Reaction of CH₃ Radicals with OH at Room Temperature and Pressure

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The kinetics of the reaction $CH_3 + OH(+M) \rightarrow CH_3OH(+M)$ have been studied by pulse radiolysis combined with transient ultraviolet absorption spectrophotometry. The radical source reactions (2) $F + CH_4 \rightarrow HF + CH_3$ and (3) $F + H_2O \rightarrow HF + OH$ were initiated by pulse radiolysis of $Ar/SF_6/CH_4/H_2O$ mixtures at a total pressure of 1 atm and room temperature. The kinetics of methyl radicals were studied by monitoring the transient absorption signals at 216.4 nm. In the absence of water vapour the observed decay was simple second order in accordance with the self-reaction (4) $CH_3 + CH_3(+M) \rightarrow C_2H_6(+M)$. The initial yield of F-atoms was derived from the observed maximum absorbance of CH_3 produced *via* reaction (2) using a consensus value of $\sigma(CH_3)$. The relative yields of CH_3 and OH were controlled by varying the $[H_2O]/[CH_4]$ concentration ratio and the ratio of the rate constants $k_2/k_3 = 3.2 \pm 0.2$ was derived from the observed variation in the yield of methyl radicals as a function of the $[H_2O]/[CH_4]$ concentration ratio. The decay kinetics of CH_3 were studied as a function of the relative radical yields, $G(OH)/G(CH_3)$. The kinetic features were analysed by computer modelling of reactions (2)–(4) combined with the reaction (1) $CH_3 + OH(+M) \rightarrow CH_3OH(+M)$, (5) $OH + OH(+M) \rightarrow H_2O_2(+M)$ and (6) $OH + OH \rightarrow O + H_2O$. A representative set of experimental decay curves could be fitted within the signal-tonoise ratio after adjustment of the cross-combination rate constant to a value of $k_1 = (9.4 \pm 1.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

Radical-radical reactions are important in chemical transformations taking place in the atmosphere and in combustion processes.¹ They have remained a challenge to the experimentalists because of the complexity inherent in the kinetic analysis which requires simultaneous information on absolute radical concentrations and lifetimes in order to establish rate constants for this class of reactions.

In the present study we have investigated the radicalradical cross-reaction between methyl and hydroxyl radicals.

$$CH_3 + OH(+M) \rightarrow CH_3OH(+M)$$
 (1)

where M is the diluent gas, argon in this case. This reaction takes place in competition with the self-reactions of CH_3 and OH, respectively.

Experimentally it has been possible to maintain a constant sum of the radical yields, $G(CH_3) + G(OH)$ while the relative yields $G(OH)/G(CH_3)$ could be varied by adjustment of the concentration ratio of the parent compounds, *i.e.* H₂O and CH₄. Thus, the decay rate of methyl radicals could be studied in the absence of hydroxyl radicals where the selfreaction dominates, as well as in the presence of an increasing excess of hydroxyl radicals where reaction (1) takes over as the main sink for methyl radicals.

Only one experiental study of reaction (1) has been reported and this under experimental conditions where a maximum 17% of the methyl radicals were consumed in reaction (1) while *ca.* 78% were lost in the competing reaction $H + CH_3$, which was unavoidable because of the simultaneous formation of H and OH by photolysis of water.² Experimental kinetic results on reaction (1) may be compared with recent theoretical studies on this reaction.³ Finally, there have been several studies of other radical cross-reactions involving the methyl radical⁴⁻⁶ and the extended data set will offer an opportunity to test further the proposed cross combination rule for radical-radical reactions.

Experimental

The experimental technique of pulse radiolysis combined with transient ultraviolet absorption spectrophotometry has been described in detail previously.7 Briefly, gas mixtures are prepared in a 1 dm³ reaction cell and irradiated with a 50 ns pulse of 2 MeV electrons from a field emission accelerator. The number of free radicals produced per irradiation pulse is typically 10¹⁴-10¹⁵ cm⁻³. The small surface-to-volume ratio of the reaction chamber combined with the high gas pressure normally employed (1 bar) ensure that wall effects are negligible. Analysing light from a pulsed xenon lamp passes through the reaction chamber which is equipped with a set of internal mirrors to obtain an optical pathlength of 80 cm by multiple reflections through the gas mixture. The spectral features are analysed using a 1 m grating monochromator (Hilger–Watts) with a reciprocal dispersion of 8 Å mm^{-1} . The light intensity is monitored with a fast photomultiplier (Hamamatsu R955) and the signals are digitised in a transient recorder (Biomation 8100) interfaced with a minicomputer (PDP-11) programmed for on-line analysis of UV spectra and chemical kinetics. Gas mixtures were prepared by admitting one component at a time and reading the corresponding partial pressure with an electronic membrane manometer with a sensitivity of 10^{-5} bar (1 bar = 1000 mb = 2.48×10^{19} molecule cm⁻³ at 294 K).

The temperature of the gas mixture is measured with a platinum resistance thermometer. The experimental work was carried out at a constant temperature of 294 K and the total pressure was maintained at 1 bar.

Materials

Research-grade gases, Ar, SF_6 and CH_4 were used without further purification. H_2O was triply distilled and thoroughly outgassed before use.

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Radical Source Reactions and Decay Kinetics

Pulse radiolysis is a very versatile technique for the production of free radicals in the gas phase. A wide range of radical species may be produced by the reaction of F atoms with suitable hydrogen-containing additives:

$$F + RH \rightarrow HF + R$$

High yields of F-atoms are obtained by pulse radiolysis of $Ar-SF_6$ mixtures:

2 MeV
$$e^- + Ar \rightarrow Ar^* + e^-$$

Ar* + SF₆ \rightarrow SF₄ + 2F (a)

$$\rightarrow$$
 SF₅ + F (b)

In addition to F atoms, reactions (a) and (b) yield SF_4 and SF_5 , respectively. Under the conditions prevalent in this study, reaction (a) dominates the F-atom production with the SF_5 route contributing <3% of the total. This value is calculated from the measured 'prompt' absorption signal at 300 nm and the literature value for the absorption cross-section of SF_5 .⁸ SF_4 is a stable product with a very low absorption cross-section in the spectral region used in this study⁹ and does not interfere with the kinetic analysis.

In the present investigation the F atoms produced initially are converted into methyl and hydroxyl radicals *via* reactions (2) and (3).

$$F + CH_4 \rightarrow HF + CH_3 \tag{2}$$

$$F + H_2O \rightarrow HF + OH$$
 (3)

At sufficiently high concentrations of CH₄ and/or H₂O all F atoms are converted quantitatively into methyl and hydroxyl radicals and with relative yields controlled by the concentration ratio of the parent compounds. Thus, the sum of the radical yields equals the initial yield of F atoms, $G(CH_3)$ + G(OH) = G(F) while the relative yields are determined by the simple competition ratio $G(CH_3)/G(OH) = k_2[CH_4]/k_3[H_2O]$. The sum of the concentrations of the parent compounds was maintained high enough to make the formation reactions (2) and (3) very much faster than the subsequent radical decay reactions (1), (4)–(6).

$$CH_3 + OH(+M) \rightarrow CH_3OH(+M)$$
 (1)

$$CH_3 + CH_3(+M) \to C_2H_6(+M)$$
 (4)

$$OH + OH(+M) \rightarrow H_2O_2(+M)$$
 (5)

$$OH + OH \rightarrow O + H_2O$$
 (6)

The overall decay rate of the methyl radicals was studied by monitoring the transient absorption at 216.4 nm using a spectral bandwidth of 4 Å. The initial yield of F-atoms was calculated from the observed maximum absorbance (A_{max}) in the absence of H₂O using a consensus value of the absorption cross-section $\sigma(CH_3)^{10,11}$ as before.⁵ The following observations confirm that there are no other sources of methyl radicals in our system. The yield of methyl radicals produced via reaction (2) was studied as a function of the methane concentration. The yield was found to increase towards a maximum value which showed that at $p(CH_{4}) > 1$ mbar all F atoms produced by the radiolysis of 50 mbar SF_6 in 1 atm of Ar are converted into methyl radicals via reaction (2). Furthermore, the observed rate of formation was found to increase monotonically as a function of the methane concentration in accordance with reaction (2). In the case of 'direct radiolysis' of methane we would expect to observe a 'prompt signal' due to formation of CH₃ via fast ionization or energy transfer reaction. The absence of such a prompt component



Fig. 1 CH₃ decay in the absence of H₂O; 5 mbar CH₄, 50 mbar SF₆ and 945 mbar Ar, and T = 294 K. The solid line is that predicted by $k_4 = 5.8 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and an initial [CH₃] of 2.8×10^{14} radical cm⁻³

in the observed formation kinetics may be taken as a safe indication for the absence of other methyl source reactions.

Fig. 1 shows the kinetics of CH₃ in the absence of OH. From the maximum absorbance observed with an optical pathlength of L = 80 cm we have calculated the constant initial yield of F atoms, $[F]_0 = A_{max}/\sigma L = 2.83 \times 10^{14} \text{ cm}^{-3}$. The decay of methyl radicals shown in Fig. 1 is simple second order in accordance with the self-reaction (4). The smooth curve going through the experimental points was obtained by computer modelling using a value of $k_3 = 5.8 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ in good agreement with the values obtained in previous investigations.^{10,11} The effect of reaction (1) on the overall decay kinetics of CH₃ was studied by pulse radiolysis of gaseous mixtures with varying concentration ratios of CH₄ and H₂O as shown in Table 1. The kinetics of the pure self-reaction (4) was obtained with the gas composition of system A in Table 1, i.e. in the absence of water vapour.

The $[H_2O]/[CH_4]$ concentration ratio was varied as shown in systems B-E in Table 1. Fig. 2 shows the variation in the yield of methyl radicals which may be expressed in terms of the simple competition formula (I)

$$[CH_3]_{max}/[F]_0 = 1/(1 + k_3[H_2O]/k_2[CH_4])$$
(I)

The smooth curve in Fig. 2 is the result of a least-squares fit of (I) to the experimental points corresponding to a value of $k_2/k_3 = 3.2 \pm 0.2$ where the error represents one standard deviation. Combining this ratio with the value of $k_2 = 6.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ obtained previously⁵ we derive an absolute value of $k_3 = 2.1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

In the presence of hydroxyl radicals the overall decay rate of methyl radicals is described by the differential equation $d[CH_3]/dt = -2k_4[CH_3]^2 - k_1[CH_3][OH]$. Owing to the

Table 1 Composition of gas mixtures (partial pressures in mbar)

system	CH₄	H ₂ O	SF ₆	Ar
A	5	0	50	945
В	1	6	50	943
С	1	12	50	937
D	1	15	50	934
E	2	4	50	944



Fig. 2 A_{max} (CH₃) as a function of the [H₂O]/[CH₄] ratio (see text)

strong absorption of methyl radicals it has been possible to study the kinetics under experimental conditions where the relative yield of OH is about five times higher than the yield of CH₃. The effect of reaction (1) is clearly observed in Fig. 3 which shows the reciprocal half-lives, $\tau_{1/2}$, of CH₃ as a function of the maximum absorbance which also represents the relative yield of CH₃. The line through the origin represents the theoretical variation of the half-life of the pure selfreaction in the absence of OH, *i.e.* $\tau_{1/2} = 1/2k_4[CH_3]_{max} =$ $\sigma L/2k_4 A_{max}$. The experimental points in Fig. 3 show clearly that the observed half-lives deviate substantially from those of the self-reaction (4). The difference is caused by the competing reaction (1) which becomes increasingly important as the relative yield of OH increases. A first estimate of the rate constant for reaction (1) was obtained by a linear leastsquares fit to the experimental points. The intercept of this line was taken as measure of the half-life of reaction (1) proceeding under pseudo-first-order conditions where $[OH]_{max} = [F]_0$ and $\tau_{1/2} = \ln 2/k_1[F]_0$. Based on the value of the intercept of $3.8 \times 10^4 \text{ s}^{-1}$ and $[F]_0 = 2.8 \times 10^{14} \text{ cm}^{-3}$ we obtain a value of $k_1 = 9.4 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹. This value, and that for k_3 derived from expression (I), are in very good agreement with the results of detailed computer simulations of the CH₃ decay kinetics taking into account all of the reactions listed in Table 2. Values of k_3 and k_1 were varied in the model to reproduce the experimental yields shown in Fig. 2, the half-lives in Fig. 3 and to fit the experimental decay curves obtained under the varying experimental conditions outlined in Table 1. Fig. 4 shows the best fit of the model curve to the experimental curve obtained with the composition of system E in Table 1. In Table 3 we have summarised the results of our computer simulations corresponding to the varying experimental conditions. In the case of system C where $[H_2O]/[CH_4] = 12$ the computer model predicts that more than 95% of the methyl radicals are consumed in reaction (1). Under these conditions where the effect of the self-reaction (4) on the overall decay rate is negligible, the fit of the computer model becomes extremely sensitive to the value of k_1 . Using the average values of k_3 and k_1 listed in Table 3 the computer model accounts well for the whole series of experiments outlined in Table 1. The quoted error limits represent the span of rate constants derived in the series and reflect unavoidable variations in the irradiation



Fig. 3 Reciprocal half-life (τ) of CH₃ decay as a function of A_{max} , (CH₃) and [H₂O]/[CH₄] (see text)

dose (\pm 5%) as well as uncertainties in the concentrations of water vapour due to the effect of adsorption on the walls of the reaction chamber.

One possible source of error lies in the high concentrations of H_2O relative to SF_6 , particularly in mixtures C and D of Table 1, which could lead to the direct reaction of Ar^* with H_2O thus reducing the production of F atoms and hence, the radicals of interest. However, reactions (a) and (b) are a simplified form of the mechanism of F-atom production. The interaction of 2 MeV electrons with Ar leads to Ar^+ and a secondary electron; the latter is captured very efficiently by SF_6 to produce SF_6^- and it is the reaction of Ar^+ , and possibly SF_6 (produced by the interaction of Ar^+ and SF_6) with SF_6^- which leads to the production of F atoms. The production of F atoms then, relies on the capture of secondary electrons by SF_6 . In comparison to SF_6 , H_2O has a very low capture potential of secondary electrons and its ability to compromise the formation of radicals is thus very much



Fig. 4 CH₃ decay in the presence of H₂O; 2 mbar CH₄, 4 mbar H₂O, 50 mbar SF₆ and 944 mbar Ar, and T = 294 K. The solid line is that predicted by the model given in Table 2

Table 2 Reactions used in modelling the CH_3/OH system

reaction		rate constant/cm ³ molecule ⁻¹ s ⁻¹	reference
$F + CH_4$	\rightarrow CH ₃ + HF	6.7×10^{-11}	5
$F + H_2O$	$\rightarrow OH + HF$		see Table 3
$CH_3 + CH_3(+M)$	$\rightarrow C_2 H_6(+M)$	5.8×10^{-11}	see text
$CH_3 + OH(+M)$	$\rightarrow CH_3OH(+M)$		see Table 3
OH + OH(+M)	\rightarrow H ₂ O ₂ (+M)	4.7×10^{-12}	13ª
OH + OH	$\rightarrow O + H_2O$	1.9×10^{-12}	13ª
$OH + CH_4$	$\rightarrow CH_3 + H_2O$	8.5×10^{-15}	14

^a Overall rate constant measured for the experimental conditions used in this study; branching ratio taken from ref. 16.

reduced. Also, the results of the kinetic analysis summarised in Table 3 show consistent results for all water concentrations.

Discussion

The value of $k_1 = (9.4 \pm 1.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in very good agreement with the value of $9.3 \times 10^{11} \text{ cm}^3$ molecule⁻¹ s⁻¹ reported by Sworski *et al.*² The agreement is quite remarkable in view of the difference in experimental techniques and the fact that these authors were dealing with a much more complex system where the predominant (78%) reaction was H + CH₃(+M) \rightarrow CH₄(+M) while only 17% of the methyl radicals were consumed in reaction (1). Nevertheless, we believe that the agreement between the experimental results obtained under different experimental conditions must be taken as a good indication of the reliability of the reported results.

According to the simple cross combination rule for mixed radical-radical reactions between the radicals R^1 and R^2 the rate of the cross reaction may be expressed by the equation^{4,12}

$$k_{12} = 2(k_{11} \times k_{22})^{1/2}$$

In the actual case we compare the rate of the cross-reaction (1) with the rates of the self-reactions (4) and (5). Using $k_4 = 5.8 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and the recommended high pressure value for $k_5 = 1.5 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹¹ ¹³ we obtain from the equation above a value of $k_1 = 5.9 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ in the high-pressure limit. In this case the value predicted by the simple cross combination rule is only 64% of the experimental value of k_1 obtained at a pressure of 1 atm. This fairly large discrepancy would seem to confirm that the simple cross combination rule only applies to similar types of radicals.⁴

A QRRK study of reaction (1) was carried out by Dean and Westmoreland³ providing expressions for k_1 for three collision partners, M = Ar, N_2 and CH_4 in the pressure range of 0.03–10 bar. For example, they suggest $k_1(Ar) = 1.12$ $\times 10^{41} (T)^{-8.44} \exp(11\,803/RT)$ cm³ molecule⁻¹ s⁻¹ applicable in the range of 600–2500 K and a pressure of 1 bar. At 600 K and 1 bar a value of $k_1(Ar) = 3.3 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ is obtained and this value is essentially unchanged at 10 bar, *i.e.* the reaction is at its high-pressure

Table 3 Rate constant values for k_1 and k_3 for mixtures B-E

mixture	$k_1/10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹	$k_3/10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹
В	10.8	1.83
С	10.0	1.92
D	8.3	2.00
Ε	8.3	2.10
mean value	9.4 ± 1.3	2.0 ± 0.2

limit at 1 bar. Also, a graphical representation of the rate constant as a function of temperature shows this value increasing slightly from 600 to 300 K. The value of k_1 determined in the present investigation at room temperature and 1 bar Ar, together with that reported by Sworski *et al.*,² confirm a value considerably higher than that predicted by theory and suggests further refinement of the theory is needed for this reaction.

The value of the rate constant for the reaction of F atoms with H₂O, $k_3 = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ extracted from computer modelling of the methyl decay curves is higher than the results of previous studies. Walther and Wagner¹⁵ obtained a value of $k_3 = 1.1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ using a discharge flow system combined with mass spectrometry to study the kinetics of H₂O in the presence of an excess of F atoms. Frost et al.¹⁶ used flash photolysis to generate F atoms in the presence of H₂O and monitored the product HF by infrared chemiluminescence. These authors reported a value of $k_3 = 1.3 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at a pressure of 150 mbar at 298 K. Recently, Stevens *et al.*¹⁷ reported $k_3 = 1.6 \times 10^{-11} \exp(-28/T)$ cm³ molecule⁻¹ s⁻¹ in the temperature range of 240-373 K using a discharge flow/resonance fluorescence method. This expression yields a value of $k_3 = 1.45 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 294 K. It is difficult to ascertain the causes for the differences in the reported values of k_3 . One possible source of error lies in the measurements of the true gas-phase concentrations of water vapour because of the effects of adsorption of H₂O on glass and metal surfaces. Also, there are major differences in the absolute water concentrations used in the different studies. In the present study $p(H_2O)_{max} = 15$ mbar whereas the maximum pressures used in the other studies were ca. 10^{-3} mbar. Problems with adsorption phenomena may well be most serious in the case of low concentrations. However, there are no obvious reasons to prefer any one of the reported values, and further work is needed before the differences in k_3 are resolved.

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