

# Rate coefficients and production of vibrationally excited HCl from the reactions of chlorine atoms with methanol, ethanol, acetaldehyde and formaldehyde

Paul W. Seakins,<sup>\*a</sup> John J. Orlando<sup>b</sup> and Geoffrey S. Tyndall<sup>b</sup>

<sup>a</sup> School of Chemistry, University of Leeds, Leeds, UK LS2 9JT

<sup>b</sup> National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80307, USA

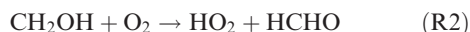
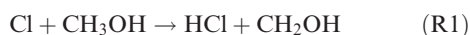
Received 12th February 2004, Accepted 13th March 2004

First published as an Advance Article on the web 26th March 2004

Room temperature rate coefficients have been determined for the reactions of Cl (<sup>2</sup>P<sub>3/2</sub>) atoms with methanol, ethanol, formaldehyde and acetaldehyde. Cl atoms were produced by laser flash photolysis of molecular chlorine, in the presence of oxygen to prevent chain chemistry. IR emission from vibrationally excited HCl was observed for all reagents. For the reactions with methanol and acetaldehyde the kinetics have been determined by both IR diode laser absorption spectroscopy ( $k_{\text{Cl}+\text{CH}_3\text{OH}} = (5.83 \pm 0.77) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{\text{Cl}+\text{CH}_3\text{CHO}} = (7.7 \pm 1.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and IR chemiluminescence ( $k_{\text{Cl}+\text{CH}_3\text{OH}} = (5.38 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_{\text{Cl}+\text{CH}_3\text{CHO}} = (8.8 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). For ethanol and formaldehyde IR chemiluminescence measurements gave  $k_{\text{Cl}+\text{HCHO}} = (6.98 \pm 0.69) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{\text{Cl}+\text{C}_2\text{H}_5\text{OH}} = (1.02 \pm 0.19) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The fraction of vibrationally excited HCl was determined relative to that of acetaldehyde and when put on an absolute scale the values for methanol, ethanol and formaldehyde were:  $0.25 \pm 0.04$ ,  $0.21 \pm 0.03$  and  $0.91 \pm 0.14$  respectively.

## 1. Introduction

The reactions of chlorine atoms with hydrocarbons or oxygenated hydrocarbons are commonly used to generate radical species. A prime example is the reaction of Cl atoms with methanol, which has been shown to selectively produce the hydroxymethyl radical<sup>1</sup> and in the presence of O<sub>2</sub> can be used to produce HO<sub>2</sub>.



The system is particularly useful as HCl and HO<sub>2</sub> (and HCHO) are generated in a 1:1 ratio allowing determination of radical concentrations from measurements of stable species. Chlorine atom reactions can also be of relevance in the lower atmosphere (especially the marine boundary layer) where their greater reactivity relative to OH can partially compensate for lower concentrations, making the chlorine reactions a significant component of hydrocarbon removal.<sup>2</sup>

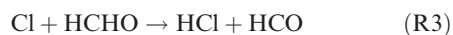
The dynamics of Cl atom abstraction reactions have been extensively studied as examples of prototypical abstraction reactions. Recent experimental<sup>3,4</sup> work based on the observation of HCl rotation distributions from the reactions of Cl with methanol and ethanol has indicated that the mechanism of H atom abstraction in oxygenated hydrocarbons may be different from simple alkanes,<sup>5</sup> with the products sampling attractive wells in the exit channels. This experimental work is supported by theoretical calculations on the Cl + methanol reaction.<sup>3,6</sup> Additionally, a number of reactions of Cl with oxygenated hydrocarbons have been studied by Taatjes and co-workers,<sup>7,8</sup> who have directly observed the time profiles of HCl( $v_2 \leftarrow v_1$ ) by IR absorption and have quantified the fraction of vibrational excitation by fitting the profiles of HCl( $v_1 \leftarrow v_0$ ) absorption. Kinetic and dynamic information on the title reactions previous to our study is summarised in Table 1.

**Table 1** Thermochemical, kinetic and fractional production of vibrationally excited HCl from the title reactions.

Reaction	$\Delta_r H_{298}^a / \text{kJ mol}^{-1}$	$k_{298} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$f(\text{HCl}, v = 1)$
Cl + CH <sub>3</sub> OH	−29.8 <sup>b</sup>	$5.6 \pm 0.2 \times 10^{-11}$ <sup>8</sup>	$0.12 \pm 0.02$ <sup>8</sup>
		$5.4 \pm 0.9 \times 10^{-11}$ <sup>9</sup>	
		$4.78 \pm 0.38 \times 10^{-11}$ <sup>10</sup>	
		$6.14 \pm 0.68 \times 10^{-11}$ <sup>11</sup>	
		$6.33 \pm 0.70 \times 10^{-11}$ <sup>11</sup>	
		$4.6 \pm 0.4 \times 10^{-11}$ <sup>12</sup>	
Cl + HCHO	−61.5	$6.1 \times 10^{-11}$ <sup>13</sup>	—
		$7.48 \pm 0.50 \times 10^{-11}$ <sup>14</sup>	
		$7.18 \pm 0.61 \times 10^{-11}$ <sup>15</sup>	
		$6.7 \pm 1.4 \times 10^{-11}$ <sup>16</sup>	
		$7.41 \pm 0.66 \times 10^{-11}$ <sup>17</sup>	
		$7.8 \times 10^{-11}$ <sup>18</sup>	
Cl + CH <sub>3</sub> CHO	−57.5	$8.3 \pm 0.1 \times 10^{-11}$ <sup>8</sup>	$0.56 \pm 0.14$ <sup>19</sup> $0.54 \pm 0.04$ <sup>8</sup>
		$7.8 \pm 1.3 \times 10^{-11}$ <sup>9</sup>	
		$7.5 \pm 0.8 \times 10^{-11}$ <sup>19</sup>	
		$6.6 \pm 1.4 \times 10^{-11}$ <sup>20</sup>	
		$6.0 \times 10^{-11}$ <sup>21</sup>	
		$8.4 \pm 0.8 \times 10^{-11}$ <sup>12</sup>	
Cl + C <sub>2</sub> H <sub>5</sub> OH	−43.3 <sup>c</sup> −11.0 <sup>d</sup> +3.0 <sup>e</sup>	$7.9 \pm 0.6 \times 10^{-11}$ <sup>22</sup>	$0.19 \pm 0.05$ <sup>7</sup> $0.14 \pm 0.04$ <sup>8</sup>
		$1.09 \pm 0.09 \times 10^{-10}$ <sup>7</sup>	
		$1.01 \pm 0.06 \times 10^{-10}$ <sup>10</sup>	
		$1.19 \times 10^{-10}$ <sup>23</sup>	
		$0.85 \pm 0.20 \times 10^{-10}$ <sup>12</sup>	
		$0.78 \pm 0.16 \times 10^{-10}$ <sup>24</sup>	

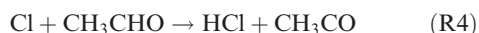
<sup>a</sup> HCl ( $v = 1$ ) = 2880 cm<sup>−1</sup> = 34 kJ mol<sup>−1</sup>. <sup>b</sup>  $\Delta_r H_{298}$  (CH<sub>2</sub>OH) = −17.2 kJ mol<sup>−1</sup>. Average value from Dobe *et al.*<sup>25</sup> and Johnson and Hudgens.<sup>26</sup> <sup>c</sup> Cl + C<sub>2</sub>H<sub>5</sub>OH → HCl + CH<sub>3</sub>CHO <sup>d</sup> Cl + C<sub>2</sub>H<sub>5</sub>OH → HCl + CH<sub>2</sub>CH<sub>2</sub>OH <sup>e</sup> Cl + C<sub>2</sub>H<sub>5</sub>OH → HCl + CH<sub>3</sub>CH<sub>2</sub>O <sup>f</sup> From reaction Cl + C<sub>2</sub>H<sub>5</sub>OH <sup>g</sup> From reaction Cl + CD<sub>3</sub>CH<sub>2</sub>OH

The reaction of chlorine atoms with formaldehyde



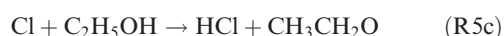
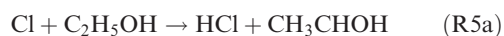
is known to generate IR emission and this was used by Fasano and Nogar<sup>17</sup> to monitor the kinetics of reaction (3), but the fractional production of HCl was not quantified. The room temperature kinetic measurements are all in good agreement but there is some uncertainty as to the temperature dependence of reaction (3).<sup>14,15</sup>

The reaction of chlorine atoms with acetaldehyde



has been investigated previously in the NCAR laboratory.<sup>9,19</sup> Tuneable IR diode laser absorption spectroscopy was used to determine a fractional production of HCl( $v=1$ ) of  $(0.56 \pm 0.14)$ .<sup>19</sup> The result is in excellent agreement with the value determined by fitting HCl ground state profiles determined by Smith *et al.* ( $0.54 \pm 0.04$ ).<sup>8</sup> Given the similarity in bond strengths of the aldehydic C–H bonds in formaldehyde and acetaldehyde, and the lower degrees of freedom in the Cl + formaldehyde system, one might expect HCl vibrational excitation from Cl + acetaldehyde to be a lower limit for the Cl + formaldehyde system.

The dynamics of the reaction of chlorine atoms and ethanol has been investigated by two groups.<sup>3,7</sup>



Rudic *et al.*<sup>3</sup> used REMPI spectroscopy to probe the rotational and vibrational distribution of HCl from reaction (5) under single collision conditions. Vibrationally excited HCl( $v=1$ ) was observed but the ratio of HCl  $v=0:v=1$  could not be determined. The measured rotational distribution of HCl in both the ground and first excited vibrational levels was significantly hotter than that observed from the reaction of chlorine atoms with hydrocarbons such as ethane. Rudic *et al.* rationalised their observations on reaction (1) using a potential energy surface in which the leaving HCl moiety forms a complex with the CH<sub>2</sub>OH group and in the break up of this complex, significantly more torque can be applied to the HCl molecule than in the nearly co-linear geometry of the simple H atom abstraction from alkanes.

Taatjes *et al.*<sup>7</sup> studied the reaction of Cl with several isotopomers of ethanol, both monitoring HCl ( $v=0,1$ ) by laser absorption in real time and studying the kinetics *via* relative rate methods. The results from both techniques show that over 90% of the reaction proceeds *via* channel 5a. The best fit to the ground state HCl time profiles was obtained with  $f(\text{HCl } v=1) = 0.19 \pm 0.05$ . A similar value  $0.14 \pm 0.04$  was obtained for the Cl + CD<sub>3</sub>CH<sub>2</sub>OH reaction. The IR laser could also be tuned to observe the production of HCl( $v=1$ ) directly; however, the similarity of the rise and fall time constants of the biexponential profile limited the quantitative information that could be extracted on the kinetics of HCl( $v=1$ ) production and vibrational quenching.

Both Rudic *et al.*<sup>3</sup> and Smith *et al.*<sup>8</sup> have studied the reaction of Cl atoms with methanol. Qualitatively the rotational distribution observed by Rudic *et al.* for reaction (1) is similar to that observed for ethanol.<sup>3,4</sup> No measurements of any vibrationally excited HCl were reported. More recently, Smith *et al.*<sup>8</sup> have reported a fractional yield of  $0.12 \pm 0.02$  for the production of vibrationally excited HCl.

During our diode laser absorption study of reaction (1), monitoring HCl and HCHO in an excess of oxygen, spontaneous IR emission was observed. Gas filter experiments suggested that a majority of the emission originates from HCl( $v=1$ ) production and we have observed absorptions

corresponding to transitions from HCl( $v=1$ ). We have characterised the fraction of total IR emission from reaction (1) relative to the reaction of Cl with acetaldehyde ( $f(\text{HCl } v=1) = 0.55 \pm 0.08$ )<sup>8,19</sup> *via* total emission measurements and also investigated the kinetics and fractional excitation of HCl in the reactions of Cl with ethanol and formaldehyde. Our total IR emission experiments also allow us to determine quenching rates for the process

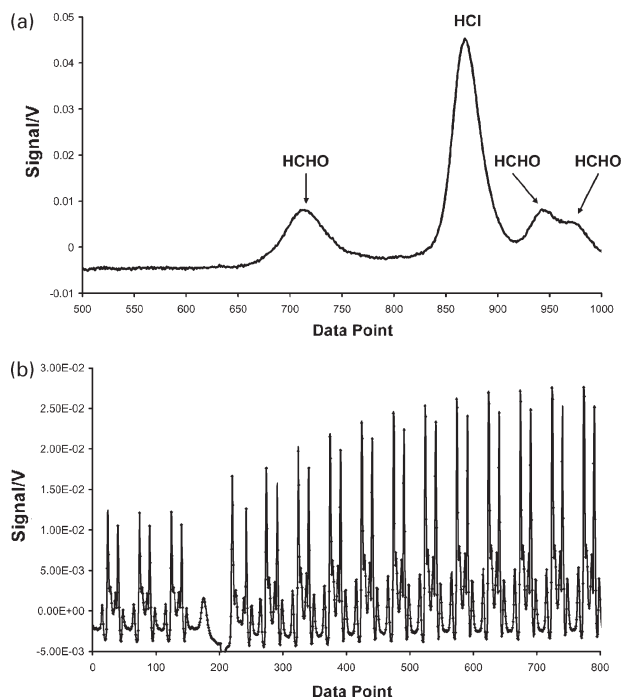


## 2. Experimental

The reactions were studied in a slow-flow, temperature controlled jacketed cell. Gases flowed through calibrated mass flow controllers (MKS) with a total flow in the region of 1000 sccm. The pressure in the cell was approximately 25 Torr, giving a residence time of  $\sim 0.5$  s. Chlorine atoms were generated from the 351 nm photolysis (Lambda Physik Compex 102,  $\sim 35$  mJ pulse<sup>-1</sup> at the reaction cell) of Cl<sub>2</sub> (Scott Specialty Gases 99.99%) producing ground state (<sup>2</sup>P<sub>3/2</sub>) fragments which will be rapidly thermalised by the bath gas on the time-scales of our measurements. The excimer light was coupled into the cell with a dichroic mirror and laser energies were measured before and after the 50 cm cell. Typical concentrations were [Cl]<sub>0</sub>  $(2\text{--}5) \times 10^{12}$  molecule cm<sup>-3</sup>, [RH]  $(2\text{--}25) \times 10^{13}$  with [RH]:[Cl]<sub>0</sub> always greater than 20:1. For total IR emission studies, IR radiation was passed through a long pass filter to block the excimer laser light and then through a quartz cell which cut off radiation below 2300 cm<sup>-1</sup> and could be used as a cold gas filter. The emission was then focused onto the 1 mm active area of an InSb detector (Cincinnati Electronics SDD-7845-S1) with a CaF<sub>2</sub> lens. The amplified output from the detector was then displayed and captured on a digital oscilloscope (LeCroy 9430) before transfer to a PC for subsequent analysis.

Details of the IR kinetic absorption spectroscopy *via* diode lasers have been presented previously<sup>19,27</sup> and hence only the major points are presented here. Output from an IR diode laser (Laser Components, Specdilas-IR-2799) housed in an Infrared Laboratories, Inc. liquid nitrogen cooled dewar was collimated, and passed twice through the cell, through the filters and onto the InSb detector as described above. The frequency of the laser was modulated by a ‘saw tooth’ current from a function generator (SRS Model DS345) operating in ‘burst mode’ allowing the laser to scan repeatedly after each excimer pulse over a sufficient frequency range to map out a complete ro-vibrational peak (or for studies of reaction (1)) closely located peaks from HCl and HCHO). HCl( $v=0$ ) was detected and quantified on the P(3) transition of either H<sup>35</sup>Cl (2821.5686 cm<sup>-1</sup>) or H<sup>37</sup>Cl (2819.5628 cm<sup>-1</sup>), while HCHO detection was mainly on a line located at 2819.5127 cm<sup>-1</sup>, adjacent to the H<sup>37</sup>Cl P(3) transition. The frequency of the modulation signal could be varied up to 20 kHz (50  $\mu$ s between points). The burst cycle is initiated by the excimer pulse and lasts for 1/laser repetition rate. The position of the trigger on the digital oscilloscope is adjusted so signal from the previous burst acts as pretrigger data for the next cycle (see Fig. 1b). Methanol (Mallinckrodt, HPLC grade), ethanol (Mallinckrodt, analytical reagent grade) and acetaldehyde (Aldrich, 99.5+%) were subjected to freeze–pump–thaw cycles before being prepared as 1–3% mixtures in N<sub>2</sub>. Formaldehyde was prepared by heating paraformaldehyde (Eastman Kodak) under vacuum. The absolute concentrations of the reagents and confirmation of purity were checked using IR absorption.

A 60:40 mix of oxygen (U.S. Welding, UHP) and nitrogen (U.S. Welding, UHP) was used as a buffer gas. Oxygen was used to ensure that the initial radicals formed from the abstraction did not go on to react with chlorine and so possibly



**Fig. 1** (a) Single scan showing absorptions by HCHO (2819.5127, 2819.5874, and 2819.5993  $\text{cm}^{-1}$ ) and HCl (2819.5608  $\text{cm}^{-1}$ ), (b) Typical scan with the diode laser working in burst mode. The photolysis laser fires at around point 200. Kinetic data were obtained from the heights of the peaks, corrected for the pre-photolysis values.

regenerate chlorine atoms. A significant concentration of nitrogen was used to ensure that the pseudo-first-order rate coefficient for vibrational relaxation was always greater than that for reaction.

### 3. Results

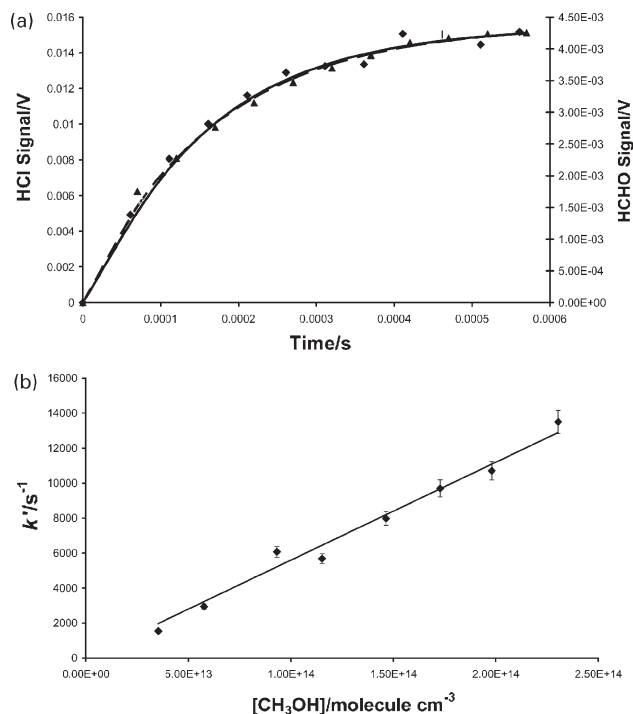
#### Cl + CH<sub>3</sub>OH

Reaction (1) was studied with an excess of oxygen and therefore essentially all the CH<sub>2</sub>OH produced in the reaction was rapidly converted into formaldehyde (typically  $k'_2/k'_1 = 550$ ) and so both HCl and HCHO were expected to be formed with the same time constant. Fig. 1a shows a single scan of the diode laser with absorptions from both HCl (2819.5608  $\text{cm}^{-1}$ ) and formaldehyde (2819.5127, 2819.5874, and 2819.5993  $\text{cm}^{-1}$ ). The spacing of the lines was confirmed using a germanium etalon and referenced to the HITRAN database.<sup>28</sup> Fig 1b shows a typical profile with the diode laser modulated at 20 kHz. Two peaks are observed corresponding to absorption during the 'ramp' and 'flyback' components of the saw-tooth modulation, analysis is based solely on the ramp scan. Flow rates for these experiments were about 400 sccm and therefore there was still some residual HCl and HCHO prior to photolysis.

The heights of each line were determined and the pre trigger background subtracted. The resulting signals for both HCl and HCHO were then fit using eqn. (1)

$$[\text{HCHO}]_t = A(1 - e^{-k't}) \quad (\text{E1})$$

using a non-linear least squares fitting program. With this simple analysis the same pseudo-first-order rate coefficient was obtained by monitoring either species for a particular methanol concentration as shown in Fig. 2a. This result confirms, as would be expected at the high [O<sub>2</sub>], that reaction (1) is the rate determining step in formaldehyde formation and therefore that either HCl or HCHO observation can be used to determine the kinetics of reaction (1). The concentration of



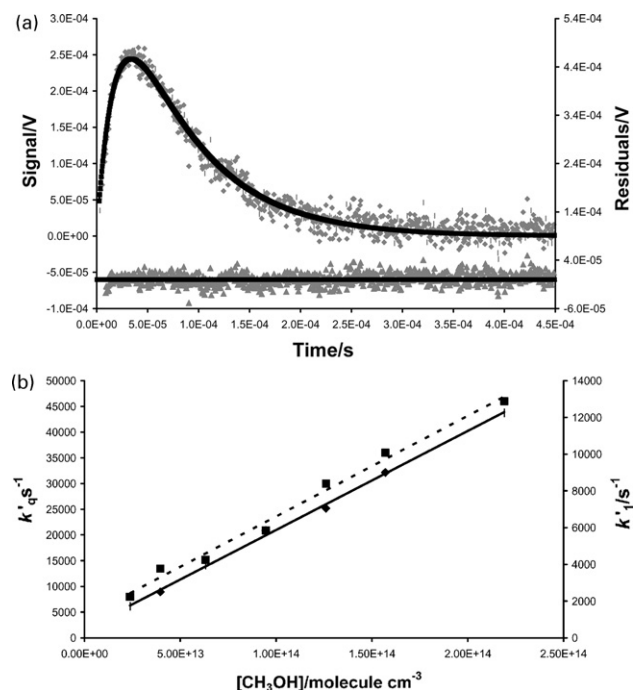
**Fig. 2** (a) Temporal dependence of normalised HCl (◆) and HCHO (▲) signals with corresponding fits to eqn. (1), (b) Bimolecular plot for Reaction (1) at room temperature from diode laser measurements.

methanol was varied and a bimolecular plot for reaction (1) monitoring HCl production (Fig. 2b) gave:

$$k_1 = (5.83 \pm 0.77) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors are 2σ from the least squares analysis of Fig. 2b.

Fig. 3a shows a typical emission profile from reaction (1). Filling the filter cell with HCl removed more than 95% of the signal, indicating that a vast majority of the emission



**Fig. 3** (a) IR chemiluminescence data from reaction (1) with biexponential fit from eqn. (2) and residuals, (b) Bimolecular plot for reaction (1) (■) and HCl(v) relaxation by methanol (◆) at room temperature from chemiluminescence measurements.

was from the  $\text{HCl}(v = 1 \rightarrow 0)$  emission. The data were fit using a biexponential function:

$$S = \frac{Ak'_1}{(k'_q - k'_1)} (e^{-k'_1 t} - e^{-k'_q t}) \quad (\text{E2})$$

where  $A = \alpha[\text{Cl}]_0$ ,  $k'_q$  is the pseudo-first-order rate coefficient for vibrational quenching of  $\text{HCl}(v = 1)$  and  $\alpha$  is the fraction of chlorine atoms producing vibrationally excited  $\text{HCl}$ . This analysis correctly accounts for a reduction in the signal height as a result of quenching.

The returned values of  $A$  scaled linearly with  $[\text{Cl}]_0$  and were invariant with the  $[\text{Cl}]_0:[\text{CH}_3\text{OH}]$  showing the emission did originate from the target reaction and not from any secondary chemistry such as  $\text{Cl} + \text{HCHO}$ .

The room temperature bimolecular plot is shown in Fig. 3b and the resulting bimolecular rate coefficient is  $k_1 = (5.38 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , in very good agreement with both the current diode laser studies and previous work (Table 1). The rate coefficient for the relaxation of  $\text{HCl}(v = 1)$  can be extracted from a plot of  $k'_q$  vs.  $[\text{CH}_3\text{OH}]$  and the resulting value is  $k_{q,\text{CH}_3\text{OH}} = (1.96 \pm 0.23) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The bimolecular plot for quenching has a significant intercept ( $4000 \pm 2800 \text{ s}^{-1}$ ) due to quenching *via* buffer gases.

The fractional production of  $\text{HCl}(v = 1)$  was determined by comparing the  $A/[\text{Cl}]_0$  from the target reaction and from the reaction of  $\text{Cl}$  with acetaldehyde.<sup>8,9,19</sup> Both diode laser studies and total emission studies were undertaken on the  $\text{Cl} + \text{acetaldehyde}$  reaction and the resulting kinetics were in good agreement with previous work.<sup>9</sup> As with the  $\text{Cl}/\text{methanol}$  system, the total emission for the  $\text{Cl}/\text{acetaldehyde}$  system scaled linearly with  $[\text{Cl}]_0$  and was invariant with the  $[\text{Cl}]_0:[\text{acetaldehyde}]$  ratio. Previous diode laser studies<sup>19</sup> have shown a fractional yield of  $0.56 \pm 0.14$  for  $\text{HCl}(v = 1)$  production from acetaldehyde in good agreement with the more precise determination of Smith *et al.*,<sup>8</sup>  $0.54 \pm 0.04$ . A value of  $0.55 \pm 0.08$  was used to normalise the methanol signal. For each system an average value of  $A/[\text{Cl}]_0$  was calculated and the resulting ratio of vibrational excitation at room temperature was  $0.44 \pm 0.04$ , giving the fractional  $\text{HCl}(v = 1)$  production from reaction (1) as  $0.25 \pm 0.04$ . Note that for a majority of experiments identical concentrations of  $[\text{Cl}]_0$  were generated. Where the initial concentrations of chlorine atoms were varied, the relative  $[\text{Cl}]_0$  (which is all that is needed) could be obtained from measured laser power and  $[\text{Cl}_2]$ .

Given the similarity of the energy required for  $\text{HCl}(v = 1)$  production and the overall exothermicity of reaction (1), the reaction was investigated *via* total emission studies at 243 K to see if there was any decrease in the fractional production of  $\text{HCl}(v = 1)$ . The bimolecular and quenching rate coefficients determined at 243 K were  $k_1 = (5.08 \pm 0.84) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{q,\text{CH}_3\text{OH}} = (1.21 \pm 0.15) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . A slight decrease in the fractional production of  $\text{HCl}(v = 1)$  was observed with  $f(\text{HCl}_{v=1}) = 0.22 \pm 0.05$ ,

but there is considerable overlap in the error bars of both determinations.

## Cl + C<sub>2</sub>H<sub>5</sub>OH, HCHO

Room temperature chemiluminescence studies were also undertaken for the reaction of  $\text{Cl}$  with ethanol and formaldehyde. Once again the returned value of  $A$  scaled linearly with  $[\text{Cl}]_0$ , the bimolecular plots were linear and both the rate coefficient for reaction and  $\text{HCl}(v = 1)$  quenching could be obtained from appropriate plots. The results of the chemiluminescence studies for all reactions are summarised in Table 2.

## 4. Discussion

### Rate coefficients for Cl abstraction reactions

In general the rate coefficients determined in this study, in some cases by more than one method, are in excellent agreement with data in the literature.

**Cl + methanol.** The room temperature measurements are in good agreement with a number of previous measurements,<sup>1,8,9,11</sup> and the recommendations of the IUPAC and NASA evaluations. The values of Dobe *et al.*,<sup>1</sup> Pagsberg *et al.*<sup>13</sup> ( $6.14 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and Michael *et al.*<sup>11</sup> are approximately 10% higher than our value, but there is considerable overlap of the error bars. Our measured value is outside the error range of an earlier relative rate measurement by Wallington *et al.*,<sup>12</sup> but in excellent agreement with a more recent relative rate determination by the same group.<sup>9</sup> No significant temperature dependence was observed in our work, consistent with the more extensive temperature measurements of Michael *et al.*<sup>11</sup> (200–500 K) using direct methods and the slightly more complex relative rate determinations of Lightfoot *et al.*<sup>29</sup> (248–573 K,  $(5.3 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), neither of whom observed any temperature dependence.

**Cl + ethanol.** The most recent study by Taatjes *et al.*<sup>7</sup> contains slight discrepancies in the room temperature rate coefficients with their direct determinations being some 15% higher than their relative rate measurements and Taatjes *et al.* highlighted the need for further measurements of reaction (5). Our measured value of  $(1.02 \pm 0.19) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is in the middle of the two determinations, suggesting that random, rather than systematic errors are responsible for the differences in the Taatjes *et al.* study.

Earlier relative rate determinations are somewhat scattered with Wallington *et al.*<sup>12</sup>  $(8.1 \pm 2.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and Edelbuttel-Einhaus<sup>24</sup>  $(7.7 \pm 1.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  reporting values lower than this determination, and Khatoun *et al.*<sup>23</sup> reporting a significantly higher value ( $1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). The 1990 study of Nelson *et al.*<sup>10</sup> ( $1.01 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is, however, in good

**Table 2** Summary of kinetic and vibrational excitation of  $\text{HCl}$

Reaction	Temperature/K	$k_{\text{bi}}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$f(\text{HCl}_{v=1})$	$k_{\text{q}}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Intercept of bimolecular quenching plot/ $\text{s}^{-1}$
$\text{Cl} + \text{CH}_3\text{OH}^a$	298	$5.83 \pm 0.77$	na	na	na
$\text{Cl} + \text{CH}_3\text{OH}$	298	$5.38 \pm 0.25$	$0.25 \pm 0.04$	$19.6 \pm 2.3$	$4000 \pm 2800$
$\text{Cl} + \text{CH}_3\text{OH}$	243	$5.08 \pm 0.84$	$0.22 \pm 0.05$	$12.1 \pm 1.5$	$10500 \pm 3000$
$\text{Cl} + \text{C}_2\text{H}_5\text{OH}$	298	$10.2 \pm 1.9$	$0.21 \pm 0.03$	$15.0 \pm 2.5$	$9900 \pm 3000$
$\text{Cl} + \text{HCHO}$	298	$6.98 \pm 0.69$	$0.91 \pm 0.14$	$5.80 \pm 1.5$	$14000 \pm 3000$
$\text{Cl} + \text{CH}_3\text{CHO}^b$	298	$7.8 \pm 1.1$	na	na	na
$\text{Cl} + \text{CH}_3\text{CHO}$	298	$8.8 \pm 1.5$	$0.55 \pm 0.08^c$	$8.2 \pm 1.5$	$12300 \pm 1200$

<sup>a</sup> Diode laser studies of  $\text{HCHO}$  and  $\text{HCl}(v = 0)$  production. <sup>b</sup> Diode laser observation of  $\text{HCl}(v = 1)$ . <sup>c</sup> Combination of references.<sup>19,8</sup>



agreement with this determination and the 1997 IUPAC recommendation.

**Cl + formaldehyde.** Despite increasing recognition of the importance of formaldehyde in both stratospheric and marine boundary layer chemistry, there have been no direct measurements of the rate coefficient for reaction (3) since 1981. The two most comprehensive studies<sup>14,15</sup> reported good agreement at room temperature, but disagreed about the temperature dependence of the rate coefficient. At lower stratospheric temperatures of  $\sim 220$  K, the two expressions differ by 25%. Our value for  $k_3$ ,  $(6.98 \pm 0.69) \times 10^{-11}$ , is in good agreement with all room temperature measurements.

**Cl + acetaldehyde.** Direct and relative rate measurements for this reaction in the literature vary from  $(5.9 \pm 0.5 - 9.2 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at room temperature. The recommendation of the most recent measurement is  $k = (7.8 \pm 1.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , in excellent agreement with our diode laser determination, but slightly lower than the present chemiluminescence measurement, however, still within experimental error. A thorough discussion on the status of this reaction can be found in Tyndall *et al.*<sup>9</sup>

### Fractional production of HCl( $v=1$ )

Diode laser studies confirm the production of HCl( $v=1$ ) from the reaction of Cl with the oxygenated hydrocarbons studied. Cold gas filter experiments suggest that a large majority of the chemiluminescence signal is HCl ( $v_1 \rightarrow v_0$ ) emission. The magnitude of the emission scales linearly with  $[\text{Cl}]_0$  and is independent of  $[\text{Cl}]:[\text{RH}]$  ratio, compatible with direct production from the primary reaction.

For ethanol the observed fractional production of vibrationally excited HCl is in excellent agreement with the measurements of Taatjes *et al.*<sup>7</sup> Vibrationally excited HCl was also observed in the single collision studies of Rudic *et al.*<sup>3</sup> although no attempt could be made to extract the ratios of ground and excited state HCl production in that study. The methodology of Taatjes and co-workers<sup>8</sup> to determine the fractional excitation of HCl from Cl + acetaldehyde also agrees well with earlier diode laser studies of Kegley-Owen *et al.*<sup>19</sup>

For methanol the observed fractional production of vibrationally excited HCl is significantly greater than that measured by Smith *et al.*<sup>8</sup> ( $0.25 \pm 0.04$  vs.  $0.12 \pm 0.02$ ). Currently we can offer no explanation for this observation especially in the light of the good agreement between various techniques for ethanol and acetaldehyde. Very recently a value of  $(0.16 \pm 0.07)$  has been measured by Camden *et al.*<sup>30</sup> but a detailed analysis is not yet available. The energy available for internal excitation,  $E_{\text{int}}$ , is given by:

$$E_{\text{int}} = -\Delta H + E_{\text{act}} + 3RT \quad (\text{E3})$$

where for reaction (1),  $E_{\text{act}} \sim 0^{11}$  (the lack of *any* experimental activation energy suggests that the average energy of the colliding molecules is the same as reagents and therefore that the additional  $\frac{1}{2}RT$  term to the translational energy component from a hard spheres approach should be ignored). Approximately  $4.7 \text{ kJ mol}^{-1}$  are required beyond the exothermicity of the reaction for the production of vibrationally excited HCl, 63% of the translational and rotational energy of the reagents. Given the relatively small amount of energy required to reach the threshold for the production of vibrationally excited HCl and the efficiency of production of vibrationally excited HCl in other reactions, neither the fractional yield of HCl( $v=1$ ) from reaction (1) or the weak temperature dependence of the fractional yield is surprising.

The exothermicity of the reaction (1) is close to the threshold for production of vibrationally excited HCl, whereas for

ethanol, there is significantly greater energy liberated (from attack on the  $-\text{CH}_2-$  grouping). One might therefore expect that the fractional HCl excitation from reaction (1) would be lower than from reaction (5a), however, our measurements suggest the opposite behaviour. This observation suggests that the size of the co-product is a determinant in the fraction of energy going into HCl vibrational excitation.

The argument that the size of the co-product affects the fractional yield of vibrationally excited HCl is supported by comparison with the formaldehyde/acetaldehyde system, where with similar exothermicities, the yield of vibrationally excited HCl is significantly higher in the smaller Cl/formaldehyde system. The fraction of reactions generating vibrationally excited HCl from reaction (3) is surprisingly high. It is possible that the thermal energy of the reagents could be utilised to generate HCl( $v=2$ );  $5.5 \text{ kJ mol}^{-1}$  are required, approximately 55% of the thermal energy of the reagents and emission from HCl( $v=2$ ) and HCO( $v$ ) could possibly contribute to the emission. Operational problems with the operation of the cold gas filter for this reaction made it difficult to realign between experiments. The filter experiments confirm that a majority of the emission is from HCl( $v=1$ ), although we cannot exclude the possibility of significant other contributions to the total emission. Further experiments are planned.

### Quenching of vibrational excitation by methanol, ethanol, formaldehyde and nitrogen

The magnitude of the vibrational relaxation rate coefficients is large for all species; however, from the limited data available, it would seem that the measurements fall into two groups, with room temperature relaxation by the alcohols being approximately a factor of two greater than that of the aldehydes. Resonant V-V transfer is expected to be similar for each quencher, all having comparable C-H stretch frequencies.<sup>31</sup> The variations between species are presumably caused by either the slight differences in frequencies or to the possibility of complex forming collisions (hydrogen bonding), which increase the probability of energy transfer in the more polar alcohols. The magnitude of the rate coefficients for all systems is very much greater than would be expected for impulsive V-R,T transfer.<sup>32</sup>

The quenching rate coefficient of HCl by acetaldehyde,  $(8.2 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is greater than a previous determination in this laboratory  $((4.8 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ <sup>19</sup> but in good agreement with Smith *et al.*  $((8.6 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ .<sup>8</sup>

The intercepts of the bimolecular plots for quenching should be equal to the quenching by the buffer gases and chlorine. The rate coefficient for vibrational relaxation of HCl by molecular chlorine is small ( $k_{\text{qCl}_2} = 5.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and the contribution made by the small concentration of chlorine can be ignored. Nitrogen relaxes HCl( $v=1$ ) approximately 10 times more efficiently than oxygen and so, to a first approximation, the predominant contribution to the intercept will come from relaxation by nitrogen.

Averaging all the intercepts gives an average intercept of  $9300 \pm 3000 \text{ s}^{-1}$  and a corresponding bimolecular rate coefficient  $k_{\text{q,N}_2} = (2.8 \pm 0.9) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in good agreement with the measurement of Chen and Moore  $(2.7 \pm 0.3) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>33</sup>

## 5. Summary

Room temperature rate coefficients have been determined for the reactions of Cl atoms with methanol, ethanol, formaldehyde and acetaldehyde *via* IR chemiluminescence. The results are in good agreement with previous work and with measurements made in this study by IR diode laser absorption studies

of the HCl product. The linear dependence of the emission intensity with  $[Cl]_0$ , the invariance with  $[Cl]_0$ : [substrate] and consistent kinetics suggest that the emission is produced from the primary reactions under study and not from any secondary reactions.

The fractional yield of vibrationally excited HCl is in good agreement with previous work for the reaction of Cl with ethanol, but significantly higher for methanol. The yield from formaldehyde has not been measured before. Measurements suggest very efficient production of HCl( $v$ ) inconsistent with a long lived complex, although even a short lived complex could provide the rotational effects observed by Orr-Ewing and co-workers. Our results suggest that the size of the substrate may have a significant effect on the fraction of vibrational excitation and therefore that the hydrocarbon radical is not a simple spectator group, a result supported by the work of Smith *et al.* on the reaction of Cl with toluene where the resonance stabilization energy of the radical appears to be available for the HCl product.

Both alcohols and aldehydes are efficient relaxers of HCl( $v = 1$ ) with alcohols approximately a factor two more efficient.

The results of the chemiluminescence experiments are in good agreement with those from other techniques demonstrating that this simple method can produce reliable kinetic data. More comprehensive studies are planned for the near future including higher precision measurements of the temperature dependence of reaction, quenching and the production of vibrationally excited products. Kinetic studies are particularly relevant for formaldehyde where current determinations of  $k_4$  differ by some 25% at stratospheric temperatures. Diode laser measurements will be particularly useful here, allowing *in situ* determinations of formaldehyde concentrations, a potentially significant uncertainty in low temperature formaldehyde studies where the substrate may be lost on the walls of the apparatus.

## Acknowledgements

PWS would like to acknowledge support from NERC (NER/T/S/2000/01092) and from NCAR for a visiting fellowship during which this work was carried out. NCAR is operated by the University Corporation for Atmospheric Research, under the sponsorship of the National Science Foundation. This work was supported in part a research grant from the NASA Upper Atmosphere Research Program.

## References

- 1 S. Dobe, M. Otting, F. Temps, H. G. Wagner and H. Ziemer, *Ber. Bunsen-Ges. Phys. Chem.*, 1993, **97**, 877.
- 2 B. T. Jobson, H. Niki, Y. Yokouchi, J. W. Bottenheim, F. Hopper and R. Leaitch, *J. Geophys. Res.*, 1994, **99**, 25 355.
- 3 S. Rudic, C. Murray, D. Ascenzi, H. Anderson, J. N. Harvey and A. J. Orr-Ewing, *J. Chem. Phys.*, 2002, **117**, 5692.
- 4 S. Rudic, D. Ascenzi and A. J. Orr-Ewing, *Chem. Phys. Lett.*, 2000, **332**, 487.
- 5 S. A. Kandel, T. P. Rakitzis, T. Lev-On and R. N. Zare, *J. Chem. Phys.*, 1996, **105**, 7550.
- 6 J. T. Jodkowski, M. T. Rayez, J. C. Rayez, T. Berces and S. Dobe, *J. Phys. Chem. A*, 1998, **102**, 9230.
- 7 C. A. Taatjes, L. K. Christensen, M. D. Hurley and T. J. Wallington, *J. Phys. Chem. A*, 1999, **103**, 9805.
- 8 J. D. Smith, J. D. DeSain and C. A. Taatjes, *Chem. Phys. Lett.*, 2002, **366**, 417.
- 9 G. S. Tyndall, J. J. Orlando, C. S. Kegley-Owen, T. J. Wallington and M. D. Hurley, *Int. J. Chem. Kinet.*, 1999, **31**, 776.
- 10 L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy and O. J. Nielsen, *Int. J. Chem. Kinet.*, 1990, **22**, 1111.
- 11 J. V. Michael, D. F. Nava, W. A. Payne and L. J. Stief, *J. Chem. Phys.*, 1979, **70**, 3652.
- 12 T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu and S. M. Japar, *Int. J. Chem. Kinet.*, 1988, **20**, 867.
- 13 P. Pagsberg, J. Munk, A. Sillesen and C. Anastasi, *Chem. Phys. Lett.*, 1988, **146**, 375.
- 14 J. V. Michael, D. F. Nava, W. A. Payne and L. J. Stief, *J. Chem. Phys.*, 1979, **70**, 1147.
- 15 P. C. Anderson and M. J. Kurylo, *J. Phys. Chem.*, 1979, **83**, 2055.
- 16 G. Poulet, G. Laverdet and G. Le Bras, *J. Phys. Chem.*, 1981, **85**, 1892.
- 17 D. M. Fasano and N. S. Nogar, *Int. J. Chem. Kinet.*, 1981, **13**, 325.
- 18 H. Niki, P. D. Maker, L. P. Breitenbach and C. M. Savage, *Chem. Phys. Lett.*, 1978, **57**, 596.
- 19 C. S. Kegley-Owen, G. S. Tyndall, J. J. Orlando and A. Fried, *Int. J. Chem. Kinet.*, 1999, **31**, 766.
- 20 W. A. Payne, D. F. Nava, F. L. Nesbitt and L. J. Stief, *J. Phys. Chem.*, 1990, **94**, 7190.
- 21 M. Bartels, K. Hoyer mann and U. Lange, *Ber. Bunsen-Ges. Phys. Chem.*, 1989, **93**, 423.
- 22 D. J. Scollard, J. J. Treacy, H. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. MacLeod and S. Teton, *J. Phys. Chem.*, 1993, **97**, 4683.
- 23 T. Khatoon, J. Edelbuttel-Einhaus, K. Hoyer mann and H. G. Wagner, *Ber. Bunsen-Ges. Phys. Chem.*, 1989, **93**, 626.
- 24 J. Edelbuttel-Einhaus, K. Hoyer mann, G. Rohde and J. Seeba, *Symp. (Int.) Combust., [Proc.]*, 1992, **24**, 661.
- 25 S. Dobe, T. Berces, T. Turanyi, F. Marta, J. Grussdorf, F. Temps and H. G. Wagner, *J. Phys. Chem.*, 1996, **100**, 19 864.
- 26 R. D. Johnson and J. W. Hudgens, *J. Phys. Chem.*, 1996, **100**, 19 874.
- 27 G. S. Tyndall, C. S. Kegley-Owen, J. J. Orlando and A. Fried, *J. Phys. Chem. A*, 2002, **106**, 1567.
- 28 L. S. Rothman, A. Barbe, D. C. Benner, L. R. Brown, C. Camy-Peyret, M. R. Carleer, K. Chance, C. Clerbaux, V. Dana, V. M. Devi, A. Fayt, J. M. Flaud, R. R. Gamache, A. Goldman, D. Jacquemart, K. W. Jucks, W. J. Lafferty, J. Y. Mandin, S. T. Massie, V. Nemtchinov, D. A. Newnham, A. Perrin, C. P. Rinsland, J. Schroeder, K. M. Smith, M. A. H. Smith, K. Tang, R. A. Toth, J. Vander Auwera, P. Varanasi and K. Yoshino, *J. Quant. Spectrosc. Radiat. Transfer*, 2003, **82**, 5.
- 29 P. D. Lightfoot, B. Veyret and R. Lesclaux, *J. Phys. Chem.*, 1990, **94**, 708.
- 30 J. P. Camdon, H. A. Bechtel and R. N. Zare, *Rev. Sci. Instrum.*, 2004, **75**, 556.
- 31 NIST Computational Chemistry Comparison and Benchmark DataBase, 2000, <http://srdata.nist.gov/cccbdb/>, accessed 2004.
- 32 J. D. Lambert, *Vibrational and Rotational Relaxation in Gases*, Clarendon Press, Oxford, 1977.
- 33 H. L. Chen and C. B. Moore, *J. Chem. Phys.*, 1971, **54**, 4080.