#### J. Chem. Soc., Faraday Trans. 2, 1988, 84(7), 913-930

# Kinetic Study of the Reactions $CH_3O_2 + CH_3O_2$ and $CH_3O_2 + HO_2$ using Molecular Modulation Spectroscopy

### Michael E. Jenkin,\* Richard A. Cox, Garry D. Hayman and Lynden J. Whyte†

Environmental and Medical Sciences Division, United Kingdom Atomic Energy Authority Harwell Laboratory, Oxfordshire OX11 0RA

> Infrared diode laser and ultraviolet spectroscopic techniques have been used to observe the behaviour of HO<sub>2</sub> and  $CH_3O_2$  radicals generated in the gas phase by the near-ultraviolet modulated photolysis of flowing  $Cl_2$ - $CH_4$ - $H_2$ - $O_2$  and  $Cl_2$ - $CH_4$ - $H_2O_2$ - $O_2$  mixtures. This has enabled measurement of the rate coefficient for the reaction

$$HO_2 + CH_3O_2 \rightarrow \text{products}$$
 (3)

which was found to have a value of  $(5.4 \pm 1.1) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 10 Torr<sup>‡</sup> and 300 K. CH<sub>3</sub>O<sub>2</sub> produced during the photolysis of Cl<sub>2</sub>-CH<sub>4</sub>-O<sub>2</sub> mixtures displayed second-order kinetic behaviour owing to a series of reactions initiated by the reaction

$$CH_3O_2 + CH_3O_2 \rightarrow \text{ products.}$$
 (1)

The parameter  $k_{obs}/\sigma$  (where  $k_{obs}$  is the observed second-order rate constant) was measured for  $210 \le \lambda/nm \le 270$  at 760 Torr and 298 K, and had a value of  $1.11 \times 10^5$  cm s<sup>-1</sup> at 250 nm.  $\sigma(250 \text{ nm})$  was determined to be  $(4.25 \pm 0.5) \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup>, leading to a value of  $(4.7 \pm 0.5) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for  $k_{obs}$ . The time dependence of HDO production during the continuous near-ultraviolet photolysis of a static Cl<sub>2</sub>, CD<sub>4</sub>, CH<sub>3</sub>OH, O<sub>2</sub> mixture has also been measured in the infrared. It seems likely that reaction (18*a*) accounts for the majority of the observed HDO with the remainder being formed following the production of OH radicals in the system. The observed results are consistent with the existence of two channels for reaction (18), with  $k_{18a}/(k_{18a} + k_{18b}) \approx 0.4$ :

$$CD_3O_2 + HO_2 \rightarrow HDO + CD_2O + O_2$$
 (18*a*)

$$\rightarrow CD_3OOH + O_2. \tag{18b}$$

#### 1. Introduction

The reactions of alkylperoxy radicals and  $HO_2$  are of interest in tropospheric photochemistry, since both are important chain carriers in hydrocarbon oxidation mechanisms, their reactions with NO to produce  $NO_2$  ultimately leading to the generation of  $O_3$ .<sup>1</sup> Evaluation of the kinetics of the mutual or self-reactions of peroxy radicals is of particular importance, since these reactions may result in radical termination and consequently influence the tropospheric  $O_3$  budget.

 $CH_3O_2$  is the most abundant of alkylperoxy radicals in the atmosphere, and its reactions have received considerable attention, particularly the self-reaction  $(1)^{2-11}$ 

$$CH_3O_2 + CH_3O_2 \rightarrow \text{products}$$
 (1)

‡ 1 Torr = 101 325/760 Pa.

<sup>†</sup> Present address: School of Chemical Sciences, University of East Anglia, Norwich NR47TJ.

and its reaction with NO<sup>2,12-15</sup>

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2.$$
 (2)

The reaction with HO<sub>2</sub> [reaction (3)] has also been studied by several groups using both direct methods,  $^{2,9,16,17}$  and by observation of the yield of the product CH<sub>3</sub>OOH:  $^{9,18}$ 

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2. \tag{3a}$$

Cox and Tyndall<sup>2</sup> obtained a value of  $k_3$  of  $6.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and 760 Torr using molecular-modulation u.v. spectroscopy to observe CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub> directly. More recently, Moortgat et al.<sup>9</sup> have determined a lower value of  $4.8 \times$  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and 700 Torr from the direct observation of CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub> during the modulated photolysis of CH<sub>3</sub>CHO-O<sub>2</sub> mixtures. The most recent studies of this reaction using flash photolysis have yielded even lower values of  $k_3$  of  $3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (760 Torr, 298 K; Veyret<sup>16</sup>) and  $2.9 \times$  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (26-600 Torr, 298 K; Kurylo *et al.*,<sup>17</sup> which are in good agreement despite large differences in the values used for the u.v. cross-sections employed to calculate the concentrations of the radicals. Two further values of  $k_3$ , estimated from the yield of CH<sub>3</sub>OOH are  $1.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (760 Torr, 298 K; Kan *et al.*<sup>18</sup>) and  $3.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (700 Torr, 298 K; Moortgat *et al.*<sup>9</sup>).

Evidently there is still a great deal of uncertainty in the value of  $k_3$ , probably arising from both inconsistencies in the measured peroxy radical spectra and from an inadequate knowledge of the chemistry producing and removing these radicals, particularly concerning the products of reaction (3). In this paper we present the results of a kinetics study of reactions (1) and (3) performed using the molecular-modulation technique, and report values for  $k_1$  at 298 K/760 Torr and for  $k_3$  at 300 K/10 Torr and 303 K/760 Torr. The study of the reaction (1) also allowed measurement of the u.v. spectrum of CH<sub>3</sub>O<sub>2</sub> in the wavelength range 210-270 nm. In addition, we present evidence for the existence of the reaction pathway CD<sub>3</sub>O<sub>2</sub>+HO<sub>2</sub>  $\rightarrow$  CD<sub>2</sub>O+HDO+O<sub>2</sub> for the reaction of CD<sub>3</sub>O<sub>2</sub> with HO<sub>2</sub> at 300 K and 10 Torr.

#### 2. Experimental

Experiments were performed either in a 19.8 dm<sup>3</sup> Pyrex reaction vessel (10 Torr experiments) or in a 1.2 dm<sup>3</sup> quartz reaction vessel (760 Torr experiments). Reagents, products and transient species could be monitored in the u.v.-visible region using deuterium or xenon lamp sources with dispersion and detection using a conventional monochromator/photomultiplier arrangement, or in the infrared using a tunable diode laser spectrometer (Spectra Physics LS3). Details of the reaction vessels and associated spectroscopic equipment have been described previously.<sup>19</sup>

In order to study the kinetics of reactions (1) and (3),  $CH_3O_2$  and  $HO_2$  radicals were produced by the following reaction scheme, initiated by the photodissociation of  $Cl_2$  in the near-u.v. using fluorescent blacklamps ( $310 < \lambda/nm < 400$ ):

$$Cl_2 + h\nu \rightarrow Cl + Cl$$
 (4)

$$Cl + CH_4 \rightarrow CH_3 + HCl$$
 (5)

$$CH_3 + O_2 \xrightarrow{+M} CH_3O_2$$
 (6)

$$C1 + H_2 \rightarrow H + HCl \bigg\}_{at \ 760 \ Torr}$$
(7)

$$H + O_2 \xrightarrow{+M} HO_2$$
 (8)

$$Cl + H_2O_2 \rightarrow HO_2 + HCl$$
 at 10 Torr. (9)

914

#### M. E. Jenkin, R. A. Cox, G. D. Hayman and L. J. Whyte 915

The lamps were powered by a square-wave modulated 250 V d.c. supply, which allowed intermittent photolysis of the reagents.  $CH_3O_2$  was detected in the wavelength range 210-270 nm, and was generally monitored at 260 nm, where the cross-section of HO<sub>2</sub> is an order of magnitude lower than that of  $CH_3O_2$ . HO<sub>2</sub> was independently measured in the infrared during experiments performed at 10 Torr, using a resolved vibration rotation line of the  $\nu_3$  band (1110.287 cm<sup>-1</sup>,  $F_16_{15} \leftarrow 5_{14}$ ) in first-derivative mode, in the manner described before.<sup>19</sup> At 760 Torr, pressure broadening precluded measurement of HO<sub>2</sub> in the infrared and HO<sub>2</sub> concentrations were determined from measurement of the composite HO<sub>2</sub>-CH<sub>3</sub>O<sub>2</sub> absorption signals in the u.v. at 210 nm. The modulated absorption signals due to HO<sub>2</sub> and  $CH_3O_2$  were accumulated and averaged using a 200 channel multichannel analyser<sup>20</sup> to provide well averaged time-resolved absorption waveforms which could be analysed to obtain the kinetic parameters.

Experiments were performed using flowing gas mixtures to minimise the build-up of products and the associated secondary chemistry. The respective flows of the constituent gases were either regulated with mass flow controllers (MKS, type 261) or metered through precalibrated rotameters. With the exception of Cl<sub>2</sub>, the concentrations of the constituent gases were determined from their flow rates and the total pressure in the vessel (MKS Baratron). Cl<sub>2</sub> concentrations were measured by conventional absorption spectroscopy  $[\sigma(330 \text{ nm}) = 2.56 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}]^{21}$ . Cl<sub>2</sub> (BOC, 5% in N<sub>2</sub> or ICI, liquid grade), H<sub>2</sub> (Air Products, high purity), O<sub>2</sub> (BOC, breathing grade) and N<sub>2</sub> (Air Products, high purity) were used as received. CH4 (BOC, research grade or commercial grade) was passed through a column of molecular sieve (type 5A) immersed in a salt-ice mixture to ensure removal of higher hydrocarbon impurities. Gas chromatographic analysis of samples of the lower grade CH<sub>4</sub> after passage through the molecular sieve indicated that all  $C_2$ - $C_6$  aliphatic hydrocarbons were reduced to levels below the detection limit of 30 ppb (3 m column, OPN on Porasil C, FID detection).  $H_2O_2$  (90%) was further purified by continuous pumping on a mercury free vacuum line to decrease the water vapour content to <5%. A flow of the H<sub>2</sub>O<sub>2</sub> vapour was achieved by diverting some of the  $O_2$  flow through a bubbler containing the concentrated sample.

Further experiments were performed in the 19.8 dm<sup>3</sup> vessel to look for HDO as a product of the reaction between  $CD_3O_2$  and  $HO_2$ .  $CD_3O_2$  was produced by a reaction scheme analogous to reactions (4)-(6) using  $CD_4$  (MSD, >99.5 atom % D) as a precursor to  $CD_3O_2$ , and with HO<sub>2</sub> produced by the following sequence, with CH<sub>3</sub>OH (Fisons, AR Grade) as a precursor:

$$Cl + CH_3OH \rightarrow CH_2OH + HCl$$
 (10)

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O.$$
(11)

HDO was monitored in the infrared at 1378.594 cm<sup>-1</sup>, which corresponds to the  $3_{03} \leftarrow 3_{12}$  transition of the  $\nu_2$  band. Calibration of the strength of this line was achieved by admitting a known concentration of an equilibrium mixture of H<sub>2</sub>O(25%)-HDO(50%)-D<sub>2</sub>O(25%) into the reaction vessel. This was done with both a static system and a flowing system, and in each case the mixture was pressurised to 10 Torr with O<sub>2</sub>. The resultant effective cross-section at this pressure was  $(1.00 \pm 0.06) \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup>.

#### 3. Analysis of the Time-resolved Absorption Waveforms

The methods of analysis used to extract the kinetic information from the time-resolved absorption waveforms have been described in detail in previous papers,<sup>19,20</sup> so the present section is restricted to a statement of expressions relevant to the current work, without derivation.

When the transient obeys second-order kinetics, the steady-state concentration achieved during illumination is given by

$$C_0 = (B/k)^{1/2}$$
(i)

where B is the radical production rate and k the second-order rate constant. The time dependence of the concentration is described by the following equations:

$$\frac{1}{C} - \frac{1}{C_0} = 2kt \qquad \text{light off} \qquad (ii)$$

$$\ln\left(\frac{C_0+C}{C_0-C}\right) = 4kC_0t \qquad \text{light on.}$$
(iii)

The measured absorptions (A) are related to the concentrations by the Beer-Lambert law ( $\sigma$  is the absorption cross-section and l is the absorption path length):

 $A + A_{\rm R} = \sigma lc$  for small absorptions. (iv)

 $A_{\rm R}$  is the residual absorption ( $\ll A$ ) which is included as a variable to account for incomplete radical decay before the illumination restarts.

The above expressions were used to obtain kinetic parameters in simple second-order systems. In more complex systems, the Harwell program FACSIMILE was employed, enabling optimisation of unknown parameters within an assumed chemical scheme using a non-linear least-squares routine.

#### 4. Photolysis Experiments

#### 4.1. Measurement of the Photolysis Constant of Cl<sub>2</sub>

Static gas mixtures consisting of a Cl atom scavenger ( $H_2$ ,  $CH_4$  or  $CH_3OH$ ),  $O_2$  and  $Cl_2$  were employed to measure the rate of photolytic decay of  $Cl_2$  under conditions appropriate to the intended experiments. During these experiments,  $Cl_2$  was monitored at 335 nm (instead of 330 nm) to minimise any absorption due to product  $CH_2O$  in the  $CH_4$  and  $CH_3OH$  systems. Concentrations of  $H_2$ ,  $CH_4$  or  $CH_3OH$  were high enough to ensure efficient scavenging, and  $O_2$  was in large excess so that complications due to reactions of intermediates such as H atoms,  $CH_3$  or  $CH_2OH$  with  $Cl_2$  were avoided, *e.g.* 

$$Cl + CH_4 \rightarrow CH_3 + HCl$$
 (5)

$$CH_3 + Cl_2 \rightarrow Cl + CH_3Cl.$$
 (12)

Photolysis rates were calculated from the gradients of plots of  $ln{[Cl_2]/[Cl_2]_0}$  vs. time.

In the experiments using  $Cl_2-CD_4-CH_3OH-O_2$  mixtures (section 4.5) at 10 Torr,  $O_2$  was necessarily not in large excess owing to the low total pressure of the system. A series of experiments was performed therefore to investigate how the decay of  $Cl_2$  is affected by changing the  $[Cl_2]/[O_2]$  ratio in a  $Cl_2-CH_3OH-O_2$  system, since as this ratio increases, the reaction of the intermediate  $CH_2OH$  with  $Cl_2$  becomes competitive and may be favoured over the reaction with  $O_2$ :

$$Cl + CH_3OH \rightarrow CH_2OH + HCl$$
 (10)

$$CH_2OH + Cl_2 \rightarrow CH_2O + HCl + Cl$$
(13)

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O.$$
(11)

At low values of the ratio  $[Cl_2]/[O_2]$ , first-order decay of  $Cl_2$  was observed, in agreement with the experiments above. As the ratio was increased, first-order decay was no longer observed, and the initial decay became more rapid. Fig. 1 shows the variation of the



Fig. 1. Variation of initial decay constant for Cl<sub>2</sub> with  $[Cl_2]/[O_2]$  during the near-u.v. photolysis of Cl<sub>2</sub> in the presence of CH<sub>3</sub>OH and O<sub>2</sub>. Slope =  $(3.13 \pm 0.18) \times 10^{-3} \text{ s}^{-1}$ ; intercept =  $(4.56 \pm 0.20) \times 10^{-4} \text{ s}^{-1}$ .

initial decay rate with  $[Cl_2]/[O_2]$ . Assuming that  $Cl_2$  is removed only by photolysis and reaction (13), then the graph should have the form:

$$k_{\rm I} = k_{\rm I}^{\circ} \left( 1 + \frac{2k_{13}}{k_{11}} \frac{[\rm Cl_2]}{[\rm O_2]} \right) \tag{v}$$

where  $k_1$  is the observed initial decay constant, and  $k_1$  is the value of  $k_1$  at  $[O_2] = \infty$  (*i.e.* the photolysis constant  $k_4$ ). The slope/intercept ratio of the graph in fig. 1 yields a value of

$$k_{13}/k_{11} = 3.4 \pm 0.3.$$

## 4.2. Photolysis of $Cl_2$ in the Presence of $CH_4$ and $O_2$ : Absorption Spectrum and the Self-reaction Kinetics of $CH_3O_2$ at 760 Torr and 298 K

During the photolysis of a flowing mixture of  $Cl_2$  ( $4.0 \times 10^{15}$  molecule cm<sup>-3</sup>),  $CH_4$  ( $6.7 \times 10^{17}$  molecule cm<sup>-3</sup>) and  $O_2$  ( $9.5 \times 10^{18}$  molecule cm<sup>-3</sup>) at 760 Torr total pressure (balance N<sub>2</sub>),  $CH_3O_2$  radicals were produced by the reaction sequence (4)-(6). Modulated absorption signals due to  $CH_3O_2$  were detected in the wavelength range 210-270 nm, and a typical example of a modulated waveform is shown in fig. 2. Analysis of the time dependence of the absorption indicated second-order kinetics implying that  $CH_3O_2$  was being removed by its self-reaction:

$$CH_3O_2 + CH_3O_2 \rightarrow \text{ products.}$$
 (1)

Using the data analysis described in the previous section, values of  $k_{obs}/\sigma$  were calculated at 10 nm intervals in the range 210-270 nm [eqn (ii) and (iii)], where  $k_{obs}$  is the observed second-order rate constant. With a knowledge of the radical production rate  $B(=k_4[Cl_2])$ , eqn (i) enabled calculation of values for both  $k_{obs}$  and  $\sigma$  at each wavelength. These results are presented in table 1. The nine experiments provided a mean value of



Fig. 2. Modulated absorption waveform obtained for  $CH_3O_2$  at 260 nm during photolysis of a  $Cl_2-CH_4-O_2$  mixture at 760 Torr and 298 K.

λ/ nm	no of determinations	$\frac{(k_{\rm obs}/\sigma)}{/10^5{\rm cms^{-1}}}$	$k_{\rm obs}/$ 10 <sup>-13</sup> cm <sup>3</sup> molecule <sup>-1</sup>	$\frac{\sigma_s^a}{10^{-18} \text{ cm}^2 \text{ molecule}^{-1}}$
210	1	1.99	5.01	2.37
220	1	1.27	4.89	3.70
230	1	0.96	4.49	4.92
240	1	0.95	5.04	4.97
250	2	1.11	4.56	4.25
260	2	1.33	4.80	3.53
270	1	1.98	4.27	2.38

Table 1. Values of  $k_{\rm obs}/\sigma$  and  $\sigma$  measured using a Cl-CH<sub>4</sub>-O<sub>2</sub> system

 $a \sigma_{\rm s} = \bar{k}_{\rm obs} / (k_{\rm obs} / \sigma)$ . T = 298 K.  $\bar{k}_{\rm obs} = (4.71 \pm 0.53) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. P = 760 Torr.

 $k_{obs}$  of  $(4.7 \pm 0.5) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (error =  $2\sigma$ ). Smoothed values of the absorption cross-sections ( $\sigma_s$ ) were determined using this mean value of  $k_{obs}$  and the respective  $k_{obs}/\sigma$  data. The resultant CH<sub>3</sub>O<sub>2</sub> absorption spectrum is displayed in fig. 3, along with other recent determinations.

The major potential source of error in this determination results from the build-up of the products of the self-reaction (1). These have been shown to include CH<sub>3</sub>OH, CH<sub>2</sub>O and CH<sub>3</sub>OOH,<sup>18,22</sup> all of which react rapidly with Cl atoms. Under the flowing conditions of the experiments, however, the concentrations of these species were low  $(<5 \times 10^{12} \text{ molecule cm}^{-3})$  so that >98% of Cl atoms reacted with CH<sub>4</sub>. A small adjustment was made in the value of the CH<sub>3</sub>O<sub>2</sub> production rate *B* to account for this. CH<sub>3</sub>OOH was also found to give a small 'triangular' product absorption<sup>23</sup> superimposed



Fig. 3. Recently published u.v. absorption spectra for  $CH_3O_2$  (-O-) this work; (-- $\bullet$ --) McAdam *et al.*<sup>10</sup> (--×--) Kurylo *et al.*<sup>26</sup>

on the radical waveform at wavelengths at the low end of the range. This was subtracted before analysis of the waveform.

# 4.3. Photolysis of Cl<sub>2</sub> in the Presence of CH<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>: the Reaction CH<sub>3</sub>O<sub>2</sub>+ HO<sub>2</sub> $\rightarrow$ Products at 10 Torr and 303 K

This series of experiments was performed to investigate the kinetics of reaction (3) at 10 Torr pressure.  $CH_3O_2$  was produced by reactions (4)-(6) as before, and addition of  $H_2O_2$  to the system allowed generation of  $HO_2$  by reaction (9).  $HO_2$  could be detected in the infrared near 1110 cm<sup>-1</sup>, and initial experiments performed in the absence of  $CH_4$  yielded modulated absorption waveforms for  $HO_2$  which were well described by eqn (ii) and (iii) indicating that  $HO_2$  was being removed by its self-reaction:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \tag{14}$$

The resultant values of  $k_{14}/\sigma$  were used to determine the effective absorption crosssection for HO<sub>2</sub> at the monitoring wavelength, using a mean recommended value of  $k_{14}$ ,  $1.6 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>24,25</sup> This experiment was repeated periodically to ensure there was no significant drift in the monitoring wavelength which would be accompanied by a change in  $\sigma$ . In the presence of CH<sub>4</sub>, a departure from second-order kinetics was observed for HO<sub>2</sub> owing to the production of CH<sub>3</sub>O<sub>2</sub> and the existence of reaction (3). CH<sub>3</sub>O<sub>2</sub> was also monitored and waveforms for both radicals were recorded for the same conditions. HO<sub>2</sub> was always monitored in the infrared, where the absorption is not complicated by the presence of CH<sub>3</sub>O<sub>2</sub>, and CH<sub>3</sub>O<sub>2</sub> was measured at 260 nm in the ultraviolet. Provided CH<sub>3</sub>O<sub>2</sub> is in excess over HO<sub>2</sub>, which was always the case, then the fraction of the absorption at 260 nm due to HO<sub>2</sub> is negligible. The relative concentration of CH<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> was varied, and as [H<sub>2</sub>O<sub>2</sub>]/[CH<sub>4</sub>] decreased, the signal due to HO<sub>2</sub> diminished. In the complete absence of H<sub>2</sub>O<sub>2</sub>, however, substantial amounts of

**Table 2.** Conditions for experiments performed at low pressure  $(Cl_2-CH_4-H_2O_2-O_2 system; concentrations in units of molecule cm<sup>-3</sup>) and resultant values of <math>k_3$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)

$10^{-16}$ [Cl <sub>2</sub> ]	$10^{-16} [CH_4]$	$10^{-15}[H_2O_2]$	$10^{-17} [O_2]$	$10^{12} k_3$
1.21	6.23	8.95	2.49	6.20
1.21	6.29	8.74	2.47	5.58
1.42	6.11	1.80	2.35	5.12
1.41	5.98	1.88	2.32	5.98
1.43	5.90	0	2.37	5.01
1.60	5.98	0	2.29	4.71

 $\vec{k_3} = (5.4 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{error} = 2\sigma).$  P = 10 Torr, T = 300 K.

 $HO_2$  were still observed. This can be explained by the relatively long residence time of the reaction mixture in the vessel (*ca.* 60 s). Products of the  $CH_3O_2$  self-reaction such as  $CH_3OH$  and  $CH_2O$  are allowed to build up, and undergo competing abstraction reactions with Cl atoms, leading to the production of  $HO_2$  by the following reactions:

$$Cl + CH_3OH \rightarrow CH_2OH + HCl$$
(10)

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O \tag{11}$$

$$Cl + CH_2O \rightarrow HCO + HCl$$
 (15)

$$HCO+O_2 \rightarrow HO_2+CO.$$
 (16)

 $CH_3O$  radicals produced in the self-reaction of  $CH_3O_2$  also contribute to the overall  $HO_2$  balance via their reaction with  $O_2$ :

$$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2 \tag{1a}$$

$$CH_3O + O_2 \rightarrow HO_2 + CH_2O.$$
(17)

Six experiments were performed in the presence and absence of  $H_2O_2$  as summarised in table 2, with primary HO<sub>2</sub> production from both reaction (9) and following the *in situ* production of CH<sub>2</sub>O and CH<sub>3</sub>OH. Examples of modulated absorption waveforms for both HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> describing their simultaneous behaviour are shown in fig. 4. FACSIMILE was employed to simulate the radical waveforms using the simplified chemical scheme listed in table 3. Three parameters were varied and optimised so that the size and shape of the waveforms could be recreated. These parameters were  $k_4$  (describing the total radical production rate),  $\alpha$  (the fraction of Cl atoms resulting in the production of CH<sub>3</sub>O<sub>2</sub>) and  $k_3$  (the rate coefficient for the reaction of CH<sub>3</sub>O<sub>2</sub> with HO<sub>2</sub>). The data for each pair of waveforms were 'fitted' with several sets of starting values for the varied parameters. The final 'best-fit values' for the parameters showed little dependence on the values adopted initially. Importantly, the final values of  $k_4$  were consistent with the measured values (section 4.1). The fitted values of  $k_3$  for the range of conditions used are displayed in table 2, and the mean of the six determinations is

$$k_3 = (5.4 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
  
(T = 300 K, P = 10 Torr, error = 2 $\sigma$ ).

# 4.4. Photolysis of $Cl_2$ in the Presence of $H_2$ , $CH_4$ and $O_2$ : the Reaction $CH_3O_2 + HO_2 \rightarrow$ Products at 760 Torr and 303 K

Five experiments were performed to study the kinetics of reaction (3) at 760 Torr, with HO<sub>2</sub> produced by reactions (7) and (8). The relative proportions of H<sub>2</sub> and CH<sub>4</sub> were





**Fig. 4.** Modulated absorption waveforms for (a) HO<sub>2</sub> and (b) CH<sub>3</sub>O<sub>2</sub> describing their simultaneous behaviour in the photolysis of a Cl<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>-O<sub>2</sub> mixture at 10 Torr and 300 K. Computed profiles represent the best fit (----) and optimised fits with  $k_3$  fixed at  $2 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (---). (a) [HO<sub>2</sub>]<sub>t=1s</sub> =  $8.8 \times 10^{11}$  molecule cm<sup>-3</sup>; (b) [CH<sub>3</sub>O<sub>2</sub>]<sub>t=1s</sub> =  $1.5 \times 10^{12}$  molecule cm<sup>-3</sup>.

varied along with the photolysis rate (*i.e.* number of lamps) and  $Cl_2$  concentration as shown in table 4. For a given set of experimental conditions, modulated absorption waveforms were recorded in two separate experiments during which the reaction mixture was monitored at 210 and 260 nm. At each wavelength the recorded waveform was made up of contributions from both radicals, since their u.v. spectra overlap:

$$A_{\lambda} = l\{\sigma_{\lambda}(\mathrm{HO}_{2})[\mathrm{HO}_{2}] + \sigma_{\lambda}(\mathrm{CH}_{3}\mathrm{O}_{2})[\mathrm{CH}_{3}\mathrm{O}_{2}]\}.$$
 (vi)

Fig. 5 shows a pair of waveforms recorded at 210 and 260 nm. The simplified chemical scheme outlined in the last section was once again used to fit the composite absorption waveforms. The values used for the absorption cross-sections were  $\sigma_{210} = 4.9 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-125}$  and  $\sigma_{260} = 3 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-110}$  for HO<sub>2</sub>, and  $\sigma_{210} = 2.4 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  and  $\sigma_{260} = 3.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  for CH<sub>3</sub>O<sub>2</sub>, which were taken from this work. The values of  $k_3$  concluded from the fitting procedure are

Table	3.	Simplified	chemical	scheme	used	for	the	fitting	of	modulated
		waveforms	for CH <sub>3</sub> O	2 and HO	$D_2$ gen	erate	d sir	nultane	ousl	ly

reaction	rate parameter	comment	
$CI + hr(x) CI + CI \rightarrow CH_3O_2$	$\alpha k_4$	а	
$Cl_2 + m\nu(\rightarrow Cl + Cl) \rightarrow HO_2$	$(1-\alpha)k_4$	а	
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (10 Torr)	$1.6 \times 10^{-12}$	b	
(760 Torr)	$2.85 \times 10^{-12}$	с	
$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$	$1.13 \times 10^{-13}$	d	
$\rightarrow$ CH <sub>3</sub> OH+CH <sub>2</sub> O+O <sub>2</sub>	$2.41 \times 10^{-13}$	d	
$\rightarrow$ CH <sub>3</sub> OOCH <sub>3</sub> +O <sub>2</sub>	$3.0 \times 10^{-14}$	d	
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$1.3 \times 10^{-15}$	с	
$CH_3O_2 + HO_2 \rightarrow products$	<i>k</i> <sub>3</sub>	а	

<sup>*a*</sup>  $\alpha$ ,  $k_4$  and  $k_3$  were optimised by fitting procedure (see text). <sup>*b*</sup> Taken as the mean of values quoted in ref. (24) and (25). <sup>*c*</sup> Taken from ref. (24). <sup>*d*</sup> Taken from the present study. The value of  $k_{obs}$  was adjusted in accordance with the literature [see ref. (22)] to allow for over-estimation of the rate constant as a result of the subsequent chemistry of CH<sub>3</sub>O (see discussion). Branching ratios taken from ref. (22).

**Table 4.** Conditions for experiments performed at atmospheric pressure  $(Cl_2-CH_4-H_2-O_2 \text{ system}; \text{ concentrations in units of molecule cm}^{-3})$  and resultant values of  $k_3$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)

no. of lamps	$10^{-15}$ [Cl <sub>2</sub> ]	$10^{-17} [H_2]$	$10^{-16}  [CH_4]$	10 <sup>-19</sup> [O <sub>2</sub> ]	[H <sub>2</sub> ]/[CH <sub>4</sub> ]	$10^{12} k_3$
1	3.88	7.02	4.76	2.42	14.7	6.5
3	4.70	6.96	8.38	2.41	8.31	7.5
5	7.48	7.29	8.92	2.40	8.17	6.5
5	7.68	7.20	5.08	2.40	14.2	7.1
5	7.14	7.01	1.52	2.41	46.1	6.3

 $\bar{k}_3 = (6.8 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{error} = 2\sigma).$  P = 760 Torr, T = 303 K.

shown in table 4 for each set of conditions used. The mean value is  $k_3 = (6.8 \pm 0.9) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (error = 2 $\sigma$ ), but there is a possibility of a small systematic error since  $k_3$  appears to decrease as  $[H_2]/[CH_4]$  increases. This probably indicates slight inaccuracies in the relative cross-sections for the species at the two monitoring wavelengths. The data were also fitted using other recently reported values for the cross-sections at 210 and 260 nm,<sup>26</sup> but the systematic error in the fitted value of  $k_3$  was significantly worse, its value falling by nearly a factor of two between  $[H_2]/[CH_4] = 8.2$  and  $[H_2]/[CH_4] = 46$ .

# 4.5. Detection of HDO during the Photolysis of $Cl_2-CD_4-CH_3OH-O_2$ : the Reaction $CD_3O_2+HO_2 \rightarrow$ Products

Four photolysis experiments were carried out on identical reaction mixtures comprised of Cl<sub>2</sub>  $(1.0 \times 10^{16} \text{ molecule cm}^{-3})$ , CD<sub>4</sub>  $(1.64 \times 10^{16} \text{ molecule cm}^{-3})$ , CH<sub>3</sub>OH  $(1.3 \times 10^{14} \text{ molecule cm}^{-3})$  and O<sub>2</sub>  $(3.29 \times 10^{17} \text{ molecule cm}^{-3})$  at a total pressure of 10.8 Torr and a temperature of 300 K. Under these conditions, HO<sub>2</sub> is generated in large excess over CD<sub>3</sub>O<sub>2</sub>, so that initially >99.8% if CD<sub>3</sub>O<sub>2</sub> reacts with HO<sub>2</sub> in preference to its self-reaction, assuming the rate coefficients for these reactions are equal to those for the CH<sub>3</sub>O<sub>2</sub> radical, as determined in sections 4.2 and 4.3.





**Fig. 5.** Modulated absorption waveforms at (a) 260 and (b) 210 nm obtained during the photolysis of a  $Cl_2-H_2-CH_4-O_2$  mixture at 760 Torr and 300 K. Computed profiles represent the best fit (----), and optimised fits with  $k_3$  fixed at  $5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (---) and  $9 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (---). (b)  $[HO_2]_{t=0.5s} = 2.0 \times 10^{-12}$  molecule cm<sup>-3</sup>;  $[CH_3O_2]_{t=0.5s} = 1.2 \times 10^{12}$  molecule cm<sup>-3</sup>.

Fig. 6 shows the formation of HDO with time during a continuous photolysis experiment. Initially an approximately linear build up is observed for *ca.* 20 s, after which the rate of build up increases dramatically. This suggests that HDO is formed as a result of the  $Cl+CD_4$  chain, since  $CH_3OH$  is expected to be depleted after *ca.* 15 s. Even though formation of one  $CH_2O$  molecule for every  $CH_3OH$  removed will prolong the primary production of  $HO_2$  [reactions (15) and (16)], after *ca.* 20 s the proportion of the flux through the  $Cl+CD_4$  channel would be expected to increase significantly.

It is possible to envisage two major gas-phase sources of HDO occurring as a result of the  $Cl+CD_4$  chain. Both of these are a result of the reaction of  $CD_3O_2$  with  $HO_2$ :

$$CD_3O_2 + HO_2 \rightarrow CD_2O + HDO + O_2$$
 (18*a*)

$$\rightarrow CD_3OOH + O_2 \tag{18b}$$

$$Cl + CD_3OOH \rightarrow CD_2O + DCl + OH.$$
 (19)



Fig. 6. HDO production during the photolysis of  $Cl_2-CD_4-CH_3OH-O_2$  mixtures: (a) time dependence up to 30 s, (b) time dependence up to 60 s. Points are measured production. Lines are results of simulations with different values of  $k_{18a}/(k_{18a}+k_{18b})$ .

Reaction (18*a*) produces HDO directly but the reaction sequence (18*b*), (19) produces OH radicals which can abstract D atoms from species such as  $CD_4$  or  $CD_2O$  to produce HDO, although this occurs in competition with hydrogen abstraction from CH<sub>3</sub>OH, *etc.* HDO may also be produced from isotopic exchange reactions involving H<sub>2</sub>O present on the reaction vessel surfaces. Photolysis of a mixture comprised of Cl<sub>2</sub>, CD<sub>4</sub> and O<sub>2</sub> (*i.e.* no CH<sub>3</sub>OH or HO<sub>2</sub>) indicated that HDO was still generated, presumably from the heterogeneous reaction of DCl and H<sub>2</sub>O:

$$Cl+CD_4 \rightarrow DCl+CD_3$$
 (20)

$$DCl(g) \rightarrow DCl(ads)$$
 (21)

$$DCl(ads) + H_2O(ads) \rightarrow HCl(ads) + HDO(ads)$$
 (22)

$$HDO(ads) \rightarrow HDO(g).$$
 (23)

At short photolysis times (up to 20 s), however, the yield of HDO was <5% compared with DCl produced. The rate of production of HDO in the system with CH<sub>3</sub>OH present

#### M. E. Jenkin, R. A. Cox, G. D. Hayman and L. J. Whyte

Table 5. Chemical model used to simulate the photolysis of  $Cl_2$  in the presence of  $CD_4$ ,  $CH_3OH$  and  $O_2$ 

reaction	rate constant	comment
$Cl_2 + h\nu \rightarrow Cl + Cl$	$4.6 \times 10^{-4}$	а
$Cl + CD_4 \rightarrow DCl + CD_3$	$7.56 \times 10^{-15}$	ь
$CD_3 + O_2 \rightarrow CD_3O_2$	$1.24 \times 10^{-13}$	c,d
$CD_3 + Cl_2 \rightarrow CD_3Cl + Cl$	$2.0 \times 10^{-12}$	с,е
$Cl + CH_3OH \rightarrow CH_2OH + HCl$	$6.3 \times 10^{-11}$	f
$CH_2OH + O_2 \rightarrow CH_2O + HO_2$	$2.0 \times 10^{-12}$	d
$CH_2OH + Cl_2 \rightarrow CH_2O + HCl + Cl$	$6.8 \times 10^{-12}$	а
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$1.6 \times 10^{-12}$	8
$CD_3O_2 + CD_3O_2 \rightarrow 2CD_3O + O_2$	$1.13 \times 10^{-13}$	c, h
$\rightarrow$ CD <sub>2</sub> O + CD <sub>3</sub> OH + O <sub>2</sub>	$2.41 \times 10^{-13}$	c,h
$\rightarrow CD_3OOCD_3 + O_2$	$3.0 \times 10^{-14}$	c,h
$CD_{3}O_{2} + HO_{2} \rightarrow CD_{3}OOH + O_{2}$ $\rightarrow CD_{2}O + HDO + O_{2}$	$5.4 \times 10^{-12}$	c, i
$CD_{2}O + O_{2} \rightarrow CD_{2}O + DO_{2}$	$1.3 \times 10^{-15}$	c,d
$Cl + CH_2O \rightarrow HCl + HO_2 + CO$	$7.3 \times 10^{-11}$	d
$Cl + CD_2O \rightarrow DCl + DO_2 + CO$	$7.3 \times 10^{-11}$	c,d
$Cl + H_2 O_2 \rightarrow HCl + HO_2$	$4.3 \times 10^{-13}$	d
$Cl + CD_3OOH \rightarrow CD_2O + DCl + OH$	$2.0 \times 10^{-10}$	с, ј
$Cl + HO_2 \rightarrow HCl + O_2$	$3.2 \times 10^{-11}$	d
$\rightarrow$ OH + CIO	$9.1 \times 10^{-12}$	đ
$OH + CD_4 \rightarrow CD_3 + HDO$	$8.0 \times 10^{-15}$	c, d
$OH + CH_2O \rightarrow H_2O + HO_2 + CO$	$1.1 \times 10^{-11}$	d
$OH + CD_2O \rightarrow HDO + DO_2 + CO$	$1.1 \times 10^{-11}$	c,d
$OH + CD_3OOH \rightarrow HDO + CD_2O + OH$	$1.0 \times 10^{-11}$	c, k
$OH + HCI \rightarrow H_2O + CI$	$6.6 \times 10^{-13}$	d
$OH + DCI \rightarrow HDO + CI$	$6.6 \times 10^{-13}$	c,d
$OH + CD_3OD \rightarrow HDO + CD_2OD$	$1.0 \times 10^{-12}$	c,d
$OH + CH_3OH \rightarrow H_2O + CH_2OH$	$1.0 \times 10^{-12}$	đ
$OH + H_2O_2 \rightarrow H_2O + HO_2$	$1.7 \times 10^{-12}$	d
$OH + HO_2 \rightarrow H_2O + O_2$	$6.7 \times 10^{-11}$	d

<sup>*a*</sup> Taken from the present study (see section 4.1). <sup>*b*</sup> Taken from ref. (27). <sup>*c*</sup> Rate constant assumed to be equal to analogous hydrogenated species. <sup>*d*</sup> Taken from ref. (24). <sup>*e*</sup> Taken from ref. (28). <sup>*f*</sup> Taken from ref. (29). <sup>*g*</sup> Taken as mean of values given in ref. (24) and (25). <sup>*h*</sup> See note <sup>*d*</sup> of table 3. <sup>*i*</sup> Overall value of rate constant taken from this study. Branching ratio varied (see text). <sup>*j*</sup> Assumed value is estimated, and represents worst case. <sup>*k*</sup> Taken from ref. (30).

was at least a factor of 10 too large to be explained by this reaction sequence. Furthermore, in the presence of CH<sub>3</sub>OH the exchange reaction of DCl and H<sub>2</sub>O [reaction (22)] will be less favoured owing to the competing exchange with CH<sub>3</sub>OH. Consequently, it appears that the majority of HDO observed during the photolysis of the Cl<sub>2</sub>-CH<sub>3</sub>OH-CD<sub>4</sub>-O<sub>2</sub> mixtures was produced by gas-phase reactions.

In order to distinguish between the two gas-phase routes for HDO production, the reaction system was simulated using the chemical model listed in table 5. The results of simulations using different branching ratios for reaction (18) are shown in fig. 6, and it was apparent that in the absence of systematic errors in the chemical model, the observed production of HDO could not be explained without including reaction channel (18*a*) as *ca.* 40% of the total. If reaction (18) was assumed to be entirely (18*b*) then HDO production in the first few seconds (*i.e.* when the chemistry was least complicated by secondary effects) was underestimated by a factor of *ca.* 5. The model also successfully

**Table 6.** Reported values of  $k_{obs}/\sigma$  (in 10<sup>5</sup> cm s<sup>-1</sup>) and  $\sigma$  (in 10<sup>-18</sup> cm<sup>2</sup> molecule<sup>-1</sup>) at 250 nm for the self-reaction of CH<sub>3</sub>O<sub>2</sub>

σ	$k_{ m obs}/\sigma$	P/Torr	ref.
3.9	1.33	760	(2)
<b>4</b> .8 <sup><i>a</i></sup>	1.15	760	(3)
2.7	1.4	760	(4)
4.8	0.96	300	(5)
2.7	1.6	50	(6)
5.0	1.2	670	(7)
2.5	1.2	75-600	(8)
3.8	1.18	700	(9)
4.4	1.34	120-400	(10)
3.3	1.11	50-400	(11)
4.0 <sup>b</sup>			(33)
4.1	1.34	250	(34)
4.25	1.11	760	this work

 $a^{a} \sigma = 5.5 \times 10^{-18} \text{ cm}^{2} \text{ molecule}^{-1} \text{ at } 238 \text{ nm}.$   $b^{b} \sigma = 3.7 \times 10^{-18} \text{ cm}^{2} \text{ molecule}^{-1} \text{ at } 254 \text{ nm}.$ 

predicted an increase in HDO production at longer reaction times although a branching ratio of ca. 20:80 would be concluded from the latter stages of the simulation. More reliance is placed on shorter reaction times, however, for the reason already stated.

#### 5. Discussion

#### 5.1. The Self-reaction of CH<sub>3</sub>O<sub>2</sub> Radicals

The quoted value of  $k_{obs}$ ,  $(4.7 \pm 0.5) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, was obtained from nine experiments performed at atmospheric pressure and 298 K whilst monitoring CH<sub>3</sub>O<sub>2</sub> at wavelengths in the range 210-270 nm. Since the self-reaction of CH<sub>3</sub>O<sub>2</sub> generates CH<sub>3</sub>O the possibility exists for further depletion of CH<sub>3</sub>O<sub>2</sub> by HO<sub>2</sub>, as discussed previously by several authors [*e.g.* ref. (3), (6) and (8)]:

$$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2 \tag{1a}$$

$$\rightarrow CH_3OH + CH_2O + O_2 \tag{1b}$$

$$\rightarrow$$
 CH<sub>3</sub>OOCH<sub>3</sub>+O<sub>2</sub> (1c)

$$CH_3O + O_2 \rightarrow HO_2 + CH_2O \tag{17}$$

$$CH_3O_2 + HO_2 \rightarrow \text{ products.}$$
 (3)

Documented branching ratios for reaction (1) attribute *ca*. 35% of the reaction to channel (1*a*) at room temperature and pressures near atmospheric,<sup>22,31,32</sup> which would suggest that the value of  $k_{obs}$  is greater than the elementary rate constant,  $k_1$ , by a factor of *ca*. 1.35.

The values obtained for  $k_{obs}/\sigma$  (250 nm) and  $\sigma$  (250 nm) are compared with those of other workers in table 6. Our value of  $k_{obs}/\sigma$  (250 nm),  $1.11 \times 10^5$  cm s<sup>-1</sup>, is in good agreement with most previous determinations. It appears that this parameter is reasonably well determined at room temperature, with little or no dependence on pressure, although it is quite possible that the branching ratios may vary with pressure. If this is the case, then it is possible that the elementary rate constant ( $=k_{1a}+k_{1b}+k_{1c}$ ) possesses

927

#### M. E. Jenkin, R. A. Cox, G. D. Hayman and L. J. Whyte

a pressure dependence which is not apparent in the observed rate constant ( $=2k_{1a}+k_{1b}+$  $k_{1c}$ ). The value of  $\sigma(250 \text{ nm})$  determined in the present study,  $(4.25 \pm 0.5) \times$  $10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup>, agrees well with the value reported recently by McAdam *et al.*<sup>10</sup> and with the very recent measurement of Moortgat et al.<sup>34</sup> The weight of evidence now favours a value nearer the high end of the range of reported values,  $(2.5-5.0) \times$  $10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup>. The absorption spectrum is also in reasonable agreement with that of McAdam et al.<sup>10</sup> (see fig. 3), but differs significantly in both size and shape from the other recent measurement of Kurylo et al.<sup>26</sup> The values of  $\sigma$  in the range 270-240 nm reported by Kurylo et al. are ca. 75% of those determined in the present work, whereas the reported values at 220 and 210 nm are 85 and 99% of our corresponding values. This discrepancy may be explained if build-up of product CH<sub>3</sub>OH, CH<sub>2</sub>O and CH<sub>3</sub>OOH occurred in the flow system of Kurylo et al., since typically  $3.5 \times 10^{14}$  Cl atoms were produced per residence time in their system.<sup>26</sup> Complete conversion into CH<sub>3</sub>OH, CH<sub>2</sub>O and CH<sub>2</sub>OOH may result in ca. 20% of Cl atoms being scavenged by these species, resulting in a general lowering of the apparent cross-sections, and an enhancement in the values at the low-wavelength end due to the production of  $HO_2$  from the reactions of Cl with CH<sub>3</sub>OH and CH<sub>2</sub>O. Consequently their reported spectrum for CH<sub>3</sub>O<sub>2</sub> may be a composite  $CH_3O_2$ -HO<sub>2</sub> spectrum.

#### 5.2. The Reaction of CH<sub>3</sub>O<sub>2</sub> with HO<sub>2</sub>

The value of  $k_3$  obtained at 10 Torr and 300 K,  $(5.4 \pm 1.1) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, was concluded from the modelling of a system in which CH<sub>3</sub>O<sub>2</sub> was generated in excess over HO<sub>2</sub>. In these experiments, the behaviour of each radical was determined independently of the other radical, and was well described by a simplified chemical scheme in which the total and relative production rates of the radicals were varied, along with the value of  $k_3$ , and these parameters were optimised by a non-linear least-squares fitting routine. Consequently, errors often incurred from the intrinsic uncertainty in the adopted values of key rate constants, and from omissions in the chemistry were significantly reduced. Examples of these are the uncertainties in reported rate constants for Cl-atom reactions which determine the relative production rates of the radicals, and the omission of reaction of intermediates such as CH<sub>3</sub> and CH<sub>2</sub>OH with Cl<sub>2</sub> at low [O<sub>2</sub>]/[Cl<sub>2</sub>], or other similar reactions which may not currently be well understood.

The value of  $k_3$  quoted above was determined without the necessity to interpret absorption profiles with contributions from both HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>, thus avoiding errors arising from uncertainties in the absorption spectra of the radicals as discussed in the last section. Consequently this is our best estimate of  $k_3$ . The results of the experiments performed at 760 Torr and 303 K had to be interpreted by the modelling of composite u.v. absorptions, however, and the mean value of  $k_3$ ,  $(6.8 \pm 0.9) \times 10^{-12}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, displayed a small systematic error, decreasing as  $[H_2]/[CH_4]$ was increased. We conclude, therefore that the value of  $k_3$  at 760 Torr is not significantly different from the value obtained at low pressure.

Recent determinations of  $k_3$  at room temperature using flash photolysis-u.v. absorption are significantly lower than the value reported here,  $3.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Veyret)<sup>16</sup> and  $2.9 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Kurylo *et al.*),<sup>11</sup> although the results may be complicated by the production of a u.v.-absorbing intermediate which has a significant lifetime on the timescales of these experiments.<sup>16</sup> Earlier direct determinations of Cox and Tyndall<sup>2</sup> ( $6.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and Moortgat *et al.*<sup>9</sup> ( $4.8 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) using molecular modulation-u.v. absorption are in better agreement with the present determination. All studies have extracted rate constants by modelling techniques, and some of the discrepancies may arise from differences in the assumed chemistry and in the values taken for rate constants for reactions such as reaction (1). Additional error must come from differences in the values of the u.v. absorption

cross-sections used for the radicals. In the present study, HO<sub>2</sub> was the minor radical and was unambiguously and independently monitored in the infrared.  $CH_3O_2$  was measured in the u.v. at 260 nm, where the cross-section was taken to be  $3.5 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup>. Since CH<sub>3</sub>O<sub>2</sub> was in excess, variation of this cross-section would result in approximately a proportionate change in the value concluded for  $k_3$ .

Reaction (3) has been shown to have a negative temperature coefficient.<sup>2,16,35</sup> Although there is some uncertainty in the magnitude, it seems clear that the reaction proceeds *via* one or more long-lived complexes, with the possibility of several product channels:

$$CH_3O_2 + HO_2 \rightarrow CH_3O + OH + O_2$$
(3b)

$$\rightarrow$$
 CH<sub>3</sub>OOH+O<sub>2</sub> (3*a*)

$$\rightarrow CH_3OH + O_3 \tag{3c}$$

$$\rightarrow CH_2O + H_2O + O_2. \tag{3d}$$

Reaction (3b) appears unlikely, partially on account of its endothermicity and also because the subsequent reaction of CH<sub>3</sub>O with O<sub>2</sub> [reaction (17)] regenerates HO<sub>2</sub>, and a complication in the observed kinetics would arise. Reaction (3a) is known to occur, since CH<sub>3</sub>OOH has been identified by both its infrared and ultraviolet spectra. The production of CH<sub>3</sub>OH and O<sub>3</sub> [reaction (3c)] almost certainly does not occur because O<sub>3</sub> has never been detected despite its strong u.v. absorption spectrum. Reaction (3d) has been cited as a possible additional channel for reaction (3),<sup>9,19</sup> but difficulties arise in attempting to identify CH<sub>2</sub>O as a product, because it is invariably produced by other routes in reaction systems used to study reaction (3). In particular, CH<sub>3</sub>OOH is easily converted into CH<sub>2</sub>O if Cl atoms are present in the system, making the source of any observed CH<sub>2</sub>O difficult to identify:

$$Cl+CH_3OOH \rightarrow CH_2O+HCl+OH.$$
 (24)

In view of these difficulties, the experiments described in section 4.5 were carried out to look for evidence for the production of water from reaction (3d). To simplify identification of the water,  $CD_4$  was used as a precursor to  $CD_3O_2$ , so that HDO would be the expected product. Diode laser spectroscopy provides a sensitive detection method for HDO at low total pressure, with no interference from atmospheric water absorption, and in our chemical system the production of water from the wall decomposition of hydrogen peroxide would be entirely  $H_2O$ . Modelling of the observed production of HDO during the photolysis of  $Cl_2-CD_4-CH_3OH-O_2$  mixtures suggested that ca. 40% of the reaction of  $CD_3O_2$  with HO<sub>2</sub> produces HDO. There is obviously the potential for systematic error, since many of the rate constants used for deuterated species were assumed to be equal to those for the analagous normal hydrogen molecules. Further error may arise from general gaps in the understanding of these reaction systems as already discussed. However, the key reaction for the production of  $CD_3O_2$  is the reaction of Cl atoms with CD<sub>4</sub>, and there are two reported values for this rate constant, both measured relative to  $Cl + CH_4$ ,<sup>27</sup> which agree to better than 15%. The accuracy of the experiments reported here is essentially governed by the degree of uncertainty in the relative rate of the  $Cl+CD_4$  and  $Cl+CH_3OH$  reactions. In the absence of large errors in this quantity, we feel that these experiments provide strong evidence for the existence of a  $CD_2O-HDO-O_2$  forming route for the  $CD_3O_2+HO_2$  reaction.

If reaction (3d) does exist, then this may have important repercussions on the interpretation of product data for reaction (1), since the branching ratios were calculated from the observed product ratios [CH<sub>3</sub>OH]/[CH<sub>2</sub>O] and [CH<sub>3</sub>OH]/[CH<sub>3</sub>OOCH<sub>3</sub>] with the assumption that reaction (1) produced only CH<sub>3</sub>OOH and O<sub>2</sub>.

929

#### M. E. Jenkin, R. A. Cox, G. D. Hayman and L. J. Whyte

#### 5.3. Atmospheric Chemistry

In the background troposphere, or marine boundary layer, the destruction of HO<sub>2</sub> by its reaction with  $CH_3O_2$  is a potentially important removal process for odd hydrogen.<sup>1</sup>  $CH_3OOH$  produced by this reaction [reaction (3*a*)] acts as a reservoir for odd hydrogen since it has a relatively long tropospheric lifetime before photolysis and regeneration of the odd hydrogen in the form of OH:

$$CH_3OOH + h\nu \rightarrow CH_3O + OH.$$
 (25)

Consequently other removal processes for  $CH_3OOH$  (*e.g.* rainout) can compete with photolysis, precluding the regeneration of odd hydrogen and possibly resulting in further removal, *e.g.*:

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O.$$
 (26)

In contrast, the production of CH<sub>2</sub>O directly from the reaction of CH<sub>3</sub>O<sub>2</sub> with HO<sub>2</sub> [reaction (3d)] represents only a very temporary reservoir for odd hydrogen since it is photolysed rapidly, with *ca.* 40% of the photolysis events producing HCO radicals and H atoms, which are rapidly converted into HO<sub>2</sub> radicals:

$$CH_2O + h\nu \rightarrow HCO + H$$
 (27)

$$HCO+O_2 \rightarrow HO_2+CO$$
 (16)

$$H+O_2 \rightarrow HO_2.$$
 (8)

Hence, if reaction (3d) represents a large fraction of the total reaction, as the results of the present study would indicate, the potential of reaction (3) for odd hydrogen destruction is significantly lower than previously thought.

This work was supported by the U.K. Department of Environment. The authors would like to thank Dr B. Veyret, Dr G. K. Moortgat, Dr T. J. Wallington and Dr M. J. Kurylo for communicating their results prior to publication.

#### References

- 1 W.M.O. Report No. 16, Atmospheric Ozone 1985—Assessment of our Understanding of the Processes Controlling its Present Distribution and Change, vol. 1, chap. 4.
- 2 R. A. Cox and G. S. Tyndall, J. Chem. Soc., Faraday Trans. 2, 1980, 76, 153.
- 3 D. A. Parkes, Int. J. Chem. Kinet., 1977, 9, 451.
- 4 C. J. Hochanadel, J. A. Ghormley, J. W. Boyle and P. J. Ogren, J. Phys. Chem., 1977, 81, 3.
- 5 C. Anastasi, I. W. M. Smith and D. A. Parkes, J. Chem. Soc., Faraday Trans. 1, 1978, 74, 1693.
- 6 C. S. Kan, R. D. McQuigg, M. R. Whitbeck and J. G. Calvert, Int. J. Chem. Kinet., 1979, 11, 921.
- 7 H. Adachi, N. Basco and D. G. L. James, Int. J. Chem. Kinet., 1980, 12, 949.
- 8 S. P. Sander and R. T. Watson, J. Phys. Chem., 1981, 85, 2960.
- 9 G. K. Moortgat, J. P. Burrows, W. Schneider, G. S. Tyndall and R. A. Cox, Proc. IVth European Symp. on the Physical and Chemical Behaviour of Atmospheric Pollutants, Stresa, September, 1986.
- 10 K. McAdam, B. Veyret and R. Lesclaux, Chem. Phys. Lett., 1987, 133, 39.
- 11 M. J. Kurylo and T. J. Wallington, Chem. Phys. Lett., 1987, 138, 543.
- 12 S. P. Sander and R. T. Watson, J. Phys. Chem., 1980, 84, 1664.
- 13 A. R. Ravishankara, F. L. Eisele, N. M. Kreutter and P. H. Wine, J. Chem. Phys., 1981, 74, 2267.
- 14 I. C. Plumb, K. R. Ryan, J. R. Steven and M. F. R. Mulcahy, J. Phys. Chem., 1981, 85, 3136.
- 15 R. Simonaitis and J. Heicklen J. Phys. Chem., 1981, 85, 2946.
- 16 B. Veyret, personal communication.
- 17 M. J. Kurylo, P. Dagaut, T. J. Wallington and D. M. Neuman, Chem. Phys. Lett., 1987, 139, 513.
- 18 C. S. Kan, J. G. Calvert and J. H. Shaw, J. Phys. Chem., 1980, 84, 3411.
- 19 F. C. Cattell, J. Cavanagh, R. A. Cox and M. E. Jenkin, J. Chem. Soc., Faraday Trans. 2, 1986, 82, 1999.
- 20 M. E. Jenkin and R. A. Cox, J. Phys. Chem., 1985, 89, 192.
- 21 D. J. Seery and D. Britton, J. Phys. Chem., 1964, 68, 2263.
- 22 H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, J. Phys. Chem., 1981, 85, 877.
- 23 R. A. Cox and J. P. Burrows, J. Phys. Chem., 1979, 83, 2560.
- 24 D. L. Baulch, R. A. Cox, R. F. Hampson Jr, J. A. Kerr, J. Troe and R. T. Watson, J. Phys. Chem. Ref. Data, 1984, 13, 1259.

- 25 NASA Panel for Data Evaluation, Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling, Evaluation No. 7, JPL Publication 85-37, 1985.
- 26 M. J. Kurylo, T. J. Wallington and P. A. Ouellette, J. Photochem., 1987, 39, 201.
- 27 CRC Handbook of Bimolecular and Termolecular Gas Reactions, ed. J. A. Kerr and S. J. Moss (CRC Press, Florida, 1981), vol. 1.
- 28 R. S. Timonen and D. Gutman, J. Phys. Chem., 1986, 90, 2987.
- 29 J. V. Michael, D. F. Nava, W. A. Payne and L. J. Stief, J. Chem. Phys., 1979, 70, 3652.
- 30 H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, J. Phys. Chem., 1983, 87, 2190.
- 31 J. Weaver, J. Meagher, R. Shortridge and J. Heicklen, J. Photochem., 1975, 4, 341.
- 32 D. A. Parkes, Proc. Fifth Symp. on Combustion, Tokyo, 1974 (The Combustion Institute, Pittsburgh, PA, 1975), p. 795
- 33 M. J. Pilling and M. J. C. Smith, J. Phys. Chem., 1985, 89, 4713.
- 34 G. K. Moortgat, F. P. Simon and W. Schneider, to be presented at the 10th Int. Symp. Gas Kinetics, Swansea, July, 1988.
- 35 P. Dagaut, T. J. Wallington and M. J. Kurylo, J. Phys. Chem., in press.

Paper 7/2132; Received 3rd December, 1987