CCI

# A kinetic and mechanistic study of the gas-phase reactions of OH radicals and Cl atoms with some halogenated acetones and their atmospheric implications

Sinéad Carr,<sup>*ab*</sup> Dudley E. Shallcross,<sup>*c*</sup> Carlos E. Canosa-Mas,<sup>*b*</sup> John C. Wenger,<sup>†*a*</sup> Howard W. Sidebottom,<sup>*a*</sup> Jack J. Treacy<sup>*a*</sup> and Richard P. Wayne<sup>\**b*</sup>

<sup>a</sup> Department of Chemistry, University College Dublin, Belfield, Dublin, Ireland

<sup>b</sup> Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ. E-mail: wayne@physchem.ox.ac.uk

<sup>c</sup> Biogeochemistry Research Centre, School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS

Received 22nd April 2003, Accepted 14th July 2003 First published as an Advance Article on the web 19th August 2003

Rate coefficients for the reactions of hydroxyl radicals and chlorine atoms with a series of halogenated acetones of the type  $CX_3COCH_3$  (X = H, Cl, F) have been determined using a photolytic relative-rate technique at T = 298 K and at 760 Torr total pressure. The reactions studied and the rate coefficients obtained are shown in the table.

Reaction	Reaction number	Rate coefficient/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
$OH + CH_3COCH_3 \rightarrow products$	(1)	$(2.2\pm0.5)\times10^{-13}$
$OH + CH_2ClCOCH_3 \rightarrow products$	(2)	$(4.2\pm0.8)\times10^{-13}$
$OH + CHCl_2COCH_3 \rightarrow products$	(3)	$(3.8\pm0.8)\times10^{-13}$
$OH + CCl_3COCH_3 \rightarrow products$	(4)	$(1.5\pm0.3)\times10^{-14}$
$OH + CH_2FCOCH_3 \rightarrow products$	(5)	$(2.1\pm0.4)\times10^{-13}$
$OH + CF_3COCH_3 \rightarrow products$	(6)	$(6.9 \pm 1.3) \times 10^{-15}$
$Cl + CH_3COCH_3 \rightarrow products$	(7)	$(2.2\pm0.4)\times10^{-12}$
$Cl + CH_2ClCOCH_3 \rightarrow products$	(8)	$(2.0\pm0.2)\times10^{-12}$
$Cl + CHCl_2COCH_3 \rightarrow products$	(9)	$(1.7\pm0.3)\times10^{-13}$
$Cl + CCl_3COCH_3 \rightarrow products$	(10)	$(1.7\pm0.3)\times10^{-14}$
$Cl + CH_2FCOCH_3 \rightarrow products$	(11)	$(8.2 \pm 1.6) \times 10^{-13}$
$Cl + CF_3COCH_3 \rightarrow products$	(12)	$(8.0 \pm 1.6) \times 10^{-15}$

The errors quoted reflect an estimate of the absolute uncertainty in the measured rate coefficients of  $\pm 20\%$ . For reactions (7)–(12), Fourier transform infrared spectroscopy was used to identify products. Qualitative ultra-violet absorption spectra were also recorded for most of the halogenated species investigated in this study, and have been used together with the kinetic data to derive atmospheric lifetimes for these species.

# Introduction

The rôle played by CFCs in stratospheric ozone depletion is well known.<sup>1,2</sup> To alleviate the impact, a number of replacement compounds, the hydrofluorocarbons and hydrofluorocchlorocarbons, HFCs and HCFCs, have been developed for short-term use. These replacement compounds are susceptible to attack by the OH radical and can therefore be broken down in the troposphere.<sup>3</sup> However, some proposed replacements (*e.g.* CF<sub>2</sub>CICH<sub>3</sub>, HCFC 142b) have been shown to have rather

† Now at the Department of Chemistry, University College Cork, Cork, Ireland.

long lifetimes and could penetrate into the lower stratosphere in significant quantities, carrying halogens with them.<sup>4</sup> In addition, it is essential that the products of the degradation of these replacements are themselves not potential carriers of chlorine or bromine to the stratosphere. In the degradation of nonhalogenated hydrocarbons, ketones such as acetone are formed, and are known to be long-lived (months).<sup>5</sup> The accumulation of acetone in the upper troposphere and lower stratosphere has recently been highlighted.<sup>6–8</sup> Acetone has been shown to be a potentially important source of HO<sub>x</sub> (OH and HO<sub>2</sub>) in these regions. Hence, there is a particular need to investigate the chemistry of some halogenated acetones. In this study we have used a photolytic relative rate technique<sup>9,10</sup> at

$$OH + CH_3 COCH_3 \rightarrow products \tag{1}$$

 $OH + CH_2ClCOCH_3 \rightarrow products$ (2)

 $OH + CHCl_2COCH_3 \rightarrow products$ (3)

 $OH + CCl_3COCH_3 \rightarrow products$ (4)  $OH + CH_2FCOCH_3 \rightarrow products$ (5)

$$OH + CF_3COCH_3 \rightarrow products$$
(6)

and the kinetics and products of the reactions

$$Cl + CH_3COCH_3 \rightarrow products$$
 (7)

$$Cl + CH_2ClCOCH_3 \rightarrow products$$
 (8)

$$Cl + CHCl_2COCH_3 \rightarrow products$$
 (9)

 $Cl + CCl_3COCH_3 \rightarrow products$ (10)

$$Cl + CH_2FCOCH_3 \rightarrow products$$
 (11)

 $Cl + CF_3COCH_3 \rightarrow products$ (12)

A comparison of the rate coefficients is combined with the investigations of the nature of the products to deduce the likely mechanism of these reactions. The lifetimes of these species and their likely impact on the atmosphere are assessed using the Cambridge 2-Dimensional model.<sup>11</sup>

# **Experimental**

A conventional photolytic relative-rate technique was used for all measurements of rate coefficients. The experimental apparatus and procedure has been described in detail elsewhere<sup>9,10</sup> and will only be summarised briefly here. The apparatus consisted of a FEP Teflon bag (volume ca. 50 litres) surrounded by a bank of discharge lamps. All experiments were performed at atmospheric pressure (730–760 Torr) and at  $T = 298 \pm 2$  K. An electric fan positioned below the reaction chamber ensured that a uniform temperature was maintained during irradiation of the mixture.

For the study of reactions (1)-(6), OH radicals were generated by the photolysis of ozone

$$O_3 + h\nu(\lambda = 254 \text{ nm}) \rightarrow O(^{1}\text{D}) + O_2$$
(13)

followed by the reaction

$$O(^{1}D) + H_{2}O \rightarrow OH + OH$$
(14)

Photolysis was effected using 20 germicidal lamps (Philips TU, 15 W), which produce  $\lambda = 254$  nm radiation.

The diluent gas used in the study of reactions (1)-(6) was always oxygen. Measured amounts of reactants, with the exception of water, were flushed from calibrated pyrex bulbs into the Teflon reaction vessel by a stream of medical-grade oxygen. Water (triply distilled, 0.5 ml), was injected in liquid form directly into the chamber. The reaction vessel was then filled to capacity with  $O_2$ . Mixtures of  $O_3/H_2O/$ CX<sub>3</sub>COCH<sub>3</sub>/reference compound were allowed to equilibrate for ca. 1 h and were then photolysed for ca. 15 min, or until about 50% depletion of the substrate or reference compound had occurred. Typical initial concentrations employed were  $[CX_3COCH_3]_0$ , [reference compound]\_0 = 10-43 ppm;  $[O_3]_0 = 100-1000$  ppm and  $[H_2O]_0 = 2000-10000$  ppm. More detailed information on the initial concentrations of the substrate and reference compound is shown in Table 1.

In the investigation of reactions (7)-(12), Cl atoms were generated by the photolysis of molecular chlorine

$$Cl_2 + h\nu(\lambda > 300 \text{ nm}) \rightarrow Cl + Cl$$
 (15)

using 10 'blacklamps' (Philips TL 20 W/08) and 10 'sunlamps' (Philips TL 20 W/09) which provided UV-visible radiation in the range  $\lambda = 300-450$  nm.

The diluent gas used was synthetic air or zero-grade nitrogen. Once equilibrated, mixtures of Cl<sub>2</sub>/CX<sub>3</sub>COCH<sub>3</sub>/reference compound/diluent gas were photolysed for up to 20-30 minutes or until approximately half the contents of the reaction bag had been sampled. A list of typical initial concentrations of the substrate and reference compound is again shown in Table 1

Quantitative analysis was carried out using gas chromatography (Shimadzu 14A GC instrument, with FID detector) and FTIR spectroscopy (Mattson, Galaxy 5000). Gastight syringes (Hamilton) or a Valco gas sampling valve were used

**Table 1** Initial concentrations of substrate and reference compounds for reactions (1)–(12)

Concentration/ppm	Reference compound	Concentration/ppm		
28	CH <sub>2</sub> ClCH <sub>2</sub> Cl	14–28		
14–28	CH <sub>2</sub> ClCH <sub>2</sub> Cl	21-28		
21–28	CH <sub>2</sub> ClCH <sub>2</sub> Cl	14–21		
28	CH <sub>3</sub> CN	42–43		
21–28	CH <sub>2</sub> ClCH <sub>2</sub> Cl	14–28		
28–43	CH <sub>3</sub> CN	21–28		
Concentration/ppm	Reference compound	Concentration/ppm	$\mathrm{Cl}_2/\mathrm{ppm}$	Diluent gas
5–20	CH <sub>3</sub> Cl	5–20	10–15	Air
5		10	10	$N_2$
10	CH <sub>3</sub> (O)CH <sub>3</sub>	5–10	10	Air
20		10	10	$N_2$
10	CH <sub>2</sub> Cl <sub>2</sub>	10-15	10-15	Air
10-20		10-20	10-15	$N_2$
5–20	CHCl <sub>3</sub>	10-15	10-15	Air
10–20		10-30	10	$N_2$
10.00	CIL CICIL CI	10.00	10	A :
10-20	CH <sub>2</sub> CICH <sub>2</sub> CI	10-30	10	Alf
	Concentration/ppm 28 14–28 21–28 28 21–28 28–43 Concentration/ppm 5–20 5 10 20 10 10–20 5–20 10–20 10 20 10–20 5–20	$\begin{tabular}{ c c c c c } \hline Concentration/ppm & Reference compound \\ \hline 28 & CH_2ClCH_2Cl \\ 14-28 & CH_2ClCH_2Cl \\ 21-28 & CH_2ClCH_2Cl \\ 28 & CH_3CN \\ \hline 21-28 & CH_2ClCH_2Cl \\ 28-43 & CH_3CN \\ \hline $	$\begin{tabular}{ c c c c c c c c } \hline Concentration/ppm & Reference compound & Concentration/ppm \\ \hline 28 & CH_2ClCH_2Cl & 14-28 \\ 14-28 & CH_2ClCH_2Cl & 21-28 \\ 21-28 & CH_2ClCH_2Cl & 14-21 \\ 28 & CH_3CN & 42-43 \\ 21-28 & CH_2ClCH_2Cl & 14-28 \\ 28-43 & CH_3CN & 21-28 \\ \hline $	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

Published on 19 August 2003. Downloaded by Illinois State University on 21/10/2014 20:53:57.

to remove samples of the reaction mixtures from the Teflon bag for GC analysis. Infrared spectra were obtained using a 2 litre evacuable Wilks Cell containing a multipass White mirror arrangement (3–10 m pathlength) and mounted in the cavity of the spectrometer. Ozone was prepared using a conventional ozoniser.

# Materials

Nitrogen 99.95% (Air products), synthetic air zero grade (Air Products), oxygen, medical grade (Air Products),  $CH_3COCH_3 > 99\%$  (Aldrich),  $CH_2CICOCH_3 90\%$  (Aldrich),  $CHCl_2-COCH_3 > 98\%$  (Aldrich),  $CCl_3CICOCH_3 97\%$  (Aldrich),  $CH_2FCICOCH_3 98\%$ ,  $Cl_2 99\%$  (Aldrich),  $CF_3COCH_3 97\%$  (Aldrich),  $CH_2CICH_2CI 98\%$  (BDH),  $CH_3CN 98\%$  (BDH),  $CHCl_3 99\%$  (Merck),  $CH_2Cl_2 99\%$  (BDH) were used as supplied.

# Results

Assuming that the losses of the substrate (S) and reference compounds (R) are due to reaction with X, where X is OH or Cl, alone and that dilution due to sampling is negligible, it can be shown that

$$\ln\left(\frac{[\mathbf{S}]_{t=0}}{[\mathbf{S}]_{t}}\right) = \frac{k_{\mathbf{S}}}{k_{\mathbf{R}}} \left[ \ln\left(\frac{[\mathbf{R}]_{t=0}}{[\mathbf{R}]_{t}}\right) \right]$$
(I)

where  $[S]_{t=0}$  and  $[S]_t$  are the concentrations of the substrate compound at an initial time, t = 0, and a time t later, and  $[R]_{t=0}$  and  $[R]_t$  are the concentrations of the reference compound at the same two times.  $k_S$  and  $k_R$  are the rate constants for reactions of X with S and R.

Both CCl<sub>3</sub>COCH<sub>3</sub> and CF<sub>3</sub>COCH<sub>3</sub> are susceptible to photolysis at 254 nm. so that a modified procedure is needed in the study of reactions (4) and (6). The photolysis rates  $(k_{\text{phot}})$  of these species were first determined in the absence of OH and the equation

$$\frac{1}{t}\ln\left(\frac{[\mathbf{S}]_{t=0}}{[\mathbf{S}]_{t}}\right) = k_{\text{phot}} + \frac{1}{t}\frac{k_{\mathbf{S}}}{k_{\mathbf{R}}}\left[\ln\left(\frac{[\mathbf{R}]_{t=0}}{[\mathbf{R}]_{t}}\right)\right] \tag{II}$$

was employed. Fig. 1 shows plots of  $(\ln\{[S]_{t=0}/[S]_t\})$  as a function of  $(\ln\{[R]_{t=0}/[R]_t\})$  for reactions (1), (2), (3) and (5); Fig. 2 shows plots of  $((1/t)\ln\{[S]_{t=0}/[S]_t\})$  as a function of  $((1/t)\ln\{[R]_{t=0}/[R]_t\})$  for reactions (4) and (6); and Fig. 3 shows plots of  $(\ln\{[S]_{t=0}/[S]_t\})$  as a function of  $(\ln\{[R]_{t=0}/[R]_t\})$  for reactions (7)–(12). Table 2 summarises the measured ratios  $k_S/k_R$  and lists the absolute rate coefficients for reaction of OH and Cl with the reference compounds used in this study.

### Products observed

FTIR spectroscopy was used to monitor products for reactions (7)–(12). Table 3 lists the oxidation products observed on photolysis of  $Cl_2$ /substrate mixtures in  $O_2$  at T = 298 K and at 1 atm total pressure. The interpretation of these findings is provided later.

# Discussion

## Comparison of kinetic results from different studies

A comparison of the rate coefficients determined in this and other studies is made in Table 4. The value obtained for  $k_7$  is in good agreement with that obtained in the work of Wallington *et al.*,<sup>29</sup> who also employed a relative-rate technique. More recently, Olsson *et al.*<sup>30</sup> have obtained a slightly lower rate coefficient than the one determined in this study, but which is consistent with ours within the combined error limits;



Fig. 1 Relative-rate plots in the form of eqn. (I) for the reactions of OH with acetone and halogenated ketones that are not photolysed: (a)  $CH_3COCH_3$ ; (b)  $CH_2CICOCH_3$ ; (c)  $CHCl_2COCH_3$ ; (d)  $CH_2FCOCH_3$ . The reference compound in each case was  $CH_2CICH_2CI$ .

Notario *et al.*<sup>31</sup> (using the flash-photolysis technique) have obtained a rate coefficient somewhat higher than that determined here. Apart from the value of  $k = (5.53 \pm 0.63) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the reaction of Cl with CH<sub>2</sub>Cl-COCH<sub>2</sub>Cl reported by Voicu *et al.*,<sup>36</sup> no other kinetic data for the reactions of Cl atoms with halogenated acetones appear to have been published previously.

A number of investigations have been made of  $k_1$  using both absolute and relative rate methods. The rate coefficients determined by Zetzsch,<sup>20</sup> Kerr and Stocker,<sup>22</sup> Wallington and Kurylo<sup>23</sup> and Le Calvé *et al.*<sup>24</sup> show good agreement with the rate coefficient obtained in this study, with the recent studies by Vasvari *et al.*<sup>25</sup> and Wollenhaupt *et al.*,<sup>26</sup> Gierczak *et al.*,<sup>27</sup> and Talukdar *et al.*,<sup>28</sup> still in broad agreement but towards the lower end of the range. However, the rate coefficients measured by Chiorboli *et al.*<sup>21</sup> and Cox *et al.*<sup>19</sup> employing a relative-rate technique are approximately a factor of two larger



Fig. 2 Relative-rate plots in the form of equation (II) for the reactions of OH with halogenated ketones that are photolytically labile: (a)  $CCl_3COCH_3$ ; (b)  $CF_3COCH_3$ . In both cases, the reference compound was  $CH_3CN$ .



Fig. 3 Relative-rate plots in the form of eqn. (I) for the reactions of Cl with acetone and halogenated ketones: (a)  $CH_3COCH_3$ : reference compound  $CH_3Cl$ ; (b)  $CH_2ClCOCH_3$ : reference compound  $CH_3COCH_3$ ; (c)  $CHCl_2COCH_3$ : reference compound  $CH_2Cl_2$ ; (d)  $CH_2FCOCH_3$ : reference compound  $CH_2Cl_2$ ; (e) ( $\bullet$ ),  $CCl_3COCH_3$  and ( $\Delta$ ),  $CF_3COCH_3$ : reference compound  $CHCl_3$  in both cases.

than that obtained in this study. In both investigations, OH radicals were generated by photolysis of HONO using radiation at wavelengths longer than 330 nm. Cox *et al.*<sup>19</sup> reported the rate coefficient as an upper limit, allowing for the possibility that some photolysis of acetone may have occurred during their experiments. The rate coefficient for the reaction of OH with CF<sub>3</sub>COCH<sub>3</sub> ( $k_6$ ) determined in this work is significantly lower than the value obtained by Wallington *et al.*<sup>35</sup> who used a flash-photolysis-resonance-fluorescence technique. In the present study, OH radicals were generated by photolysis of ozone at  $\lambda = 254$  nm in the presence of water vapour. The reference compounds used are not susceptible to photolysis at these wavelengths. It is thus difficult to envisage how the rate coefficient obtained in the present relative-rate study could be erroneously low, as any loss of the substrate *via* photolysis would be expected to yield a rate coefficient larger than the true value. The reaction of OH with  $CF_3COCH_3$  is quite slow and it is possible that the presence of reactive impurities in the sample used by Wallington *et al.*<sup>35</sup> may have led to an overestimation of the rate coefficient.

### Mechanistic implications of kinetic results

It is apparent from the kinetic data for OH radicals that the reactivity of methyl groups in acetone is similar to that in ethane.<sup>13</sup> This behaviour may be expected because the C–H bond dissociation energies in both compounds are approximately equal.<sup>37,38</sup> However, the carbonyl group is strongly electron withdrawing, so that reaction of the electrophilic OH radical with acetone may be considerably less facile than

Table 2 Summary of the ratios  $k_{\rm S}/k_{\rm R}$  obtained and the rate coefficients obtained from them

CX <sub>3</sub> COCH <sub>3</sub>	OH $k_{\rm S}/k_{\rm R}$	Reference compound	$10^{14} k_{\rm R}/{\rm cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Ref.	$10^{14}k_{\rm S}/{\rm cm}^3 {\rm molecule}^{-1} {\rm s}^{-1}$
CH <sub>3</sub> COCH <sub>3</sub>	$0.94\pm0.015$	CH2ClCH2Cl	$23.1 \pm 4.2$	12	$22\pm5$
CH <sub>2</sub> ClCOCH <sub>3</sub>	$1.81\pm0.12$	CH <sub>2</sub> ClCH <sub>2</sub> Cl	$23.1 \pm 4.2$	12	$42\pm8$
CHCl <sub>2</sub> COCH <sub>3</sub>	$1.66\pm0.11$	CH <sub>2</sub> ClCH <sub>2</sub> Cl	$23.1 \pm 4.2$	12	$38\pm8$
CCl <sub>3</sub> COCH <sub>3</sub>	$0.70\pm0.07$	CH <sub>3</sub> CN	$2.16\pm0.5$	13	$1.5 \pm 0.3$
CH <sub>2</sub> FCOCH <sub>3</sub>	$0.89 \pm 0.02$	CH <sub>2</sub> ClCH <sub>2</sub> Cl	$23.1 \pm 4.2$	12	$21\pm4$
CF <sub>3</sub> COCH <sub>3</sub>	$0.32\pm0.05$	CH <sub>3</sub> CN	$2.16\pm0.5$	13	$0.69\pm0.13$
CX <sub>3</sub> COCH <sub>3</sub>	Cl $k_{\rm S}/k_{\rm R}$	Reference compound	$10^{14}k_{\rm R}/{\rm cm}^3 {\rm molecule}^{-1} {\rm s}^{-1}$		$10^{13}k_{\rm S}/{\rm cm}^3 {\rm molecule}^{-1} {\rm s}^{-1}$
CH <sub>3</sub> COCH <sub>3</sub>	$4.42 \pm 0.11$	CH <sub>3</sub> Cl	$49.5\pm25$	14	$22\pm4$
CH <sub>2</sub> ClCOCH <sub>3</sub>	$0.91\pm0.05$	CH <sub>3</sub> COCH <sub>3</sub>	$220\pm44$	This work	$20\pm2$
CHCl <sub>2</sub> COCH <sub>3</sub>	$0.52\pm0.04$	$CH_2Cl_2$	$32.2 \pm 9$	15	$1.7 \pm 0.3$
CCl <sub>3</sub> COCH <sub>3</sub>	$0.18\pm0.02$	CHCl <sub>3</sub>	$9.6 \pm 2.3$	16	$0.17\pm0.03$
CH <sub>2</sub> FCOCH <sub>3</sub>	$0.64\pm0.01$	CH <sub>2</sub> ClCH <sub>2</sub> Cl	$129 \pm 40$	15	$8.2 \pm 1.6$
CF <sub>3</sub> COCH <sub>3</sub>	$0.084 \pm 0.004$	CHCl <sub>3</sub>	$9.6 \pm 2.3$	16	$0.080\pm0.016$

Compound	Frequency of absorption band /am <sup>-1</sup>	Assignment	Dof
Compound	balld/clii	Assignment	Kel.
CH <sub>3</sub> COCH <sub>3</sub>	2143	СО	17
	2349, 668	$CO_2$	17
	1105, 1775	HCOOH	This work
	2885	HC1	17
	1177, 1800	CH <sub>3</sub> COCHO	This work
	1249	CH <sub>3</sub> COOH	This work
	1451	Unidentified	
CH <sub>2</sub> ClCOCH <sub>3</sub>	2143	CO	17
	2349, 668	$CO_2$	17
	1782, 738	HCOCl	This work
	2885	HCl	17
CHCl <sub>2</sub> COCH <sub>3</sub>	2143	CO	17
	2349, 668	$CO_2$	17
	1826, 849	COCl <sub>2</sub>	This work
	2885	HCl	17
CCl <sub>3</sub> COCH <sub>3</sub>	2143	CO	17
	2349, 668	$CO_2$	17
	1826, 849	COCl <sub>2</sub>	This work
	2885	HC1	17
CH <sub>2</sub> FCOCH <sub>3</sub>	2143	CO	17
	2349, 668	$CO_2$	17
	1835, 1065	HCOF	This work
	2885	HC1	17
CF <sub>3</sub> COCH <sub>3</sub>	2349	$CO_2$	17
	2885	HC1	17
	774, 1942	$COF_2$	This work
	1200, 1809	CF <sub>3</sub> COCHO <sup>a</sup>	This work <sup>a</sup>
	1170, 1256, 1294	CF <sub>3</sub> O <sub>3</sub> CF <sub>3</sub>	18
	1117, 984	unidentified	

**Table 3** Oxidation products observed upon photolysis of  $Cl_2/sub-$ strate mixtures in O<sub>2</sub> at 1 atm total pressure and T = 298 K

<sup>*a*</sup> An authentic sample of this compound could not be obtained; the presence of this compound in the product spectrum is therefore an assumption based on a comparison with a spectrum of a sample of CH<sub>3</sub>COCHO. 'This work' denotes that the spectra were verified with an authentic sample.

Table 4 Comparison of rate coefficients at 298 K

CX <sub>3</sub> COCH <sub>3</sub>	$10^{14}k_{\rm OH}/{\rm cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	$10^{13}k_{\rm Cl}/{\rm cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	Technique	Reference
CH <sub>3</sub> COCH <sub>3</sub>	$22\pm5^a$		RR	This work
	<53		RR	19
	$23\pm3$		FR-RF	20
	$62 \pm 9$		RR	21
	$26\pm 8$		RR	22
	$21.6 \pm 1.6$		RR	23
	$18 \pm 2.4$		FP-RF	24
	$17.3\pm0.5$		DF-RF	25
	$17.5\pm0.9$		PLP	26
	$17.7\pm1.6$		PLP	27
			DF-CIMS	28
		$22 \pm 4^a$	RR	This work
		$23.7 \pm 1.2$	RR	29
		$16.9\pm3.2$	RR	30
		$30.6\pm3.8$	FP-RF	31
		$20\pm3$	RR	32
		$22\pm4$	RR	33
		$29.3\pm2.0$	PLP-RF	34
CF <sub>3</sub> COCH <sub>3</sub>	$0.69 \pm 0.13^{a}$		RR	This work
	$1.52\pm0.14$		FP-RF	35
		$0.080 \pm 0.016^a$	RR	This work

<sup>*a*</sup> Errors are twice the standard deviation and represent precision only. RR, relative rate; FP-RF, flash photolysis–resonance fluorescence; PLP, pulsed laser photolysis; DF-CIMS, discharge flow-chemical–ionization mass spectrometry.

reaction with ethane. It is interesting to note that the rate coefficient for reaction of the electrophilic Cl atom with acetone is around four times smaller than that for reaction with ethane,<sup>14</sup> suggesting that the reaction of OH and Cl with acetone may have different mechanistic features.

It has generally been assumed that the reaction of OH radicals with acetone leads to the formation of the  $CH_3COCH_2$ radical following H-atom abstraction

$$OH + CH_3COCH_3 \rightarrow CH_3COCH_2 + H_2O$$
 (16)

However, Wollenhaupt and Crowley<sup>39</sup> and Vasvari *et al.*<sup>25</sup> have reported indirect evidence for production of acetic acid. These workers suggested that addition of the OH radical to the carbon atom of the carbonyl group followed by elimination of a methyl radical from the adduct

$$OH + CH_3COCH_3 \rightarrow CH_3CO(OH)CH_3 \rightarrow CH_3COOH + CH_3$$
(17)

could be an important reaction channel. In contrast, several recent studies have provided compelling evidence that the major product is in fact  $CH_3COCH_2$ , and that formation of acetic acid is negligible below 350 K.<sup>27,28,40,41</sup>

A number of theoretical studies of the reaction of OH with acetone have also been reported.<sup>25,40,42</sup> Three possible reaction pathways have been considered: adduct formation by the addition of OH to the carbonyl carbon atom; direct H-atom abstraction; and indirect H-atom abstraction via a sixmembered hydrogen-bonded OH-acetone complex. The results show that the barrier for OH addition is sufficiently high that, in agreement with experimental results, H-atom abstraction will dominate at low temperatures. The calculations also indicate that the most likely pathway for abstraction involves the initial formation of a hydrogen-bonded complex involving the oxygen atom of the carbonyl group and the hydrogen atom of the attacking OH radical. Intramolecular transfer of a hydrogen atom from a -CH3 group to OH results in the formation of H<sub>2</sub>O and CH<sub>3</sub>COCH<sub>2</sub>. Investigations of the temperature dependence of the reaction of OH with acetone show that the reaction exhibits strong non-Arrhenius behaviour, with the overall rate coefficient increasing above room temperature, but becoming essentially constant below 250 K.<sup>24,26,27</sup> This behaviour, together with the large primary isotope effect observed by Gierczak et al.,<sup>27</sup> provides support for a mechanism involving formation of an H-bonded complex.<sup>28,43</sup> On this basis, the transition state for reaction of OH with acetone is stabilised by hydrogen bonding in a sixmembered structure so that the deactivating inductive effect of the carbonyl group is offset to some extent. Reaction of Cl atoms has also been shown to involve H-atom abstraction.<sup>44</sup> However, in this case stabilisation of the transition state is not possible and, as expected, the rate coefficient for reaction of Cl with acetone is significantly lower than that for reaction with ethane.13

Inspection of Table 2 shows that complete substitution of the hydrogens of one of the methyl groups of acetone by chlorine or fluorine atoms results in a decrease in the rate coefficient for reaction with both OH and Cl. The rate coefficients for the reactions of Cl atoms with CCl<sub>3</sub>COCH<sub>3</sub> and CF<sub>3</sub>COCH<sub>3</sub> (reactions (10) and (12)) are significantly lower (by factors of 65 and 138) than the rate coefficient for reaction of Cl with acetone (taking a per methyl rate coefficient of  $1.1 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). The corresponding reactions with OH, reactions (4) and (6), are lower by factors of approximately 7 and 16 with respect to reaction (1). The reduction in reactivity observed on halogenation of acetone may be due to the changes in the overall enthalpy and/or to destabilising polar effects in the transition state. The C–H bond strength<sup>37</sup> for CH<sub>3</sub>COCH<sub>3</sub> is 411.3 ± 7.5 kJ mol<sup>-1</sup> and thus reactions with both OH radicals and Cl atoms are appreciably exothermic<sup>38</sup>

 $(D{H-OH} = 491 \text{ kJ mol}^{-1}, D{H-Cl} = 425 \text{ kJ mol}^{-1}).$ Bond dissociation energies have not been determined for the halogenated acetones. Information on the bond dissociation energies for halocarbons is somewhat limited,37 but it would appear that halogenation of the  $\beta$ -carbon does not lead to significant changes in the C-H bond energies. It is therefore reasonable to assume that, for CF<sub>3</sub>COCH<sub>3</sub> and CCl<sub>3</sub>COCH<sub>3</sub>, halogenation will not sufficiently strengthen the C-H bonds to account for the observed changes in reactivity. We suggest that the relatively large decreases in reactivity on substitution are mainly a consequence of polar effects in the transition states. The transition states of highly exothermic reactions are normally assumed to be similar in structure and energy to the reactants.45 Charge separation in the halogenated acetones would therefore be expected to persist in the transition state for the reactions with both OH radicals and Cl atoms. Assuming that these reactions involve overall hydrogen-atom abstraction, the transition states involve a hydrogen atom positioned between the attacking OH radical or Cl atom and the CX<sub>3</sub>COCH<sub>2</sub> radical. Halogen substitution will reduce the electron density around the abstracted H atom, and thus destabilise the transition states compared with those formed with CH<sub>3</sub>COCH<sub>3</sub>. Furthermore, these transition states will be increasingly destabilised as the degree of the charge separation increases. The reduction in reactivity upon substitution by the more electronegative fluorine atoms is greater than that observed in Cl atom substitution, as would be expected.

In order to investigate further the electron-withdrawing inductive effect of halogen substitution on the reactivity of halogenated acetones, we examined the possibility of a correlation between the rate coefficients and the electronegativities of the halogenated methyl group. The simple sum of the Pauling electronegativities of substituent atoms can be a useful measure of the withdrawal of valence electrons from a central carbon atom, as demonstrated by Thomas.<sup>46</sup> In a study by Seetula and Gutman,<sup>47</sup> a linear relationship was found between the reactivities towards hydrogen iodide of a series of substituted methyl radicals and the sum of the Pauling electronegativities of the substituents on the methyl group. Fig. 4 shows our data displayed in a similar way: the logarithms of the room-temperature rate coefficients (per CH<sub>3</sub> group) for the reaction of the halogenated species towards OH and Cl are plotted against the group electronegativities of the halogen-substituted CX<sub>3</sub> group. Pauling electronegativities of Cl, F and H are taken to be<sup>48</sup> 3.16, 3.98 and 2.20. Examining first the kinetics of

00

Δ

Δ

-32

\*-3 ∦u

-28

 $\wedge$ 



9

Group electronegativity

10

11

12

°

Δ

8

the reactions with OH, Fig. 4 (circles) shows that there is a good correlation for the reactions with  $CH_3COCH_3$ ,  $CCl_3COCH_3$  and  $CF_3COCH_3$ . However, the rate-coefficient data for the mono- and di-halogenated acetones do not fit on the same line, and appear to belong to a different correlation. Hydroxyl radicals could attack substituted acetones containing a partially halogenated methyl group in two ways

$$OH + CH_2 XCOCH_3 \rightarrow CH XCOCH_3 + H_2 O$$
 (18)

$$OH + CH_2XCOCH_3 \rightarrow CH_2XCOCH_2 + H_2O (X = F \text{ or } Cl)$$
(19)

It is possible that different correlations for fully and partially substituted acetones arise because of OH attack at the carbon atom bonded to the chlorine or fluorine atoms. Substitution of a hydrogen atom by Cl or F atoms in a methyl group reduces the bond dissociation energies of the remaining C–H bonds.<sup>37</sup> Hence, on the basis of the reaction enthalpies, it might be expected that hydrogen-atom abstraction will be dominated by removal from the halogenated methyl group rather than the unsubstituted methyl group. The rate coefficients  $(k_1)$ – $(k_6)$  provide some support for this argument, since the rate coefficients per methyl group for the reactions of OH with CH<sub>2</sub>ClCOCH<sub>3</sub>, CHCl<sub>2</sub>COCH<sub>3</sub> and CH<sub>2</sub>FCOCH<sub>3</sub> are larger than that for the reaction of OH with acetone.

We consider now the reactivity of Cl atoms towards the ketones. Fig. 4 shows that, although there is still an evident decrease in reactivity with increased group electronegativity, the case for a linear correlation is less clear than it is for the reactions of OH. Nevertheless, if a trend of reactivity is drawn as a curve through the data points for the CH<sub>3</sub>-, CCl<sub>3</sub>- and CF<sub>3</sub>- compounds, it is clear that the mono- and di-substituted acetones are substantially more reactive than the compounds that do not have both hydrogen and halogen attached to the same carbon atom. The products detected for reaction (9) provide strong evidence that hydrogen abstraction by Cl occurs almost exclusively at the CHCl<sub>2</sub> group for CHCl<sub>2</sub>COCH<sub>3</sub>, as explained subsequently in the section discussing the observed products. Tschuikow-Roux *et al.*<sup>49,50</sup> have carried out studies of the kinetics and products of the photochlorination of a series of halogenated ethanes. The rate-coefficient ratios for abstraction at the halogenated methyl group relative to the methyl group determined at 298 K for CH<sub>2</sub>ClCH<sub>3</sub>, CHCl<sub>2</sub>CH<sub>3</sub><sup>49</sup> and CH<sub>2</sub>FCH<sub>3</sub><sup>50</sup> are approximately 6, 12 and 10, respectively. These results provide further support for the assertion that abstraction is occurring at the halogenated methyl group for reactions (8), (9) and (11).

Table 5 displays our values for the rate coefficients determined in the present study alongside those reported for the reactions of Cl atoms and OH radicals with the corresponding halogenated ethanes. Similar reactivity trends in the Cl atom and OH radical data for the ketones and alkanes are expected on the basis of the structural similarities of the  $\alpha$ -halogenated acetones, CX<sub>3</sub>COCH<sub>3</sub>, with the  $\alpha$ -halogenated ethanes, CX<sub>3</sub>CH<sub>3</sub>, (X = H, F, Cl). Fig. 5 shows logarithmic plots of rate coefficients for reaction with the halogenated acetone as a function of those for reaction with the corresponding halogenated ethanes for reaction with both OH and Cl. In both cases, the apparent linearity of the correlations confirms the suspected similarity in trends for the two reaction series.

The experimental data indicate that the reactions of OH or Cl with  $CH_2ClCOCH_3$ ,  $CHCl_2COCH_3$  and  $CH_2FCOCH_3$  involve abstraction mainly from the halogenated methyl group. As Table 5 shows, the rate coefficients for reaction of OH with acetone and these halogenated acetones are quite similar to those for reaction with the corresponding halogenated alkanes. Assuming that the C–H bond strengths in the acetones and the alkanes do not differ greatly, the similarities in the rate coefficients imply that, as for the reaction of OH with acetone, the deactivating effect of the carbonyl group is

CX <sub>3</sub> COCH <sub>3</sub>	$10^{14}k_{\rm OH}/{\rm cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	CX <sub>3</sub> CH <sub>3</sub>	$10^{14}k_{\rm OH}/{\rm cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	Ref.
CH <sub>3</sub> COCH <sub>3</sub>	$22\pm5$	CH <sub>3</sub> CH <sub>3</sub>	25.5	13
CH <sub>2</sub> ClCOCH <sub>3</sub>	$42\pm 8$	CH <sub>2</sub> ClCH <sub>3</sub>	42.3	51
CHCl <sub>2</sub> COCH <sub>3</sub>	$38\pm8$	CHCl <sub>2</sub> CH <sub>3</sub>	25.9	51
CCl <sub>3</sub> COCH <sub>3</sub>	$1.5 \pm 0.3$	CCl <sub>3</sub> CH <sub>3</sub>	1.0	16
CH <sub>2</sub> FCOCH <sub>3</sub>	$21\pm4$	CH <sub>2</sub> FCH <sub>3</sub>	20	13
CF <sub>3</sub> COCH <sub>3</sub>	$0.69\pm0.13$	CF <sub>3</sub> CH <sub>3</sub>	0.13	13
CX <sub>3</sub> COCH <sub>3</sub>	$\frac{10^{13}k_{\rm Cl}/\rm cm^3}{\rm molecule^{-1}~s^{-1}}$	CX <sub>3</sub> CH <sub>3</sub>	$10^{13}k_{\rm Cl}/{\rm cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	Ref.
CX <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> COCH <sub>3</sub>	$\frac{10^{13}k_{\rm Cl}/{\rm cm}^3}{{\rm molecule}^{-1}~{\rm s}^{-1}}$ $22 \pm 4$	CX <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	$\frac{10^{13}k_{\rm Cl}/{\rm cm}^3}{\rm molecule}^{-1}{\rm s}^{-1}$ 569	Ref. 14
CX <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> COCH <sub>3</sub> CH <sub>2</sub> CICOCH <sub>3</sub>	$ \frac{10^{13}k_{Cl}/cm^{3}}{molecule^{-1} s^{-1}} \\ \frac{22 \pm 4}{20 \pm 2} $	CX <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> ClCH <sub>3</sub>	$\frac{10^{13}k_{Cl}/cm^{3}}{molecule^{-1} s^{-1}}$ 569 128	Ref. 14 49
CX <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> COCH <sub>3</sub> CH <sub>2</sub> ClCOCH <sub>3</sub> CHCl <sub>2</sub> COCH <sub>3</sub>	$\frac{10^{13}k_{\rm Cl}/\rm cm^3}{\rm molecule^{-1}~\rm s^{-1}}$ $\frac{22 \pm 4}{20 \pm 2}$ $1.7 \pm 0.3$	CX <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> ClCH <sub>3</sub> CHCl <sub>2</sub> CH <sub>3</sub>	$ \begin{array}{c} 10^{13}k_{\rm Cl}/{\rm cm}^{3} \\ \text{molecule}^{-1} {\rm s}^{-1} \\ 569 \\ 128 \\ 12.0 \end{array} $	Ref. 14 49 49
CX <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> COCH <sub>3</sub> CH <sub>2</sub> ClCOCH <sub>3</sub> CHCl <sub>2</sub> COCH <sub>3</sub> CCl <sub>3</sub> COCH <sub>3</sub>	$     \begin{array}{r} 10^{13}k_{\rm Cl}/{\rm cm}^{3} \\                                   $	CX <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> ClCH <sub>3</sub> CHCl <sub>2</sub> CH <sub>3</sub> CCl <sub>3</sub> CH <sub>3</sub>	$ \begin{array}{c} 10^{13}k_{\rm Cl}/{\rm cm}^{3} \\ \text{molecule}^{-1} \ {\rm s}^{-1} \\ 569 \\ 128 \\ 12.0 \\ 0.1 \end{array} $	Ref. 14 49 49 52
CX <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> COCH <sub>3</sub> CH <sub>2</sub> ClCOCH <sub>3</sub> CHCl <sub>2</sub> COCH <sub>3</sub> CCl <sub>3</sub> COCH <sub>3</sub> CCl <sub>3</sub> COCH <sub>3</sub>	$\frac{10^{13}k_{\rm Cl}/\rm cm^3}{\rm molecule^{-1}\ s^{-1}}$ $\frac{22 \pm 4}{20 \pm 2}$ $1.7 \pm 0.3$ $0.17 \pm 0.03$ $8.2 \pm 1.6$	CX <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> ClCH <sub>3</sub> CHCl <sub>2</sub> CH <sub>3</sub> CCl <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> FCH <sub>3</sub>	$ \begin{array}{c} 10^{13}k_{\rm Cl}/{\rm cm}^{3} \\ \text{molecule}^{-1}  {\rm s}^{-1} \\ 569 \\ 128 \\ 12.0 \\ 0.1 \\ 65.1 \end{array} $	Ref. 14 49 49 52 50

counterbalanced by stabilisation of the reaction transition state through hydrogen bonding in an OH–halogenatedacetone complex possessing a six-membered ring. The rate coefficients for reaction of OH with CCl<sub>3</sub>CH<sub>3</sub> and CF<sub>3</sub>CH<sub>3</sub> are much smaller than for reaction with ethane and can be rationalised largely in terms of the electron-withdrawing effect of the –CCl<sub>3</sub> and –CF<sub>3</sub> groups. In a similar manner, the reduction in reactivity of CCl<sub>3</sub>COCH<sub>3</sub> and CF<sub>3</sub>COCH<sub>3</sub> compared to acetone is largely a function of the inductive effect of the halogenated methyl group. As expected, the reduction in reactivity is less than for the halogenated ethanes since the abstracted H atoms are positioned  $\beta$  to the halogenated methyl group as opposed to the  $\alpha$  position in the case of the halogenated ethanes.

Whereas the rate coefficients for reaction of OH with  $CH_3COCH_3$ ,  $CH_2CICOCH_3$ ,  $CHcl_2COCH_3$  and  $CH_2F$ -COCH<sub>3</sub> are similar to those for reaction with the corresponding ethanes, the rate coefficients for the reaction of Cl with the ketones and the corresponding alkanes are quite different (see Table 5). In all cases, the rate coefficients for the reaction with the halogenated acetones are much smaller than for reaction with the analogous ethanes and can be explained in terms of the inductive effect of the carbonyl group. As for the reaction



Fig. 5 Reactivity of OH and Cl towards halogenated acetones as a function of their reactivity towards halogenated alkanes: ( $\bigcirc$ ), OH; ( $\Delta$ ), Cl.

of OH with  $CCl_3COCH_3$  and  $CF_3COCH_3$ , the rate coefficients for reaction of Cl with these compounds are larger than with  $CCl_3CH_3$  and  $CF_3CH_3$ , thus providing further evidence for the role of the carbonyl group in attenuating the reactivity of the halogenated acetones compared to the corresponding halogenated alkanes.

As expected for reactions having different mechanistic features, the slope of Fig. 5 is different for the reactions of OH and Cl. The slope of the plot for OH is near unity, whereas that for Cl atoms has a slope of around 0.5.

# **Products of reactions**

In this section, we attempt to rationalise in terms of acceptable chemical reactions the products observed by FTIR spectroscopy (see Table 3) in the Cl-initiated oxidation of the ketones. We commence the discussion with reference to the general cases of the mono- and di-halogenated species, and then turn to the special cases of  $CH_3COCH_3$ ,  $CCl_3COCH_3$  and  $CF_3COCH_3$ .

Consider first the compound  $CHCl_2COCH_3$ . If abstraction occurs at the unsubstituted methyl group, HCOCl would be expected as a product from the following mechanism

 $Cl + CHCl_2COCH_3 \rightarrow CHCl_2COCH_2 + HCl \qquad (20a)$ 

$$CHCl_2COCH_2 + O_2 + M \rightarrow CHCl_2COCH_2O_2 + M$$
(21)  
2 CHCl\_2COCH\_2O\_2 \rightarrow 2 CHCl\_2COCH\_2O + O\_2 (22)

$$CHCl_2COCH_2O \rightarrow CHCl_2CO + HCHO$$
 (23)

$$CHCl_2CO \rightarrow CHCl_2 + CO$$
 (24)

$$CHCl_2 + O_2 + M \rightarrow CHCl_2O_2 + M \tag{25}$$

$$2 \text{ CHCl}_2\text{O}_2 \rightarrow 2 \text{ CHCl}_2\text{O} + \text{O}_2 \tag{26}$$

$$CHCl_2O \rightarrow HCOCl + Cl$$
 (27)

On the other hand, if abstraction occurs at the halogenated methyl group,  $COCl_2$  is the expected product

 $Cl + CHCl_2COCH_3 \rightarrow CCl_2COCH_3 + HCl$  (20b)

$$CCl_2COCH_3 + O_2 + M \rightarrow CCl_2O_2COCH_3 + M \equal (28)$$

$$2 \operatorname{CCl}_2 \operatorname{O_2COCH}_3 \to 2 \operatorname{CCl}_2 \operatorname{OCOCH}_3 + \operatorname{O_2}$$
(29)

$$CCl_2OCOCH_3 \rightarrow COCl_2 + CH_3CO$$
 (30)

 $COCl_2$  and not HCOCl is observed in the oxidation of  $CHCl_2COCH_3$ , so that abstraction must, indeed, occur at the halogenated methyl group. The nature of the products arising from the oxidation of the monohalogenated acetones gives no information on the site of reaction since abstraction at either the unsubstituted or substituted methyl group produces HCOX (X = F or Cl). The reaction sequence initiated in the first case is

$$Cl + CH_2XCOCH_3 \rightarrow CH_2XCOCH_2 + HCl$$
 (31a)

$$CH_2XCOCH_3 + O_2 + M \rightarrow CH_2XCOCH_2O_2 + M$$
 (32)

$$2 \text{ CH}_2 \text{XCOCH}_2 \text{O}_2 \rightarrow 2 \text{ CH}_2 \text{XCOCH}_2 \text{O} + \text{O}_2 \tag{33}$$

$$CH_2XCOCH_2O \rightarrow CH_2XCO + HCHO$$
 (34)

$$CH_2XCO \rightarrow CH_2X + CO$$
 (35)

$$CH_2X + O_2 + M \rightarrow CH_2XO_2 + M \tag{36}$$

$$2 \operatorname{CH}_2 \operatorname{XO}_2 \to 2 \operatorname{CH}_2 \operatorname{XO} + \operatorname{O}_2 \tag{37}$$

$$CH_2XO + O_2 \rightarrow HCOX + X$$
 (38)

and in the second

$$Cl + CH_2XCOCH_3 \rightarrow CHXCOCH_3 + HCl$$
 (31b)

$$CHXCOCH_3 + O_2 + M \rightarrow CHXO_2COCH_3 + M$$
 (39)

$$2 \text{ CHXO}_2 \text{COCH}_3 \rightarrow 2 \text{ CHXOCOCH}_3 + \text{O}_2$$
 (40)

$$CHXOCOCH_3 \rightarrow HCOX + CH_3CO$$
 (41)

We now turn to a discussion of the products observed in the oxidation of  $CH_3COCH_3$ ,  $CCl_3COCH_3$  and  $CF_3COCH_3$ . In addition to CO and  $CO_2$ , methyl glyoxal ( $CH_3COCHO$ ), formic acid (HCOOH) and acetic acid ( $CH_3COOH$ ) were observed as products of the oxidation of acetone. Formation of methyl glyoxal is expected in two reactions of oxy- and peroxy-radicals that will be intermediates in the oxidation

$$Cl + CH_3COCH_3 \rightarrow CH_3COCH_2 + HCl$$
 (42)

$$CH_3COCH_2 + O_2 + M \rightarrow CH_3COCH_2O_2 + M$$
 (43)

$$2 \text{ CH}_3\text{COCH}_2\text{O}_2 \rightarrow 2 \text{ CH}_3\text{COCH}_2\text{O} + \text{O}_2$$
(44)

 $2 \text{ CH}_3\text{COCH}_2\text{O}_2 \rightarrow \text{CH}_3\text{COCHO} + \text{CH}_3\text{COCH}_2\text{OH} + \text{O}_2$ 

$$CH_3COCH_2O + O_2 \rightarrow CH_3COCHO + HO_2$$
 (46)

Generation of formic acid requires a secondary oxidation process involving the hydroxyacetone (CH<sub>3</sub>COCH<sub>2</sub>OH) produced in reaction (45)

$$Cl + CH_3COCH_2OH \rightarrow CH_3COCHOH + HCl$$
 (47)

$$CH_3COCHOH + O_2 + M \rightarrow CH_3COCH(O_2)OH + M$$
 (48)

$$CH_3COCH(O_2)OH + RO_2 \rightarrow CH_3COCH(O)OH + RO + O_2$$

(49)

(55)

(45)

$$CH_3COCH(O)OH + O_2 \rightarrow CH_3COO_2 + HCOOH$$
 (50)

 $RO_2$  here represents generically any of the peroxy radicals generated in the system. A possible source of acetic acid is the cross reaction between the two peroxy radicals<sup>53</sup>

$$\label{eq:COO2} \begin{split} CH_3COO_2 + CH_3COCH_2O_2 &\rightarrow CH_3COOH \\ &+ CH_3COCHO + O_2 \quad (51) \end{split}$$

In the oxidation of  $CCl_3COCH_3$ , the major carbonyl species observed was  $COCl_2$  (phosgene) with a yield close to 100% based on the loss of  $CCl_3COCH_3$ . Formation of phosgene is consistent with a mechanism in which the radical  $CCl_3O$  is the ultimate source

$$Cl + CCl_3COCH_3 \rightarrow CCl_3COCH_2 + HCl$$
 (52)

$$CCl_3COCH_2 + O_2 + M \rightarrow CCl_3COCH_2O_2 + M$$
 (53)

$$2 \text{ CCl}_3\text{COCH}_2\text{O}_2 \rightarrow 2 \text{ CCl}_3\text{COCH}_2\text{O} + \text{O}_2 \tag{54}$$

$$2 \text{ CCl}_3\text{COCH}_2\text{O}_2 \rightarrow \text{CCl}_3\text{COCHO} + \text{CCl}_3\text{COCH}_2\text{OH} + \text{O}_2$$

$$CCl_3COCH_2O + O_2 \rightarrow CCl_3COCHO + HO_2 \qquad (56)$$

$$CCl_3COCH_2O \rightarrow CCl_3CO + HCHO$$
 (57)

$$CCl_3CO \rightarrow CCl_3 + CO$$
 (58)

$$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$$
<sup>(59)</sup>

$$CCl_3O_2 + RO_2 \rightarrow CCl_3O + RO + O_2 \tag{60}$$

$$CCl_3O \rightarrow COCl_2 + Cl$$
 (61)

The absence of CCl<sub>3</sub>COCHO suggests either that reactions (55) and (56) are unimportant or that the carbonyl is rapidly photo-oxidised

$$CCl_3COCHO + h\nu \rightarrow CCl_3CO + HCO$$
 (62)

The presence of CO could be evidence that photo-oxidation of  $CCl_3COCHO$  is occurring *via* reaction (58), a process in which decomposition of  $CCl_3CO$  has been observed to dominate over addition of  $O_2$ .<sup>54</sup> Oxidation of HCO (derived from reaction

$$HCO + O_2 \rightarrow HO_2 + CO$$
 (63)

The main products identified from the oxidation of  $CF_3COCH_3$  were  $CF_2O$ ,  $CF_3O_3CF_3$ , HCl and  $CO_2$ . The yield of  $CF_2O$  was approximately 10% of the loss of  $CF_3COCH_3$ . In addition, a major degradation product showed strong absorption bands in the 1100–1300 cm<sup>-1</sup> region and at 1813 cm<sup>-1</sup>. This product was tentatively identified as trifluoromethyl-glyoxal on the basis of a comparison with the spectrum of  $CH_3COCHO$ . A mechanism which is consistent with the observed products is

$$Cl + CF_3COCH_3 \rightarrow CF_3COCH_2 + HCl$$
 (64)

$$CF_3COCH_2 + O_2 + M \rightarrow CF_3COCH_2O_2 + M \eqno(65)$$

$$2 \text{ CF}_3\text{COCH}_2\text{O}_2 \rightarrow 2 \text{ CF}_3\text{COCH}_2\text{O} + \text{O}_2$$
 (66)

$$2\ CF_3COCH_2O_2 \rightarrow CF_3COCHO + CF_3COCH_2OH + O_2$$

$$CF_3COCH_2O + O_2 \rightarrow CF_3COCHO + HO_2$$
 (68)

$$CF_3COCH_2O \rightarrow CF_3CO + HCHO$$
 (69)

$$CF_3CO + O_2 + M \rightarrow CF_3COO_2 + M$$
(70)

The dominant reaction for the alkoxy radical,  $CF_3COCH_2O$  will probably be C–C bond cleavage to produce  $CF_3CO$  and HCHO. This process is certainly dominant in the case of  $CH_3COCH_2O$ .<sup>32</sup> Hence, it is more likely that the trifluoromethylglyoxal arises from reaction (67), rather than from reaction (68). Zabel *et al.*<sup>54</sup> have shown that  $CF_3CO$  adds to  $O_2$  in preference to decomposition (producing CO). We observe little or no CO, in accord with this conclusion.  $CF_3O_3CF_3$  and  $COF_2$  will be formed in a sequence of reactions starting from the  $CF_3COO_2$  radical

$$CF_3COO_2 + RO_2 \rightarrow CF_3COO + RO + O_2$$
 (71)

$$CF_3COO \rightarrow CF_3 + CO_2$$
 (72)

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \tag{73}$$

$$CF_3O_2 + RO_2 \rightarrow CF_3O + RO + O_2 \tag{74}$$

$$CF_3O \rightarrow COF_2$$
 (75)

$$CF_3O_2 + CF_3O + M \rightarrow CF_3O_3CF_3 + M$$
 (76)

Reaction (75) is written as shown specifically to indicate the formation of COF<sub>2</sub>, which is always found in systems containing CF<sub>3</sub>O. In the present instance, the process might involve interaction with Cl atoms, water clusters, or a heterogeneous reaction. Several of the reactions in the schemes that we have proposed involve the interaction of two peroxy radicals, and we now compare some of these processes. Lightfoot et al.53 have discussed in some detail possible mechanisms for the self-reaction of peroxy radicals, and have shown that there are two main channels, one forming two alkoxy radicals (e.g. reaction (66)), and one forming a carbonyl and an alcohol (e.g. reaction (67)), which may proceed via a complex intermediate. The products that we have observed in the present study are consistent with the hypothesis that the self reaction for CCl<sub>3</sub>COCH<sub>2</sub>O<sub>2</sub> proceeds mainly via the alkoxy channel followed by decomposition via reaction (57) of the alkoxy radical (since CCl<sub>3</sub>COCHO is not observed), whereas the self reaction of CF<sub>3</sub>COCH<sub>2</sub>O<sub>2</sub> proceeds at least in part via the carbonyl/ alcohol channel (since CF<sub>3</sub>COCHO is observed). We have considered the possibility that photolysis of CCl<sub>3</sub>COCHO may prevent its detection, but, at least to a first approximation, the photolysis rates for CCl<sub>3</sub>COCHO and CF<sub>3</sub>COCHO can be assumed to be comparable. It is interesting that in the case of the self-reaction of CH<sub>2</sub>ClO<sub>2</sub> the alkoxy channel accounts for nearly 100% of the reaction, whereas for CH<sub>2</sub>FO<sub>2</sub> it only accounts for roughly 70%.53 Perhaps this difference indicates that the  $RO_4R$  intermediate discussed by Lightfoot *et al.*<sup>53</sup> is particularly stable when R contains fluorine atoms.<sup>55</sup>

### Atmospheric lifetimes

The most likely fate of the halogenated acetones in the Earth's atmosphere is either reaction with OH or photolysis. We have used the Cambridge 2-dimensional model<sup>11</sup> to determine lifetimes for the species studied with respect to loss via reaction with OH. Fig. 6 shows the globally averaged loss rate constant (1/lifetime) for these species in reaction with OH. It can be seen readily that in the troposphere the lifetimes of these species with respect to loss via reaction with OH are quite large (many months). The absorption spectrum of only acetone is known quantitatively. To provide an estimate of the photolysis rates, ultra-violet absorption spectra for most of the halogenated acetones were recorded at low resolution (ca. 1 nm) using 10 torr of the compound in a cell of pathlength 10 cm; Fig. 7 shows the spectra. It is possible to estimate the absolute absorption cross-sections and hence the photolysis rates for the halogenated acetones by simple scaling to the cross section<sup>1</sup> for acetone over the wavelength range of interest (300-400 nm). This analysis suggests that the photolysis rates for all the halogenated acetones are larger than that for acetone. If it is assumed that the quantum yields for decomposition are the same as those for acetone as published,<sup>56</sup> then rates of photolysis of CF3COCH3 and CCl3COCH3 are about two and three times that for acetone, respectively. The photolysis rates for the other halogenated acetones lie somewhere between these extremes. The calculations show that, for acetone itself, photolysis is at least five times more rapid than attack by OH (at an altitude of ca. 30 km), and up to 100 times faster at other altitudes. It follows, then, that photolysis dominates over chemical reaction with OH as the primary sink of all the halogenated acetones. Indeed, if the quantum yield for dissociation were to approach unity for the halogenated species, then the photolysis rates become very much greater than that for acetone (40 and 80 times for CF<sub>3</sub>COCH<sub>3</sub> and CCl<sub>3</sub>COCH<sub>3</sub>), and the lifetimes against photolysis correspondingly shorter. There is some support for a relatively high quantum yield for loss of halogenated acetones, as described<sup>57</sup> by Lee and Lewis: Bowles et al., 58,59 for example, find quantum yields for CO formation to be 0.74-0.92 for the photolysis of two fully halogenated acetones at  $\lambda = 313$  nm and 254 nm. Recent work by Burkholder *et al.*<sup>60</sup> has shown that the quantum yield for



Fig. 6 Globally averaged loss rate constants and lifetimes for attack by OH radicals on the ketones studied. These rates were calculated using the Cambridge 2-dimensional model:<sup>11</sup> (a)  $CF_3COCH_3$ ; (b)  $CCl_3COCH_3$ ; (c)  $CH_2FCOCH_3$ ; (d)  $CH_3COCH_3$ ; (e)  $CHCl_2COCH_3$ ; (f)  $CH_2CICOCH_3$ .





**Fig. 7** UV spectra of acetone and four of its halogenated derivatives. Optical path = 10 cm; pressure of compound = 10 Torr:<sup>11</sup> (a)  $CF_3COCH_3$ ; (b)  $CCl_3COCH_3$ ; (c)  $CH_3COCH_3$ ; (d)  $CHCl_2COCH_3$ ; (e)  $CH_2CICOCH_3$ .

photodissociation of CH<sub>2</sub>ClCOCH<sub>3</sub> is 0.5 at both  $\lambda = 308$  nm and at  $\lambda = 351$  nm (while the quantum yield for CH<sub>2</sub>BrCOCH<sub>3</sub> loss is unity at the longer wavelength and apparently greater than unity at the shorter one). It seems reasonable to suppose, therefore, that the quantum yields for the halogenated acetones studied in this work are also most likely near to unity. Unpublished results from Pilling and coworkers<sup>61</sup> suggest an atmospheric rate of photolysis of acetone itself that is roughly two times smaller than has been calculated previously. Even so, it is clear that photolysis is by far the most important tropospheric loss process. In summary, then, it would appear that the halogenated acetones studied in this work will have tropospheric lifetimes of less than a month, and photolysis will be the dominant loss process for the halogenated species, particularly for CF<sub>3</sub>COCH<sub>3</sub>.

# Acknowledgements

The authors acknowledge with gratitude the partial support of this research by the European Commission in the project 'HALOBUD' (ENV4-CT97-0393). They also wish to thank Forbairt and the British Council for the award of a grant under their joint research scheme.

The Biogeochemistry Research Centre at Bristol is a joint initiative between the School of Chemistry and the Departments of Geology and Geography.

### References

- 1 M. J. Molina and F. S. Rowland, *Nature*, 1974, 249, 810.
- 2 J. C. Farman, B. G. Gardiner and J. D. Shanklin, *Nature*, 1985, 315, 207.
- 3 R. P. Wayne, *Chemistry of Atmospheres*, Oxford University Press, Oxford, 3rd edn., 2000.
- 4 O. Wild, O. V. Rattigan, R. L. Jones, R. A. Cox and J. A. Pyle, J. Atmos. Chem., 1996, 25, 167.
- 5 H. B. Singh, D. O'Hara, D. Herlth, W. Sachse, D. R. Blake, J. D. Bradshaw, M. Kanakidou and P. J. Crutzen, J. Geophys. Res., 1994, 99, 1805.
- 6 H. B. Singh, M. Kanakidou, P. J. Crutzen and D. J. Jacob, *Nature*, 1995, **378**, 50.
- 7 F. Arnold, G. Knop and H. Zierens, Nature, 1986, 321, 505.
- 8 F. Arnold, V. Burger, B. Drost-Fanke, F. Grimm, J. Schneider, A. Krieger and T. Stile, *Geophys. Res. Lett.*, 1997, 24, 3017.

- S. Carr, J. J. Treacy, H. W. Sidebottom, R. K. Connell, C. E. Canosa-Mas, R. P. Wayne and J. Franklin, Chem. Phys. Lett., 1994, 227, 39
- D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. MacLeod and S. Téton, 10 I. Phys. Chem., 1993, 97, 4683.
- K.S. Law and J.A. Pyle, J. Geophys. Res., 1993, 98, 18377.
- S.-B. Xing, S.-H. Shi and L.-X. Qiu, Int. J. Chem. Kinet., 1992, 12 24, 1.
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. 13 Kerr, M. J. Rossi and J. Troe, J. Phys. Chem. Ref. Data, 1997, 26, 521.
- 14 R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr and J. Troe, J. Phys. Chem. Ref. Data, 1989, 18, 881.
- E. Tschuikow-Roux, F. Faraji, S. Paddison, J. Niedzielski and K. Miyokawa, J. Phys. Chem., 1988, 92, 1488.
   S. P. Sander, M. J. Kurylo, V. L. Orkin, D. M. Golden, R. E.
- Huie, B. J. Finlayson-Pitts, C. E. Kolb, M. J. Molina, R. R. Friedl, A. R. Ravishankara and G. K. Moortgat, Chemical kinetics and photochemical data for use in atmospheric studies, JPL Publication No. 02-25, JPL/NASA, Pasadena, CA, 2003.
- 17 G. Herzberg, Molecular Structure and Molecular Structure, II: Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold, New York, 1945; K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules, Van Nostrand Reinhold, New York, 1979.
- 18 E. C. Tuazon and R. Atkinson, J. Atmos. Chem., 1993, 17, 179.
- 19 R. A. Cox, R. G. Derwent and M. R. Williams, Environ. Sci. Technol., 1980, 14, 57.
- C. Zetzsch, Rate constants for the reactions of OH with acetone and 20 methylethylketone in the gas phase, Abstracts, Seventh Inter-national Symposium on Gas Kinetics, Göttingen, Aug., 1982.
- 21 C. Chiorboli, C. A. Bignozzi, A. Maldotti, P. F. Giardini, A. Rossi and V. Carassiti, Int. J. Chem. Kinet., 1983, 15, 579.
- J. A. Kerr and D. W. Stocker, J. Atmos. Chem., 1986, 4, 253. 22
- 23 T. J. Wallington and M. J. Kurylo, J. Phys. Chem., 1987, 91, 5050.
- S. Le Calvé, D. Hitier, G. Le Bras and A. Mellouki, J. Phys. 24 Chem. A, 1998, 102, 4579.
- G. Vasvari, I. Szilagyi, A. Bencsura, S. Dobe, T. Berces, E. Henon, S. Canneaux and F. Bohr, *Phys. Chem. Chem. Phys.*, 25 2001, 3, 551.
- M. Wollenhaupt, S. A. Carl, A. Horowitz and J. N. Crowley, 26 J. Phys. Chem. A, 2000, 104, 2695.
- 27 T. Gierczak, M. K. Gillies, S. Bauerle and A. R. Ravishankara, J. Phys. Chem. A, 2003, 107, 5014.
- R. K. Talukdar, T. Gierczak, D. C. McCab Ravishankara, J. Phys. Chem. A, 2003, 107, 5021. 28 McCabe and A. R.
- 29 T. J. Wallington, J. M. Andino, J. C. Ball and S. M. Japar, J. Atmos. Chem., 1990, 10, 301.
- 30 B. E. R. Olsson, M. Hallquist, E. Ljungström and J. Davidsson, Int. J. Chem. Kinet., 1997, 29, 195.
- A. Notario, A. Mellouki and G. Le Bras, Int. J. Chem. Kinet., 31 2000. 32. 62.

- J. J. Orlando, G. S. Tyndall, L. Vereecken and J. Peeters, J. Phys. 32 Chem A. 2000. 104 11 578
- L. K. Christensen, J. C. Ball and T. J. Wallington, J. Phys. Chem. 33 A, 2000, 104, 345.
- 34 J. Albaladejo, A. Notario, C. A. Cuevas, B. Ballesteros and E. Martínez, J. Atmos. Chem., 2003, 45, 35.
- 35 T. J. Wallington, P. Dagaut and M. J. Kurylo, J. Phys. Chem., 1988, 92, 5024.
- I. Voicu, I. Barnes, K. H. Becker, T. J. Wallington, Y. Inoue and M. Kawasaki, J. Phys. Chem. A, 2001, 105, 5123. 36
- CRC Handbook of Chemistry and Physics, ed. D. R. Lide, CRC 37 Press, Boca Raton, FL, 74th edn., 1993.
- 38 D. F. McMillen and D. M. Golden, Annu. Rev. Phys. Chem., 1982, 33, 493.
- 39 M. Wollenhaupt and J. N. Crowley, J. Phys. Chem. A, 2000, 104, 6429.
- 40 S. Vandenberk, L. Vereecken and J. Peeters, Phys. Chem. Chem. Phys., 2002, 4, 461.
- 41 G. S. Tyndall, J. J. Orlando, T. J. Wallington, M. D. Hurley, M. Goto and M. Kawasaki, Phys. Chem. Chem. Phys., 2000, 4, 2189.
- S. Aloisio and J. S. Francisco, J. Phys. Chem. A, 2000, 104, 3211. 42
- 43 I. W. M. Smith and A. R. Ravishankara, J. Phys. Chem. A, 2002, 106, 4798.
- O. J. Nielsen, M. S. Johnson, T. J. Wallington, L. K. Christensen 44 and J. Platz, Int. J. Chem. Kinet., 2002, 34, 283. A. Pross, Adv. Phys. Org. Chem., 1977, 14, 69.
- 45
- T. D. Thomas, J. Am. Chem. Soc., 1970, 92, 4184. 46
- 47 J. A. Seetula and D. Gutman, J. Phys. Chem., 1991, 95, 3626.
- 48 P. W. Atkins, Physical Chemistry, OUP, Oxford, 6th edn., 1998.
- 49 E. Tschuikow-Roux, J. Niedzielski and F. Faraji, Can. J. Chem., 1985, 63, 1093.
- 50 E. Tschuikow-Roux, T. Yano and J. Niedzielski, J. Chem. Phys., 1985. 82. 65.
- 51 N. Cohen and K. R. Westberg, J. Phys. Chem. Ref. Data, 1991, 20, 1211.
- 52 J. Platz, O. J. Nielsen, J. Sehested and T. J. Wallington, J. Phys. Chem., 1995, 99, 6570.
- 53 P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat and F. Zabel, Atmos. Environ., 1992, 26A, 1805.
- F. Zabel, F. Kirchner and K.-H. Becker, Int. J. Chem. Kinet., 54 1994, 26, 827.
- 55 P. Biggs, C. E. Canosa-Mas, J.-M. Fracheboud, C. J. Percival, R. P. Wayne and D. E. Shallcross, J. Chem. Soc., Faraday Trans., 1997, 93, 379.
- 56 T. Gierczak, J. B. Burkholder, S. Bauerle and A. R. Ravishankara, Chem. Phys., 1998, 231, 229.
- 57
- E. K. C. Lee and R. S. Lewis, *Adv. Photochem.*, 1980, **12**, 1. R. Bowles, J. R. Majer and J. C. Robb, *Trans. Faraday Soc.*, 1962, 58 58. 1541.
- 59 R. Bowles, J. R. Majer and J. C. Robb, Trans. Faraday Soc., 1962, 58, 2394.
- 60 J. B. Burkholder, M. K. Gilles, T. Gierczak and A. R. Ravishankara, Geophys. Res. Lett., 2002, 29, 3-1.
- D. E. Heard, personal communication, 2003.