Kinetics and Mechanism of the Reaction of CH_3 and CH_3O with CIO and OCIO at 298 K

Peter Biggs, Carlos E. Canosa-Mas, Jean-Marc Fracheboud, George Marston,† Dudley E. Shallcross‡ and Richard P. Wayne*

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

A discharge-flow system equipped with a laser-induced fluorescence cell to detect the methoxyl radical and a quadrupole mass spectrometer to detect both the chlorine monoxide and chlorine dioxide radicals has been used to measure the rate constants for the reactions

 $CH_3 + CIO \rightarrow products$ (1)

 $CH_3O + CIO \rightarrow products$ (2)

 $CH_3 + OCIO \rightarrow products$ (3)

 $CH_3O + OCIO \rightarrow products$ (4)

at T = 298 K and P = 1-3 Torr. The observed products of these reactions are CH₃O for reaction (1), HOCI for reaction (2), and CH₃O and CIO for reaction (3). For reaction (4), CH₃OCI is a possible product. The rate constants derived for reactions (1)-(4) are: $k_1 = (1.3 \pm 0.4) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹; $k_2 = (1.3 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; $k_3 = (1.6 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; $k_4 = (1.5 \pm 0.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. The likely mechanisms for reactions (1)-(4) are briefly discussed.

It is now well established that the rapid depletion of stratospheric ozone over Antarctica during the austral spring is due in the main to catalytic cycles involving the ClO radical.¹

In this study, rate constants are presented for reactions (1)–(4). Of these reactions, only process (2) appears to have been studied previously (see Discussion section). Although it is not envisaged that any of these reactions plays a role in stratospheric ozone chemistry, they are nevertheless worthy of study. The processes are radical-radical reactions where there is the possibility that several product channels exist.² Kinetic and mechanistic information for reactions (1) and (2) is also essential for our laboratory study³ of the reaction

$$CH_3O_2 + ClO \rightarrow products$$
 (5)

which is believed to be important in stratospheric ozone depletion.³⁻⁸ In addition, chlorine dioxide (OCIO) is often used as a precursor for the formation of CIO in laboratory systems,⁹ and it is therefore important to characterise the kinetics of reactions (3) and (4) in order that OCIO may be used as a source of CIO in the study of reaction (5). Furthermore, OCIO is itself an important species in the polar lower stratosphere during winter. Chlorine dioxide is formed from one channel of the reaction between CIO and the BrO radical¹⁰

$$BrO + ClO \rightarrow Br + Cl + O_2$$
 (6a)

$$BrO + ClO \rightarrow Br + OClO$$
 (6b)

$$BrO + ClO \rightarrow BrCl + O_2$$
 (6c)

Channel (6b) is the only known source of chlorine dioxide (OCIO) in the stratosphere and measurements of this species can be used as a quantitative indicator of BrO levels, and as a qualitative indicator for CIO concentrations.¹¹

Experimental

A conventional discharge-flow apparatus was used (Fig. 1) with a double sliding-injector arrangement, consisting of two concentric movable inlets. The details of the flow tube have been given previously.^{12,13} The flow tube was coupled to a fluorescence cell and a quadrupole mass spectrometer. Experiments were performed at T = 298 K and at P = 1-3 Torr total pressure, with helium as the carrier gas. Typical flow velocities employed in this study ranged from 10 to 25 m s⁻¹. Halocarbon wax (KMZ Chemicals Ltd) was used to coat the walls.

Methyl radicals were prepared in the sliding injector by the reaction of methane with fluorine atoms, generated by a microwave discharge passed through a mixture of F_2 in helium, in the reaction

$$F + CH_4 \rightarrow CH_3 + HF \tag{7}$$

Chlorine monoxide radicals were prepared in the main flow upstream of the sliding injector by the reaction of chlorine atoms with ozone (introduced into the main flow *via* a fixed injector)

$$Cl + O_3 \rightarrow ClO + O_2$$
 (8)

The chlorine atoms were prepared by the reaction of hydrogen chloride with fluorine atoms, in the reaction

$$F + HCl \rightarrow Cl + HF$$
 (9)

Sufficient HCl was added to the main flow to titrate out all the fluorine atoms, so that none remained to react with ozone.

In the set of experiments involving ClO, the methyl radicals were allowed to react with an excess of ClO radicals (*i.e.* under pseudo-first-order conditions) and, as we shall show, produced methoxyl radicals and chlorine atoms in the reaction

$$CH_3 + ClO \rightarrow CH_3O + Cl$$
 (1a)

The methoxyl radical was detected by laser-induced fluorescence (LIF; see later), while the Cl atoms were scavenged by

[†] Present address: Department of Chemistry, University of Leicester, University Road, Leicester, UK LE1 7RN.

[‡] Present address: Centre for Atmospheric Science, Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW.

J. CHEM. SOC. FARADAY TRANS., 1995, VOL. 91



Fig. 1 Schematic diagram of the apparatus

ozone, which was in excess, to reform CIO in reaction (8). The methoxyl radicals so produced also reacted with the CIO in the reaction

$$CH_3O + ClO \rightarrow products$$
 (2)

Some experiments were performed where CH_3O was generated directly in the sliding injector by the reaction of fluorine atoms with methyl nitrite^{14,15}

$$F + CH_3ONO \rightarrow CH_3O + FNO$$
 (10)

and the CH₃O was allowed to react with an excess of ClO. However, it has been noted previously¹⁶ that methanol impurities in the methyl nitrite samples can lead to complications in the chemistry. These experiments were therefore used only as a guide to the kinetics of reaction (2), and the generation of CH₃O from reaction (1) was preferred.

In the set of experiments involving OCIO, methyl radicals prepared in the sliding injector were allowed to react under pseudo-first-order conditions with chlorine dioxide, which was the only species added to the main flow. In a similar manner to reaction (1), reaction (3) also produced CH_3O (see later), which was detected by LIF, but in addition it produced CIO radicals, which were detected by mass spectrometry (see later)

$$CH_3 + OCIO \rightarrow CH_3O + CIO$$
 (3*a*)

Once again, CH₃O could itself react with the species in excess, here OCIO. Some experiments were performed where CH₃O was generated in the sliding injector by reaction (10) and allowed to react with OCIO. These experiments provided an independent estimate of k_4 .

Detection and Calibration of Species

The methoxyl radical was detected by LIF at $\lambda = 292.4$ nm, corresponding to the A²A₁($v'_3 = 4$) \leftarrow X²E($v''_3 = 0$) vibronic transition.^{17,18} The details of the generation of the laser radiation necessary for the LIF technique and the optical system used to detect the fluorescence from CH₃O can be found elsewhere.¹² The method for determining the absolute concentration of CH₃O has been described previously.¹⁶ In the present work, we used the measured depletion of either ClO or OClO, together with the kinetic model, to obtain a calibration factor for CH₃O (see Results section). The minimum detectable concentration of CH₃O was *ca.* 10¹⁰ molecule cm⁻³, for a signal-to-noise ratio of unity and a 10 s

integration time. Ozone, chlorine monoxide and chlorine dioxide were all detected using a quadrupole mass spectrometer. The mass spectrometer has been described in detail in a previous paper.¹⁹ The O_3^+ (m/z = 48), ClO⁺ (m/z = 51) and OClO⁺ (m/z = 67) ions were generated by electron bombardment (19–23 eV) and detected by a channel electron multiplier. Gas mixtures of known concentration of O_3 and OClO were prepared prior to experiments; hence their concentrations in the flow tube could be determined from flow-rate measurements. The determination of the absolute ClO concentration was necessary for kinetic analysis. Two methods were used to determine this concentration. First, the drop in the O_3^+ ion signal on addition of Cl atoms to the flow could be used. Secondly, ClO can be titrated with NO

$$ClO + NO \rightarrow Cl + NO_2$$
 (11)

Sufficient NO was added so that the NO₂⁺ ion signal (m/z = 46) was constant on further addition. The NO₂ signal was calibrated in a straightforward manner.⁷ Since a Cl atom is produced in reaction (11), it is necessary to perform the titration under conditions where O₃ has been completely converted to ClO, otherwise ClO will be regenerated by reaction (8). Thus, Cl atoms were added incrementally to a flow of ozone until the O₃⁺ ion (m/z = 48) signal was no longer detectable, implying that its concentration was near to zero. Then NO was added to the system. Typical minimum detectable concentrations were *ca*. 10¹¹ molecule cm⁻³ for ClO, OClO, and O₃, for a signal-to-noise ratio of unity and a 10 s accumulation time.

Typical initial concentrations of species used in these experiments were: $[CIO] = (5-13) \times 10^{12}$ molecule cm⁻³, $[CH_4] = (1-10) \times 10^{13}$ molecule cm⁻³, $[O_3] = (5-15) \times 10^{12}$ molecule cm⁻³ and $[OCIO] = (3-20) \times 10^{12}$ molecule cm⁻³.

Materials

Helium (BOC) was passed through an Oxisorb cartridge (Messer Griesheim) to remove oxygen and then through two traps held at 77 K containing molecular sieve (BDH type 4A) to remove water.

The method followed for the synthesis and purification of methyl nitrite has been described in detail by Biggs *et al.*¹⁶ Sulfuric acid (33%) was added to a mixture of water, methanol and sodium nitrite, held at 273 K. The product was then pumped through two traps, one containing calcium carbonate powder and the other potassium hydroxide, to remove

residual acid. In order to remove residual methanol, methyl nitrite was vacuum distilled from 196 to 77 K several times (typically three), until the level of impurity, as determined mass spectrometrically, was less than 5%.

Ozone was prepared by exciting a 12 kV silent electric discharge through a stream of dried O_2 . The emerging gas mixture of O_2 and O_3 was passed through a trap held at 196 K to remove NO_2 impurities. Ozone was then adsorbed onto silica gel at 196 K. In order to remove most of the O_2 trapped on the silica gel, the trap was pumped on for 5 min. The ozone was then carefully desorbed into a darkened storage bulb and was diluted with helium (*ca.* 10% mixture). The concentration of the ozone mixture was determined by its UV absorption at $\lambda = 254$ nm.

Chlorine dioxide was synthesised by slowly flowing chlorine (BDH, 99.7%) through a column containing slightly moistened sodium chlorite (NaClO₂, BDH) supported on glass beads. OClO and unreacted Cl₂ were then trapped at 77 K. In order to remove the unreacted Cl₂, the mixture was carefully allowed to warm to 196 K and the Cl₂ gas was pumped away. The purification of the OClO was repeated until it contained no more than a 3% Cl₂ impurity, as determined mass spectrometrically. Chlorine dioxide was then carefully transferred to a darkened storage bulb, and diluted with helium. The concentration of OClO in the storage bulb was determined by its UV absorption at $\lambda = 351$ nm. Great care was exercised when handling both ozone and chlorine dioxide, in view of their explosive nature.

Nitric oxide (Messer Griesheim, 99%) was admitted into the vacuum line via a trap held at 196 K and then transferred to a trap held at 77 K. The gas was purified by repeated freeze-pump-thaw cycles at 77 K until a pure white solid was obtained. Nitrogen dioxide (Matheson) was vacuum distilled from 196 to 77 K several times until a white solid was obtained. A correction was made to the calculated NO₂ flow rate to allow for the presence of the N₂O₄ dimer. Methane (BOC, >99%), hydrogen chloride (BDH, 99.9%) and fluorine (BDH, 5% in He) were used without further purification.

Results

Reaction between ClO and CH₃ and CH₃O

Reactions (1) and (2) were studied as a pair of consecutive reactions, and the pseudo-first-order rate constants k'_1 and k'_2 were obtained by non-linear least-squares fitting to the experimental methoxyl concentration-time profiles in the same manner as explained in previous papers.^{12,13} The CH₃O concentration-time profile can be expressed as

$$[CH_{3}O]_{t} = \frac{k'_{1a}[CH_{3}]_{0}}{k'_{1} - k'_{2}} \left[\exp(-k'_{2}t) - \exp(-k'_{1}t) \right]$$
(I)

where $[CH_3O]$, is the concentration of CH_3O at a time t and $[CH_3]_0$ is the initial methyl concentration. It is assumed that the initial methoxyl radical concentration is zero. The three parameters k'_1 and k'_2 and k'_{1a} [CH₃]₀, are optimised to fit the observed concentration-time profile. The mathematical procedure cannot determine which of the two reactions is the faster. However, some experiments were performed in which CH₃O was generated directly by reaction (10) and then allowed to react with ClO. The value of k_2 determined in this way was ca. 10^{-11} cm³ molecule⁻¹ s⁻¹. Using this value to provide a first trial input of k'_2 shows immediately that $k'_1 >$ k'_2 . This result is in accord with our previous work^{12,13} in which it was shown that the rates of the reactions of CH₃ with both NO_2 and NO_3 were faster than the rates of the corresponding reaction of CH₃O. A typical concentrationtime profile is shown in Fig. 2; the solid line in the figure is



Fig. 2 Typical concentration-time profile for CH_3O in the reaction $CH_3 + ClO$ (experiment 9 in Table 3). (-----) Profile generated by the numerical model; \bigcirc , the experimental values.

derived from application of a numerical model (see later), but is virtually identical to that from the non-linear least-squares fitting. Note that the absolute scale for [CH₃O] emerges only as an outcome of the modelling procedure to be presented later, but has no bearing on the three-parameter fit, which can use arbitrary units for the calculation. In some experiments, only the decay portion of the curve was observed. In this case, a semi-logarithmic plot of ln[CH₃O] vs. reaction time yielded just the pseudo-first-order rate constant k'_2 . Table 1 summarises the values of k'_1 and k'_2 obtained using the non-linear least-squares fitting technique (and from semilogarithmic plots where appropriate), together with the flowtube pressure and the concentrations of ClO and O₃ employed in each experiment. The corresponding secondorder plots for reactions (1) and (2) are shown in Fig. 3 and 4, from which the rate constants $k_1 = (1.3 \pm 0.4) \times 10^{-10} \text{ cm}^3$ molecule⁻¹ s⁻¹ and $k_2 = (1.7 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (error limits $\pm 2 \sigma$) were derived. The secondorder plots suggest that there is no significant pressure dependence for k_2 between 1 and 3 Torr. It can be seen, however, that the points in both second-order plots (Fig. 3 and 4) are somewhat scattered. The scatter of the points in Fig. 3 arises because there were usually only a few points in the rise part of the CH₃O concentration-time curves; consequently, some scatter in the plot of k'_1 against [ClO] is inev-



Fig. 3 Second-order plot of k'_1 against [ClO], using data presented in Table 1

Published on 01 January 1995. Downloaded by Otto von Guericke Universitaet Magdeburg on 27/10/2014 13:21:21

3047

View Article Online

J. CHEM. SOC. FARADAY TRANS., 1995, VOL. 91

Table 1	Summary of	experiments for	the determination of	pseudo-first-order	constants k'_1	and k'_{2}
---------	------------	-----------------	----------------------	--------------------	------------------	--------------

expt.	P/Torr	$[CIO]_0/10^{12}$ molecule cm ⁻³	$[O_3]_{res}/10^{12}$ molecule cm ⁻³	<i>k</i> ' ₁ /s ⁻¹	k'_2/s^{-1}
1	1.6	10.6	22.6		174
2	1.6	13.6	23.3		308
3	2.0	3.0	7.6		60
4	2.7	8.1	8.2	1297	135
5	2.8	5.7	18.0	1996ª	72
6	2.8	2.5	14.8	—	44
7	2.8	5.2	23.2	1043	119
8	2.8	11.0	9.6	1440	209
9	2.8	4.3	21.1	813	106
10	2.8	4.8	14.2	1648ª	119
11	2.8	6.1	15.7	1404	104
12	2.8	10.6	13.7	1517	244
13	2.8	6.1	18.0	714	156
14	2.9	4.7	13.8	937	76
15	2.9	4.1	14.6	738	50
16	2.9	9.2	7.7	901	164
17	2.9	7.1	10.4	974	148
18	2.9	4.3	17.9	1430ª	84
19	2.9	4.9	21.9	1142	98
20	2.9	6.8	18.3	628	103
21	2.9	7.1	12.5	717	89
22	2.9	14.4	9.3	1383	229
23	2.9	3.0	25.4		137
24	3.0	6.8	12.9	2277 °	189
25	3.0	5.6	18.3		100

 $[ClO]_0$ is the concentration of ClO without methyl radicals and $[O_3]_{res}$ is the concentration of O_3 in the presence of ClO but in the absence of methyl radicals (see text). ^a These values were omitted from the calculation of k_1 .

itable. The reason for the scatter in Fig. 4 is rather more involved. In all experiments, Cl atoms are generated in reaction (1*a*); if the reaction is rapid $(k_{12} \approx 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$, some Cl may react with CH₃O in the reaction

$$Cl + CH_3O \rightarrow HCl + HCHO$$
 (12)

and not be scavenged by ozone in reaction (8), thereby increasing the observed rate of removal of CH_3O , and thus the apparent value of k'_2 . In order to test the hypothesis that the scatter in Fig. 4 was due to varying contributions from reaction (12), further experiments were performed where the residual ozone concentration (*i.e.* that remaining after reaction with Cl atoms to produce ClO upstream of the sliding injector) was reduced to $(2-5) \times 10^{12}$ molecule cm⁻³, 50% to 25% of its previous value. It was found that k'_2 apparently increased as the residual ozone concentration was reduced, thus confirming our assertion. The scatter is thus not



Fig. 4 Second-order plot of k'_2 against [ClO], using data presented in Table 1

random, and the least-squares line reflects an upper limit for the rate coefficient, as we shall discuss shortly.

A numerical model, containing the reactions listed in Table 2, was used to simulate the methoxyl concentration-time profiles from all the experiments listed in Table 1. A BASIC program employing a second-order single-step backwarddifferentiation method was used to integrate the differential equations of the model.²⁰ The quality of the fits was largely determined by eye, but the sum of the square residuals was taken into consideration. In order to use the numerical model, the initial methyl concentration $([CH_3]_0)$ was required. In all the experiments, a drop in the ClO concentration on the addition of methyl radicals was observed. This drop (termed Δ [ClO]) could be attributed almost totally to reactions (1) and (2), and allowed an estimate of $[CH_3]_0$ to be made. In any case, the derived values of the rate constants are fairly insensitive to the absolute value of [CH₃]₀ and thus to the calibration factor, because the system operates very close to pseudo-first-order conditions. The experimental and modelled values of Δ [ClO], together with the best fit values for k_1

Table 2 Summary of the rate constants used in the numerical model of the reaction of CH_3 and CH_3O with ClO

reaction		k/cm^3 molecule ⁻¹ s ⁻¹	ref.
$CH_3 + ClO \rightarrow CH_3O + Cl$	(1 <i>a</i>)	1.3×10^{-10}	this work
$CH_3O + ClO \rightarrow products$	(2)	1.3×10^{-11}	this work
$CH_3 + CH_3 \rightarrow C_2H_6$	(13)	4.0×10^{-11}	21
$CH_3O + CH_3O \rightarrow products$	(14)	1.0×10^{-11}	22
$CH_3 + CH_3O \rightarrow products$	(15)	4.0×10^{-11}	a
$CH_{3}O + CI \rightarrow HCHO + HCl$	(16)	2.0×10^{-10}	this work
$Cl + O_3 \rightarrow ClO + O_2$	(8)	1.2×10^{-11}	23
$Cl + CH_{4} \rightarrow HCl + CH_{3}$	(17)	2.0×10^{-13}	23
$CH_3O \rightarrow products$	(18)	$20-40 \text{ s}^{-1}$	this work
$Cl \rightarrow products$	(19)	$30 \mathrm{s}^{-1}$	19

^a The rate constant k_{15} was taken to be twice the geometric mean of k_{13} and k_{14} .

Table 3 Summary of the results obtained from the application of the numerical model to the experimental CH₃O concentration-time profiles, showing a comparison of the experimental Δ [ClO] (Δ [ClO]_{expl}) and the modelled value (Δ [ClO]_{model}), and the 'best-fit' model values for the rate coefficients k_1 and k_2

expt.	Δ [ClO] _{expl} /10 ¹² molecule cm ⁻³	Δ [ClO] _{model} /10 ¹² molecule cm ⁻³	$k_1/10^{-10} \text{ cm}^3$ molecule ⁻¹ s ⁻¹	$k_2/10^{-11} \text{ cm}^3$ molecule ⁻¹ s ⁻¹
1	2.7	2.7	1.30	1.35
2	3.3	3.3	1.30	1.35
3	1.2	1.1	1.30	1.40
4	3.1	2.9	1.30	1.30
5	2.4	2.2	1.30	1.20
6	0.9	0.9	1.30	1.35
7	0.5	0.6	1.30	1.30
8	1.8	1.3	1.30	1.30
9	0.5	0.6	1.30	1.30
10	0.7	0.7	1.30	1.40
11	0.7	0.7	1.30	1.30
12	1.1	1.6	1.20	1.20
13	0.7	0.7	1.30	1.40
14	0.4	0.4	1.25	1.10
15	0.4	0.4	1.30	1.40
16	2.3	2.2	1.30	1.35
17	1.6	1.5	1.30	1.30
18	1.1	1.1	1.40	1.50
19	0.5	0.5	1.40	1.40
20	1.1	1.0	1.25	1.30
21	0.8	0.7	1.40	1.40
22	3.4	2.8	1.00	1.30
23	0.3	0.5	1.40	1.70
24	2.4	2.2	1.40	1.50
25	2.2	2.1	1.25	1.25

and k_2 for each experiment, are shown in Table 3. The concentration-time profiles for CH₃O derived from the numerical model reproduced all the experimental profiles well. The values of k_1 and k_2 obtained from the numerical model are: $k_1 = (1.3 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and}$ $k_2 = (1.3 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, where the error quoted reflects the range of values for k_1 and k_2 that gave reasonable fits to the experimental data. The value derived from the numerical model for k_1 is, within error, the same as that derived from the analytical method. The application of the numerical model indicates that the value for k_2 determined by the non-linear least-squares method is larger than the true value because reaction (12) makes a significant contribution to the overall loss of CH₃O. An estimate for the rate constant k_{12} for the reaction between Cl atoms and CH₃O, $k_{12} = (2 \pm 1) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, was also obtained from the modelling procedure. Model runs further suggested that, if experiments were performed with residual ozone concentrations typically used in these experiments (ca. 10^{13} molecule cm⁻³), and with high methane concentrations (ca. 10^{14} molecule cm⁻³), a decrease in the observed rate of loss of CH₃O should be observed. This decrease would result from the reaction between Cl atoms and methane

$$Cl + CH_4 \to CH_3 + HCl \tag{17}$$

which now becomes important. The methyl radicals produced by reaction (17) can then react with ClO, regenerating CH₃O by reaction (1*a*), thereby reducing the observed rate of loss of CH₃O. Such a decrease in the observed rate of loss of CH₃O with methane concentrations of the order of 10^{14} molecule cm⁻³ was found experimentally.

Losses of CH₃O radicals at the halocarbon-wax coated tube were derived from the model; the rate coefficients (20–40 s^{-1}) were similar to those found previously.^{12,15} Wall losses of Cl were also included.¹⁹ Heterogeneous losses of CH₃ cannot be of any importance in our system because the homogeneous processes are so fast; there is no evidence from our work for any wall losses of ClO or OClO.

Product Study

There are several product channels available for both reactions (1) and (2), as explained in the discussion. CH₃O was observed as a product of reaction (1) by LIF. Chlorine atoms were inferred to be the complementary product. No ion signals were observed at m/z = 66 or 68 (CH₃OCl⁺) or m/z = 50 (CH₃Cl⁺). Product ion signals were detected at m/z = 52 and 54, and were assigned to the HOCl⁺ ion, thus suggesting strongly the occurrence of the channel

$$CH_3O + ClO \rightarrow HOCl + HCHO$$
 (2*a*)

It was not possible to detect the HCHO⁺ ion at either m/z = 30 or 29, but the background signal level was high for these masses. It would be very difficult to detect CH₃O₂ if it were a product of reaction (2)

$$CH_3O + ClO \rightarrow CH_3O_2 + Cl$$
 (2b)

since it is not possible to observe this radical directly with the mass spectrometer used in our experiments. It is possible to titrate the CH_3O_2 with NO, converting it to CH_3O in the reaction

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
 (20)

and then to determine the increase in the CH_3O LIF signal. However, CIO is in excess, so that any added NO will react preferentially with this species, liberating Cl atoms in reaction (11), further complicating the chemistry. Nevertheless, if the channel forming CH_3O_2 and Cl, reaction (2b), was important, the CH_3O_2 formed would be expected to react with either CIO

$$CH_3O_2 + ClO \rightarrow CH_3O + Cl + O_2$$
 (5a)

$$CH_{3}O_{2} + ClO \rightarrow CH_{3}OCl + O_{2}$$
(5b)

or with Cl atoms²³

$$CH_3O_2 + Cl \rightarrow CH_2O_2 + HCl$$
 (21*a*)

$$CH_3O_2 + Cl \rightarrow CH_3O + ClO$$
 (21b)

where reaction (21b) is the reverse of reaction (2b). Although there is some debate^{3,4,6-8,24} about the value of the branching ratio for reaction channel (5a), the total rate constant is quite well established:⁶⁻⁸ $k_5 = 2.0 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K, independent of pressure. DeMore *et al.*²³ have recommended as rate constants for reactions (21a) and (21b) at 298 K $k_{21a} = 7.4 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $k_{21b} =$ 7.7×10^{-11} cm³ molecule⁻¹ s⁻¹. The reactions (2b), (5a), (5b), (21a) and (21b) were added to the numerical model described earlier and further computation was carried out. The initial results of the model indicated that the major loss of CH₃O₂ is *via* reaction with CIO [reaction (5)], although reaction with Cl atoms was a minor loss process. The following reaction sequence

$$CH_3O + ClO \rightarrow CH_3O_2 + Cl$$
 (2b)

$$CH_3O_2 + ClO \rightarrow CH_3O + Cl + O_2$$
 (5a)

$$CH_3O_2 + ClO \rightarrow CH_3OCl + O_2 \tag{5b}$$

is therefore likely to occur if the production of CH_3O_2 is significant. However, if reaction (5a) is the dominant product channel for reaction (5), CH₃O will be regenerated in this system at longer contact times. Since we measure [CH₃O] directly, an upper limit for the rate of reaction (2b) was sought, so that the lowest value determined³ to date for $k_{5a}/(k_{5a} + k_{5b})$, 0.4, was used in the model. The results then showed that, if $k_{2b}/(k_{2a} + k_{2b})$ was greater than 0.2, detectable concentrations of CH₃O would persist until contact times approaching 60 ms, because of the regeneration of CH₃O via reactions (2b) and (5a). In no experiment was such a regeneration observed. Further, modelling shows that setting $k_{5a}/(k_{5a})$ $(k_{2a} + k_{2b})$ to 0.4 forces $k_{2b}/(k_{2a} + k_{2b})$ to be less than 0.1, and most likely zero, in order to obtain reasonable fits to the experimental CH₃O concentration-time profiles. It can thus be concluded that channels (1a) and (2a) are the dominant product channels for reactions (1) and (2).

Reaction between OCIO and CH₃ and CH₃O

In exactly the same manner as we investigated the kinetics of reactions (1) and (2), we studied reactions (3) and (4) as a pair of consecutive reactions, and the pseudo-first-order rate constants k'_{3} and k'_{4} were obtained by non-linear least-squares fitting to the experimental methoxyl concentration-time profiles as explained in previous papers.^{12,13} In the experiments where CH₃O was generated directly by reaction (10) and then allowed to react with OClO, k_4 was determined to be *ca*. 4×10^{-12} cm³ molecule⁻¹ s⁻¹. For the fitting procedure, it is then necessary that $k'_3 > k'_4$. A typical non-linear leastsquares fit to an experimental CH₃O concentration-time profile is shown in Fig. 5. Table 4 summarises the values of k'_3 and k'_4 obtained using the non-linear least-squares fitting technique, together with the pressure and the concentration of OClO employed in each experiment. The corresponding second-order plots for reactions (3) and (4) are shown in Fig. 6 and 7, from which the rate constants $k_3 = (1.8 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $k_4 = (3.1 \pm 1.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ (error limits $\pm 2\sigma$), were derived. It is evident that some scatter of the points exists in the secondorder plot for k_3 , which is probably due to the generally small number of points in the rise part of the curve. Some scatter of the points in the second-order plot for k_4 (Fig. 7) also exists. A possible explanation for this scatter is that ClO radicals, generated as a co-product alongside CH₃O in reaction (4a), react with CH_3O [reaction (2a)], there being no other process of significance to remove them in this system. The net effect of reaction (2a) would be to increase the observed rate of loss of CH₃O.

J. CHEM. SOC. FARADAY TRANS., 1995, VOL. 91



Fig. 5 Typical concentration-time profile for CH_3O in the reaction $CH_3 + OCIO$ (experiment 6 in Table 4). (-----) Fit obtained from the application of the non-linear least-squares three-parameter technique.

In order to check the hypothesis that the scatter in Fig. 7 was due to reaction (2a), a numerical model, containing the reactions listed in Table 5, was used to simulate the methoxyl concentration-time profiles for all the experiments listed in

Table 4 Summary of experiments for the determination of pseudofirst-order rate constants k'_3 and k'_4

expt.	P/Torr	$[OClO]_0/10^{12}$ molecule cm ⁻³	k'_{3}/s^{-1}	k'_{4}/s^{-1}
1	1.4	5.4	96	94ª
2	1.4	2.2		30
3	1.4	10.2	150	60
4	1.4	13.5	185	59
5	1.3	16.4	255	97
6	1.3	8.4	189	65
7	1.3	17.8	302	100
8	1.3	4.0	128	30
9	1.3	20.0	400	80
10	1.0	3.4	118	63
11	1.4	1.7	34	23
12	1.4	3.4	175	59

[OCIO]₀ is the concentration of OCIO in the absence of methyl radicals. ^a This point was omitted from the calculation of k_4 .



Fig. 6 Second-order plot of k'_3 against [ClO], using data presented in Table 4

J. CHEM. SOC. FARADAY TRANS., 1995, VOL. 91



Fig. 7 Second-order plot of k'_4 against [ClO], using data presented in Table 4

Table 4 in a similar way to that used for the analysis of data for reaction (2). In all the experiments, there was a drop in the OClO concentration on the addition of methyl radicals; this drop (termed Δ [OClO]) was mainly due to reaction (3) and allowed an estimate of [CH₃]₀ to be made. The concentration-time profiles for both CH₃O and ClO derived from the numerical model reproduced all the experimental profiles well. The ClO signal was off-set by approximately 30 ms from the CH₃O signal because of the difference in distances from the tip of the sliding-injector to the LIF cell and mass spectrometer. Typical CH₃O and ClO concentrationtime profiles produced by the model (solid lines) and the experimental results (triangles for CH₃O and squares for ClO) are shown in Fig. 8. It was apparent that, once formed, ClO reacted only very slowly with OClO and itself, and that reaction with CH₃O was a significant loss process for ClO for the first 20 ms of the reaction. The results of the numerical modelling procedure indicate that the rate constant k_4 determined by the non-linear least-squares method is larger than the true value, being enhanced by the loss of CH₃O through reaction (2a). The value of k_3 produced by fitting to the numerical model is in agreement with that from the nonlinear least-squares method. The results from the numerical model are: $k_3 = (1.6 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and} k_4 = (1.5 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$



Fig. 8 The same concentration-time profile for CH_3O as shown in Fig. 5. \triangle , [CH₃O]; \square , [ClO]; (—) result from numerical model described in the text.

Product Study

There are several product channels available for both reaction (3) and (4); possibilities are identified explicitly in our discussion. Methoxyl radicals were observed as a product of reaction (3) by LIF. Chlorine monoxide radicals, the complementary product to CH₃O in reaction (3*a*), were identified by the observation of the ClO⁺ ion at m/z = 51. No ion signals were observed at m/z = 66 or 68 (CH₃OCl⁺), m/z = 52 or 54(HOCl⁺) or m/z = 50 or 52 (CH₃Cl⁺), the other possible products of reaction (3). Just as in the product study for reaction (2), it would be very difficult to detect CH₃O₂ as a product of reaction (4). It is possible to titrate the CH₃O₂ with NO back to CH₃O [reaction (20)], but, with OClO in great excess, any added NO will react preferentially with this species, liberating ClO radicals in the reaction

$$OCIO + NO \rightarrow CIO + NO_2$$
 (25)

When CH₃O was generated directly by reaction (10), an ion signal was observed at m/z = 66, but was very small. There is thus only tentative evidence from our work that a product of reaction (4) is CH₃OCl.

Discussion

It is apparent that the reaction between CH_3 and ClO is fast, with the major (if not the only) channel being process (1a).

Table 5 Summary of the rate constants used in the numerical model of the reaction of CH₃ and CH₃O with OClO

reaction		k/cm^3	ref
$CH_3 + ClO \rightarrow CH_3O + Cl$	(1a)	1.3×10^{-10}	this work
$CH_3O + ClO \rightarrow products$	(2)	1.3×10^{-11}	this work
$CH_3 + CH_3 \rightarrow C_2H_6$	(13)	4.0×10^{-11}	21
$CH_3O + CH_3O \rightarrow products$	(14)	1.0×10^{-11}	22
$CH_3 + CH_3O \rightarrow products$	(15)	4.0×10^{-11}	а
$CH_{3}O + CI \rightarrow HCHO + HCI$	(16)	2.0×10^{-10}	this work
$Cl + OClO \rightarrow ClO + ClO$	(22)	5.8×10^{-11}	23
$CH_3 + OCIO \rightarrow CH_3O + CIO$	(3 <i>a</i>)	1.6×10^{-11}	this work
$CH_3O + OClO \rightarrow products$	(4)	1.5×10^{-12}	this work
$CH_3O \rightarrow products$	(18)	$20-40 \text{ s}^{-1}$	12, 15
$Cl \rightarrow products$	(19)	30 s^{-1}	19
$OClO + ClO \rightarrow products$	(23)	3.0×10^{-15}	25
$CIO + CIO \rightarrow CI + OCIO$	(24a)	2.4×10^{-15}	26
$ClO + ClO \rightarrow Cl + Cl + O_2$	(24b)	4.9×10^{-15}	26
$ClO + ClO \rightarrow Cl_2 + O_2$	(24 <i>c</i>)	4.7×10^{-5}	26

" The rate constant k_{15} was taken to be twice the geometric mean of k_{13} and k_{14} .

Although four possible channels can be envisaged

CH₃ + ClO → CH₃O + Cl;

$$\Delta_r H^{298} = -111 \text{ kJ mol}^{-1}$$
 (1*a*)
CH₃ + ClO → CH₃Cl + O;
 $\Delta_r H^{298} = -81 \text{ kJ mol}^{-1}$ (1*b*)

$$CH_3 + ClO + M \rightarrow CH_3OCl + M;$$

$$\Delta_{\rm r} H^{298} = -309 \text{ kJ mol}^{-1} \quad (1c)$$

 $CH_3 + ClO \rightarrow HCHO + HCl;$

$$\Delta_{\rm r} H^{298} = -447 \text{ kJ mol}^{-1} \quad (1d)$$

there was no evidence from product studies that channels (1b)and (1c) make a significant contribution at pressures between 1 and 3 Torr. In addition, there was no evidence of a pressure dependence for k_1 . It is impossible to distinguish whether reaction (1) proceeds via a direct abstraction mechanism or through an energised adduct of the type [CH₃-OCl]*. It is easy to show from simple RRK-type calculations that if the mechanism of reaction (1) involves an energised adduct, the vast majority of energised adducts so formed will dissociate to form CH₃O and Cl and will not be stabilised at the pressures used in these experiments. Production of CH₃Cl and O atoms from an energised adduct is unlikely, since it requires the formation of a three-centred intermediate, which is energetically unfavourable. Our inability to observe CH₃Cl is consistent with this picture. Although the formation of HCHO and HCl is highly exothermic, the reaction pathway must involve a four-centred intermediate, which is also likely to be energetically unfavourable. One way to establish the mechanism would be to detect the stabilised adduct CH₃OCl, but stabilisation is likely to require very high pressures.²⁷

Three possible product channels can be envisaged for reaction (2),

CH₃O + ClO → HOCl + HCHO;
$$\Delta_r H^{298} = -303 \text{ kJ mol}^{-1} \quad (2a)$$

CH₃O + ClO → CH₃O₂ + Cl;
$$\Delta_r H^{298} = +19 \text{ kJ mol}^{-1} \quad (2b)$$

CH₃O + ClO → CH₃Cl + O₂;

$$A H^{298} = -201 \text{ kI mol}^{-1} \quad (2c)$$

No CH₃Cl was observed as a product of this system, and it was not identified either in an indirect study of this system by Helleis *et al.*⁷ Numerical modelling (see Results section) has shown that reaction (2*b*) is not a significant channel. The indirect study of Helleis *et al.*⁷ also argues against reaction (2*b*) being of any significance. Hence, the slightly endothermic channel (2*b*) is not important. It is therefore concluded that channel (2*a*) is the dominant (if not the only) channel of reaction (2). The mechanism of reaction (2*a*) seems to be a simple abstraction. In a recent study, Kukui *et al.*⁸ made an indirect measurement of k_2 ; their value $[(1-3) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹] is in broad agreement with the results of this study. Daële²⁸ has also obtained a rate coefficient of $(2.2 \pm 0.2) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹, slightly higher than our result.

During the course of this work, numerical modelling of the kinetics of reactions (1) and (2) has indicated that the rate of reaction between Cl atoms and CH₃O [reaction (12)] is very fast, comparable to the rate of reaction suggested by Bogan *et al.*²⁹ for the reaction of F atoms with CH₃O. Recent measurements³⁰ have also indicated that reaction (12) does proceed at a rate near to the hard-sphere collision rate.

Although several possible reaction channels exist for reaction (3)

CH₃ + OClO → CH₃O + ClO;

$$\Delta_r H^{298} = -124 \text{ kJ mol}^{-1}$$
 (3*a*)
CH₃ + OClO → CH₃OCl + O;

J. CHEM. SOC. FARADAY TRANS., 1995, VOL. 91

$$\Delta_{\rm r} \, H^{298} = -54 \, \rm kJ \, mol^{-1} \quad (3b)$$

$$CH_3 + OCIO \rightarrow HOCI + HCHO;$$

$$\Delta_{\rm r} H^{298} = -427 \text{ kJ mol}^{-1} \quad (3c)$$

CH₃ + OCIO → CH₃Cl + O₂;
$$\Delta_r H^{298} = -345 \text{ kJ mol}^{-1}$$
 (3d)

product studies indicate that channel (3a) is the only reaction pathway. The mechanism of the reaction is most likely to be a simple abstraction.

For reaction (4), the two channels

CH₃O + OClO → CH₃OCl + O₂;

$$\Delta_r H^{298} = -173 \text{ kJ mol}^{-1}$$
 (4a)
CH₃O + OClO → CH₃O₂ + ClO;
 $\Delta_r H^{298} = +6 \text{ kJ mol}^{-1}$ (4b)

can be envisaged. There is tentative evidence for the formation of CH₃OCl from our study. If CH₃O₂ were formed, it could either react with ClO, leading to regeneration of CH₃O *via* reaction (5*a*), or CH₃O₂ could react with OClO. However, the reaction between CH₃O₂ and OClO is likely to be slow. Maguin³¹ has shown that the rate constant for the reaction between OClO and HO₂

$$OCIO + HO_2 \rightarrow HOCl + O_3$$
 (26)

is 1.9×10^{-14} cm³ molecule⁻¹ s⁻¹ at 298 K, and that the products are HOCl and O₃, formed most likely from a sixmembered intermediate. The rate constant for the reaction between CH₃O₂ and OClO might be expected to be comparable to k_{26} . Thus, if reaction (4b) is important, the CH₃O₂ formed will almost certainly react with any ClO present in the system and not with OClO. Since in this study we observed no regeneration of CH₃O, which would be expected if reaction (5a) were occurring, it is extremely unlikely that channel (4b) is in operation.

Comparison with Similar Reactions

The rate constants for the reaction of ClO and OClO with H, CH₃, OH and CH₃O are collected in Table 6. It would appear that the mechanism (abstraction) is the same for the reactions of H and CH₃ with OClO, and that the difference in reactivity can be explained in terms of simple steric arguments. The reaction between OH and OCIO is thought to proceed via a cyclic intermediate,³² since the major products are HOCl and O₂ and because the rate constant increases with decreasing temperature. Some evidence exists from our study that CH₃OCl is a product of the reaction between CH₃O and OClO, suggesting the involvement of a fivemembered intermediate. Further studies of the kinetics of reaction (4) and of the products at low temperatures are warranted to investigate whether or not the mechanism of this reaction is indeed similar to that of the reaction between OH and OCIO. The rate constants for the reactions between OH and ClO and CH₃O and ClO are virtually identical, but the major products suggest that the mechanisms are not the same. For the reaction between OH and ClO, HO₂ and Cl

Table 6 Summary of the known rate constants at 298 K for the reactions of H, CH_3 , OH and CH_3O with ClO and OClO, and also for the reactions of HO₂ and CH₃O₂ with ClO

reaction	k/cm^3 molecule ⁻¹ s ⁻¹	ref.
$CH_3 + CIO \rightarrow CH_3O + CI$	1.3×10^{-10}	this work
$OH + ClO \rightarrow HO_2 + Cl$	1.7×10^{-11}	234
$CH_3O + CIO \rightarrow HCHO + HOCI$	1.3×10^{-11}	this work
$HO_2 + ClO \rightarrow HOCl + O_2$	5.0×10^{-12}	23
$CH_3O_2 + ClO \rightarrow CH_3O + ClOO$	2.0×10^{-12}	7, 8°
$\rightarrow CH_3OCl + O_2$		
$H + OCIO \rightarrow OH + CIO$	5.7×10^{-11}	9
$CH_3 + OCIO \rightarrow CH_3O + CIO$	1.6×10^{-11}	this work
$OH + OCIO \rightarrow HOCI + O_2$	7.2×10^{-12}	32°
$CH_3O + OClO \rightarrow products$	1.5×10^{-12}	this work

^a The dominant channel; a minor channel forming $HCl + O_2$ also exists. ^b The rate constant at 298 K is reasonably well established but the branching ratio for the two channels is the subject of much debate at the present time, with the suggestion that a third channel as yet unknown may exist.³ 'The dominant channel; a second channel (<15%) forming HO₂ + ClO may also exist.³²

are the major products, whereas for the reaction between CH₃O and ClO, the formation of CH₃O₂ and Cl is an endothermic process. The rate constant for reaction (1) is extremely high; however, a study of the reaction between H and CIO has not been reported to date, so that no comparisons can be made. It has already been stated that the mechanism of reaction (1) could involve an energised adduct or could proceed via direct abstraction; it is impossible to distinguish between the two from the results of this study.

We would like to thank the SERC (NERC), CEC and the Institut Français du Pétrole, under whose auspices this and related work was carried out. D.E.S. would like to thank the SERC for a research studentship during the tenure of which this work was conducted. We thank Richenda Connell for assistance with the preparation of the methyl nitrite samples used in this work.

References

- Scientific Assessment of Ozone Depletion: 1991, WMO Global 1 Ozone Research and Monitoring Project, Report No. 25, 1992, Geneva, Switzerland.
- I. W. M. Smith, J. Chem. Soc., Faraday Trans., 1991, 87, 2271.
- 3 P. Biggs, C. E. Canosa-Mas, J-M. Fracheboud, D. E. Shallcross and R. P. Wayne, Geophys. Res. Lett., 1995, 22, 1221.
- F. G. Simon, J. P. Burrows, W. Schneider, G. K. Moortgat and P. J. Crutzen, J. Phys. Chem., 1989, 93, 7807.

- P. J. Crutzen, R. Müller, Ch. Brühl and Th. Peter, Geophys. Res. 5 Lett., 1992, 19, 1113.
- R. D. Kenner, K. R. Ryan and I. C. Plumb, Geophys. Res. Lett., 1993, 20, 1571.
- F. Helleis, J. N. Crowley and G. K. Moortgat, J. Phys. Chem., 7 1993, 97, 11 464.
- A. S. Kukui, T. P. W. Jungkamp and R. N. Schindler, Ber. 8 Bunsen-Ges. Phys. Chem., 1994, 98, 1298.
- P. P. Bemand, M. A. A. Clyne and R. T. Watson, J. Chem. Soc., Faraday Trans. 1, 1973, 69, 1356.
- R. R. Friedl and S. P. Sander, J. Phys. Chem., 1989, 93, 4756.
- J. Sessler, M. P. Chipperfield, J. A. Pyle and R. Toumi, Geophys. 11 Res. Lett., 1995, 22, 687.
- P. Biggs, C. E. Canosa-Mass, F. Caralp, J-M. Fracheboud, A. D. Parr, D. E. Shallcross and R. P. Wayne, J. Chem. Soc., Faraday Trans., 1993, 89, 4163.
- 13 P. Biggs, C. E. Canosa-Mas, J-M. Fracheboud, D. E. Shallcross and R. P. Wayne, J. Chem. Soc., Faraday Trans., 1994, 90, 1197.
- P. Biggs, C. E. Canosa-Mas, J-M. Fracheboud, D. E. Shallcross and R. P. Wayne, in preparation.
- S. Dóbé, T. Bérces and I. Szilágyi, J. Chem. Soc., Faraday Trans., 15 1991, **87**, 2331.
- P. Biggs, C. E. Canosa-Mas, J-M. Fracheboud, D. E. Shallcross 16 and R. P. Wayne, J. Chem. Soc., Faraday Trans., 1994, 90, 1205.
- G. Inoue, H. Akimoto and M. Okuda, Chem. Phys. Lett., 1979, 17 63, 213.
- 18 S. C. Foster and T. A. Miller, J. Phys. Chem., 1989, 93, 5986.
- P. Biggs, M. H. Harwood, A. D. Parr and R. P. Wayne, J. Phys. 19 Chem., 1991, 95, 7746.
- 20 C. F. Curtis and J. O. Hirschfelder, Proc. Natl. Acad. Sci., 1952, **38**, 735.
- M. J. Pilling, Int. J. Chem. Kinet., 1989, 21, 267. R. Zellner, D. Hartmann, J. Karthauser, D. Rhasa and G. 22 Weibrug, J. Chem. Soc., Faraday Trans. 2, 1988, 84, 549.
- W. B. DeMore, S. P. Sander, D. M. Golden, M. J. Molina, R. F. Hampson, M. J. Kurylo, C. E. Kolb, C. J. Howard and A. R. Ravishankara, Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling, NASA Evaluation No. 11, Jet Propulsion Laboratory Publication 94-26, Pasadena, CA, USA, 1994.
- F. Helleis, J. N. Crowley and G. K. Moortgat, Geophys. Res. 24 Lett., 1994, 21, 1795.
- 25 J. B. Burkholder, R. L. Mauldin, R. J. Yokelson, S. Solomon and A. R. Ravishankara, J. Phys. Chem., 1993, 97, 7597.
- 26 A. Horowitz, J. N. Crowley and G. K. Moortgat, J. Phys. Chem., 1994, 98, 11924.
- 27 J. Troe, J. Chem. Soc., Faraday Trans., 1994, 90, 2303.
- V. Daële, Ph.D. Thesis, Université de Paris VII, 1994. 28
- 29 D. J. Bogan, M. Kaufman, C. W. Hand, W. A. Sanders and B. E. Brauer, J. Phys. Chem., 1990, 94, 8128.
- T. P. W. Jungkamp. Christian Albrechts University, Kiel, 30 Germany, personal communication.
- F. Maguin, Ph.D. Thesis, University of Orléans, France, 1993.
- 32 G. Poulet, H. Zagogianni and G. Le Bras, Int. J. Chem. Kinet., 1986, 18, 847.

Paper 5/02310F; Received 10th April, 1995