The reaction of CH₃ radicals with CH₃OH as a function of temperature: (---) ref. (3); (\cdots) ref. (4); (---) this work.

with that given in the present work but the activation energy is lower.

Of the low temperature studies, our results are more in line with the high-temperature values of Spindler and Wagner. In fact, a long extrapolation of our measurements to this higher temperature regime yields rate constants that are lower by about a factor of 3; this is fair agreement when one considers the long extrapolation involved and the errors in both studies.

There are two pathways possible in the reaction of CH₃ radicals with methanol and this raises the possibility of non-Arrhenius behaviour. However, any curvature is likely to be small since Kerr and Parsonage³ in their review and, more recently, Tsang⁹ in his review, suggest that $k_{5b}/k_{5a} \approx 2.5$ in the lower temperature regime, rising to *ca*. 3.0 at the higher temperatures. This small change cannot rationalise the large differences between the corrected Kerr and Parsonage expression and the shock-tube data, but may help to minimise further the smaller differences between this work and the higher-temperature work.

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