Rate Coefficient for the Reaction of CH₂OH Radicals with Cl₂ and Infrared Spectra of Chloromethanol and Dichloromethanol

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Quantitative infrared spectra have been recorded for chloromethanol and dichloromethanol, formed from the reactions of Cl₂ with CH₂OH and CHClOH, respectively. Chloromethanol decomposes quantitatively to HCHO and HCl, probably via a heterogeneous mechanism. The lower limit for the homogeneous gas-phase lifetime thus measured is 660 s. The rate coefficient for the reaction of CH₂OH with Cl₂ has been determined by measuring the products formed in experiments where O₂ was allowed to compete with Cl₂ for the CH₂OH radicals. The rate coefficient is $(2.7 \pm 0.7) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 295 ± 2 K. The rate coefficient for the reaction of Cl atoms with chloromethanol was estimated to be $(4 \pm 2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 295 ± 2 K.

Introduction

The hydroxymethyl radical, CH_2OH , is an important intermediate in combustion chemistry.¹ It is also formed in the atmospheric degradation of many natural and anthropogenic hydrocarbons.² In both atmospheric and combustion systems, its major fate is reaction with molecular oxygen, O_2 .³

$$CH_{2}OH + O_{2} \rightarrow HCHO + HO_{2}$$
(1)

This reaction can be used as a convenient source of HO₂ in kinetics studies.⁴ Direct measurements of the rate coefficients for CH₂-OH reactions with O₂, NO₂, and NO have been made using laser magnetic resonance,^{4.5} mass spectrometry,⁶⁻¹¹ and ultraviolet absorption spectroscopy.¹²

The reaction of Cl atoms with CH₃OH is the most convenient source of CH₂OH in kinetics studies. It has been demonstrated that abstraction of a methyl hydrogen atom accounts for greater than 97% of the reaction.^{4,13}

$$CI + CH_{3}OH \rightarrow HCI + CH_{2}OH$$
 (2)

In kinetics studies in which reaction 2 is used as a source of CH₂OH radicals, one potential interfering reaction is the reaction of CH₂OH with molecular chlorine;^{7,14} this reaction is the subject of the present study.

$$CH_2OH + Cl_2 \rightarrow Cl + ClCH_2OH$$
 (3)

Reaction 3 is interesting from the standpoint of both the kinetics of the elementary reaction and the thermochemistry and stability of the product, chloromethanol.

$$ClCH_{2}OH \rightarrow HCl + HCHO$$
 (4)

Estimates of the rate coefficient for reaction 3 have been derived by Grotheer and co-workers? $(k_3 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ and Jenkin et al.¹⁴ $(k_3 = 3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$. However, neither of these studies was specifically designed to measure k_3 .

We have investigated the chain reaction of CH_2OH with Cl_2 by FTIR spectrometry. The major product is expected to be chloromethanol, ClCH₂OH, which has never been observed in the gas phase. Kunttu et al. reported infrared features in a lowtemperature matrix which they attributed to chloromethanol formed from the ultraviolet photolysis of chloromethyl formate.¹⁵

$$HCOOCH_2Cl + h\nu \rightarrow CO + ClCH_2OH$$

Lin observed HCl infrared laser emission from the reaction of $O(^1D)$ with CH₃Cl, which he attributed to the decomposition of the transient chloromethanol molecule formed by insertion of the oxygen atom into one of the C-H bonds.¹⁶

$$O(^{1}D) + CH_{3}CI \rightarrow (CICH_{2}OH)^{1}$$

(CICH_{2}OH)^{1} \rightarrow HCHO + HCI

We have produced ClCH₂OH from the photochlorination of methanol and investigated the stability of the chloromethanol produced in this way. The photochlorination of alcohols offers an attractive method of generating unusual multisubstituted molecules in the gas phase, and this study serves as a prototype to see whether the method has general applicability.

Gutman and co-workers have studied the kinetics of a series of halogen-substituted methyl radicals and other organic radicals with halogen molecules.¹⁷ They have attempted to correlate the observed reactivity with some intrinsic molecular parameter (electronegativity of substituent, enthalpy of reaction, ionization potential of radical). It is of interest to see whether the reactivity of hydroxymethyl conforms to any of the trends detected in the haloalkyl radicals.

We report here the rate coefficient for the reaction of CH_2OH with molecular chlorine at 295 ± 2 K, measured relative to the reaction of CH_2OH with molecular oxygen. The gas-phase infrared spectrum of $ClCH_2OH$ is described for the first time, along with a lower limit for its homogeneous lifetime. The rate coefficient for the reaction of chlorine atoms with chloromethanol has been estimated, and the infrared spectrum of dichloromethanol is reported. Further, we report ab initio Hartree-Fock calculations of the infrared spectra of chloromethanol and dichloromethanol, as well as calculations of the thermodynamics of their decomposition reactions. Finally, the results are discussed in terms of reactivity trends for substituted alkyl radicals and implications for atmospheric chemistry.

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Experimental Section

The experiments are conceptually similar to those carried out by Wallington et al.¹⁸ on the reaction of C_2H_5 with O_2 and Cl_2 . Parallel experiments were carried out in the laboratories at NCAR and Ford; both systems have been described in detail previously^{19,20} and are only briefly discussed here. The experiments involved the photolysis of Cl_2 - CH_3OH-N_2 mixtures with various amounts of O_2 added in experiments to determine the relative rate coefficients of reactions 1 and 3.

The experiments at NCAR were carried out in a 47-L stainless steel reactor fitted with a quartz window at one end to allow photolysis using a filtered xenon arc lamp. Those at Ford were performed in a 140-L Pyrex reactor surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Chloromethanol and dichloromethanol were prepared by the irradiation of CH₃OH-Cl₂ mixtures in 700 Torr of nitrogen diluent. To study the relative rates of reactions 1 and 3, oxygen was added to the reaction mixtures in varying amounts. All experiments were performed at 295 K.

$$Cl_2 + h\nu \rightarrow 2Cl$$
 (5)

$$Cl + CH_3OH \rightarrow CH_2OH + HCl$$
 (2)

$$CH_2OH + Cl_2 \rightarrow ClCH_2OH + Cl$$
(3)

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$
 (1)

The loss of methanol and the formation of products were monitored by Fourier transform infrared spectroscopy using infrared path lengths of 32.6 (NCAR) or 26.6 m (Ford), with spectral resolutions of 0.5 and 0.25 cm⁻¹, respectively. Products were identified and quantified by fitting reference spectra of the pure compounds to the observed product spectra using integrated absorption features over the following wavelength ranges (in cm⁻¹): methanol, 950-1100; HCHO, 1700-1800; HCOCl, 1700-1850; HCl, 2600-2800; and HCOOH, 1050-1150 and 1700-1900. Initial concentrations of the gas mixtures were as follows: at NCAR, $[CH_3OH] =$ 21-34 mTorr, $[Cl_2] = 16-66$ mTorr, and $[O_2] = 10-125$ mTorr; at Ford, $[CH_3OH] = 7-15 \text{ mTorr}$, $[Cl_2] = 100 \text{ mTorr}$, and $[O_2]$ = 0-501 mTorr; total pressure = 700 Torr with nitrogen diluent. Frequent experiments were carried out in the NCAR chamber to calibrate the Cl_2 photolysis rate, reaction 5. These experiments involved the photolysis of Cl2-CH3OH mixtures in a large excess of O_2 and equating the loss of methanol to the amount of chlorine atoms produced. Ultrahigh-purity nitrogen and oxygen were obtained from U.S. Welding or Airco.; methanol was procured from Baker or Aldrich at >99.9% purity and used after repeated freeze-pump-thaw cycles to remove dissolved air.

Computational Details. All calculations were performed with the Gaussian 88 program employing standard basis sets.²¹ Gradient-optimized geometries and analytical force constants for ClCH₂OH and CHCl₂OH were obtained at the RHF/6- $31G^{**}$ level assuming C_1 and C_s symmetries, respectively. The structural results for ClCH₂OH are identical to those reported earlier.¹⁵ The optimized geometric parameters for Cl₂CHOH are as follows: (distances in angstroms) r(C-O) = 1.3458, r(C-O) = 1.3458Cl) = 1.7856, r(C-H) = 1.0726, r(O-H) = 0.9466; (angles in degrees) a(Cl-C-O) = 111.93, a(H-C-O) = 108.69, a(H-O-C-O) = 108.69, a(H-O-O) = 108.69, a(H-O-C-O) = 108C) = 111.14, a(Cl-C-O-H) = 118.30. Kunttu et al. used two adjustable parameters to fit the RHF/6-31G** vibrational spectrum of ClCH₂OH to that obtained experimentally.¹⁵ We have chosen rather to report frequencies scaled by a constant factor of 0.87 to account for the systematic overestimation inherent in the Hartree-Fock and harmonic oscillator approximations;²² the results of the two scaling methods for ClCH₂OH are not substantially different.



Figure 1. Infrared spectra acquired before (A) and after (B) a 2-s irradiation of a mixture of 98 mTorr of Cl_2 and 14.8 mTorr of methanol in 700 Torr of nitrogen diluent. Subtraction of the features attributable to CH_3OH results in spectrum C, which we assign to $ClCH_2OH$.

To evaluate the heats of decomposition of ClCH₂OH and CHCl₂OH, the electronic energies of these two molecules, as well as HCl, HCHO, and HCOCl, were obtained at the MP2/6-311G(2d,p) level using the RHF/ $6-31G^{**}$ optimized geometries. The larger basis set decreases the energy of decomposition slightly, but the results with either basis set are similar. The (unscaled) RHF/ $6-31G^{**}$ vibrational frequencies were used to generate zero-point corrections to the electronic energies, and standard statistical mechanical methods were used to adjust the energies to 298.15 K, as well as to obtain reaction enthalpies and entropies at 298.15 K.^{22,23}

Results

Chloromethanol and dichloromethanol were prepared by the UV irradiation of CH_3OH-Cl_2 mixtures in N₂ diluent. Figure 1A,B shows spectra acquired at Ford before and after a 2-s irradiation of a mixture of 98 mTorr of Cl_2 and 14.8 mTorr of methanol. The loss of methanol was 4.07 mTorr (28%). Subtraction of CH_3OH features from Figure 1B yields the product spectrum C. Product features were observed at 959, 1083, 1318, and 1374 cm⁻¹. These are in very good agreement with those given by Kunttu et al. for $ClCH_2OH$ in the condensed phase.¹⁵ These features decayed in the dark and two extra products were formed: HCHO and HCl. We ascribe the initial product features to $ClCH_2OH$, which subsequently decays in the dark to give HCHO and HCl.

$$ClCH_{2}OH \rightarrow HCHO + HCl$$
 (4)

In the Ford chamber (glass surface, diameter 30 cm) the ClCH₂-OH was found to be relatively long lived. The loss of ClCH₂OH in the dark followed first-order kinetics as shown in Figure 2. Linear least-squares analysis of the data in Figure 2 gives a value of $k_4 = (1.6 \pm 0.1) \times 10^{-3} \, \mathrm{s}^{-1}$ under these experimental conditions. The yields of HCHO and HCl products formed in the dark were identical, as expected from the decomposition of ClCH₂OH in reaction 4. In the stainless steel chamber at NCAR (diameter 20 cm) ClCH₂OH decayed more rapidly (lifetime ~ 1 min), with a decay coefficient which varied from day to day. Thus, the decay of ClCH₂OH in the NCAR chamber was probably heterogeneous. Such behavior has often been observed for hydroperoxides in this chamber. The observed decay of ClCH₂-OH in the Ford chamber, although slower and more reproducible,



Figure 2. Decay of $ClCH_2OH$ and $CHCl_2OH$ as a function of time in the dark. The solid lines are linear least-squares fits.



Figure 3. Infrared spectra acquired before (A) and after (B) a 2-s irradiation of a mixture of 7.3 mTorr of CH_3OH and 101 mTorr of Cl_2 in 700 Torr of nitrogen. Subtraction of features attributable to $ClCH_2OH$ results in spectrum C, which we assign to $CHCl_2OH$.

may also contain a heterogeneous component. For this reason, the lifetime of $ClCH_2OH$ we report (660 s) is probably a lower limit.

The primary goal of the present work is to investigate the IR spectrum and the kinetic behavior of chloromethanol. For this reason, in the majority of our experiments conditions were chosen such that consumption of methanol was moderate (10-50%), and hence, subsequent chlorination reactions would be of minor importance. Nevertheless, a limited number of experiments were performed using lower initial methanol concentrations with larger conversions of methanol, to investigate the possibility of preparing dichloromethanol. A sequence of spectra from one such experiment carried out at Ford is shown in Figure 3. Figure 3A is the spectrum of a mixture of 7.3 mTorr of CH₃OH with 100 mTorr of Cl_2 in 700 Torr total pressure of nitrogen. UV irradiation for 2 s leads to spectrum B. As seen from Figure 3B, in this experiment essentially all of the methanol was consumed. Careful examination of the spectrum in Figure 3B showed that less than 1% of the methanol remained. Two products were observed. As seen by comparison of Figures 1C and 3B, ClCH₂OH is one product. Using our reference spectrum of $ClCH_2OH$ (derived from Figure 1C), we have subtracted features attributable to $ClCH_2OH$ to give Figure 3C. Infrared product features at 1003, 1105, 1221, and 1388 cm⁻¹ (see Figure 3C) decayed in the dark at the same rate, indicating that they are directly related. Two products were observed to form in the dark, HCOCl and HCl. We ascribe spectrum C to dichloromethanol, which decomposes to give HCOCl and HCl in reaction 6.

$$CHCl_{OH} \rightarrow HCOCl + HCl$$
(6)

As seen from Figure 2, the loss of CHCl₂OH in the dark followed first-order kinetics in the Ford chamber. Linear least-squares analysis of the data in Figure 2 gives $k_6 = (9.0 \pm 0.8) \times 10^{-3} \, \text{s}^{-1}$. Identical spectra were obtained in the NCAR chamber, but the decay was too fast to allow reliable measurement of the lifetime.

The observed formation of HCHO and HCOCl from the decomposition of ClCH₂OH and CHCl₂OH provides a means for both calibrating our reference spectra for these chloromethanols and estimating the reactivity of ClCH₂OH toward Cl atoms. By quantifying the absolute increase in HCHO and HCOCl observed in the dark and relating these changes to the corresponding decrease of IR features ascribed to ClCH₂OH and CHCl₂OH, we derive $\sigma_{\text{ClCH}_2\text{OH}}(1094 \text{ cm}^{-1}) = (6.2 \pm 0.4) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ and $\sigma_{\text{CHCl}_2\text{OH}}(1109 \text{ cm}^{-1}) = (1.8 \pm 0.2) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$; uncertainties are 2 standard deviations.

We have calculated the infrared spectra of both ClCH₂OH and CHCl₂OH at the RHF/ $6-31G^{**}$ level, and the results are presented in Table I. The four observed bands for chloromethanol are satisfactorily reproduced by the calculations, and both the calculated and observed spectra agree well with previously reported results.¹⁵ The observed and calculated relative intensities are also in good agreement. On the basis of the calculated intensities, we assign the band observed at 1318 cm⁻¹ to the methylene wag and the band at 1374 cm⁻¹ to the hydroxyl bend. These assignments differ from those reported earlier.¹⁵ For dichloromethanol, agreement between three of the observed bands and the calculations is excellent: the band at 1105 cm⁻¹ is assigned to the C-O stretch, calculated at 1100 cm⁻¹; the band at 1221 cm⁻¹ to the H-C asymmetric rock, calculated at 1206 cm⁻¹; and the band at 1388 cm⁻¹ to the C-O-H in-plane bend, calculated at 1342 cm⁻¹. Thus, the calculations strongly support the assignment of this spectrum to CHCl₂OH. The observed band at 1003 cm⁻¹ is problematic, however. It is clearly too weak to be the C-O stretch, which we have already assigned anyway, and much too high in energy to belong to one of the C-Cl stretching modes. Presumably, the 1003-cm⁻¹ feature is either a combination or difference band.

The ratio of the total increase in HCHO on standing in the dark to that of the increase in HCOCl provides a measure of the concentration ratio $[ClCH_2OH]_0/[CHCl_2OH]_0$ formed during the irradiation period. This concentration ratio, together with the measured consumption of CH₃OH, can be used with a simple mechanism consisting of reactions 2, 3, 7, and 8 to extract the rate constant ratio k_7/k_2 .

$$Cl + CH_3OH \rightarrow CH_2OH + HCl$$
 (2)

$$CH_2OH + Cl_2 \rightarrow ClCH_2OH + Cl$$
 (3)

$$ClCH_2OH + Cl \rightarrow CHClOH + HCl$$
(7)

$$CHClOH + Cl_2 \rightarrow CHCl_2OH + Cl$$
(8)

For example, in an experiment in which a mixture of 14.8 mTorr of CH_3OH and 101 mTorr of Cl_2 in 700 Torr of N_2 was irradiated for 2 s, the loss of CH_3OH was 12.6 mTorr (85% of

TABLE I: Experimentally Observed Infrared Frequencies, Along with Calculated Frequencies (RHF/6-31G**, Scaled by 0.87), Relative Intensities (Scaled to 100), and Approximate Descriptions for Chloromethanol and Dichloromethanol

$CICH_2OH(C_1)$				CHCl ₂ OH (C _s)				
exptl (cm ⁻¹)	calcd (cm ⁻¹)	rel int	approx description	exptl (cm ⁻¹)		calcd (cm ⁻¹)	rel int	approx description
	329	36	OH torsion		a'	266	<1	CCl ₂ O asym bend
	405	38	CICO bend		a″	311	19	OH torsion
	647	65	CCl stretch		a″	428	27	CCl ₂ O asym bend
959	920	8	CH ₂ rock		a'	431	6	CCl ₂ O sym bend
1083	1081	100	CO stretch		a'	652	8	CCl ₂ sym stretch
	1134	4	CH ₂ twist		a″	726	100	CCl ₂ asym stretch
				1003				
1318	1293	16	CH_2 wag	1105	a'	1100	89	CO stretch
1374	1327	38	COH bend		a'	1200	<1	HC sym rock
	1438	1	CH ₂ scissor	1221	a″	1206	19	HC asym rock
	2837	19	CH_2 sym stretch	1388	a'	1342	27	COH bend
	2923	6	CH ₂ asym stretch		a'	2944	1	CH stretch
	3629	32	OH stretch		a'	3605	29	OH stretch

initial concentration), and after standing in the dark for 25 min 11.9 mTorr of HCHO and 1.2 mTorr of HCOCl were formed. Assuming reactions 3 and 8 to be rapid compared to the time scale of the irradiation (2 s), a ratio of $k_7/k_2 = 0.07$ is required to explain the observed ClCH₂OH and CHCl₂OH yields. We estimate the uncertainty on k_7/k_2 to be 50%. Using the literature value for $k_2 = 5.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ then leads to $k_7 =$ $(4 \pm 2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. In our experiments to study dichloromethanol we did not observe any phosgene, COCl₂, either immediately after photolysis or after the reaction mixtures sat for 20 min in the dark. The lack of phosgene suggests that the formation of trichloromethanol, from the reaction of Cl atoms with dichloromethanol, is of negligible importance in the present work.

To derive the rate constant ratio k_3/k_1 , oxygen was added to the reaction mixtures. With both Cl₂ and O₂ present there is a competition between reactions 3 and 1 for the available CH₂OH radicals. Reaction with Cl₂ leads to the formation of ClCH₂OH, while reaction with O₂ leads to the formation of HCHO. Provided that HCHO is formed only by reaction 1 and that it is not lost by any process, then

$$\frac{\Delta[\text{CH}_3\text{OH}]}{\Delta[\text{HCHO}]} = 1 + \frac{k_3}{k_1} \frac{[\text{Cl}_2]}{[\text{O}_2]}$$

where Δ [CH₃OH] and Δ [HCHO] are the observed loss of methanol and formation of HCHO, k_3 and k_1 are the rate constants for reactions 3 and 1, and [Cl₂] and [O₂] are the concentrations of Cl₂ and O₂, respectively.

Since $ClCH_2OH$ was relatively stable in the Ford chamber, the above equation could be used to analyze the data. The rapid decay of $ClCH_2OH$ to HCHO in the NCAR chamber necessitated an approach based on numerical simulation of the consumption of methanol. This will be described later.

Experiments To Determine k_3 at Ford. In the Ford experiments, [Cl₂] was held fixed at 100 mTorr and [O₂] was varied over the range 125-501 mTorr. As noted above, the simple analysis assumes that the only source of HCHO is reaction 1 and that HCHO is not lost in any process. In reality, a small amount of HCHO is also formed by the decomposition of ClCH₂OH, and HCHO is lost in our chamber by reaction with Cl atoms.

$$Cl + HCHO \rightarrow HCO + HCl$$
 (9)

To minimize complications in our kinetic analysis caused by formation of HCHO via reaction 4, spectra were acquired immediately following UV irradiation. The time taken for the acquisition of eight coadded interferograms was 13 s. Typical irradiation times were 2–10 s. Hence, the maximum time that ClCH₂OH had to decompose in our chamber was 23 s. Using the value of $k_4 = 1.6 \times 10^{-3} \text{ s}^{-1}$ measured in the present work, we calculate that 3–4% of the initially formed ClCH₂OH will

TABLE II: Reaction Mechanism

reaction	rate constant ^a	ref ^d
$Cl_2 + h\nu \rightarrow Cl + Cl$	measured	this work
$Cl + CH_3OH \rightarrow CH_2OH + HCl$	5.7 × 10 ⁻¹¹	
$CH_2OH + Cl_2 \rightarrow ClCH_2OH + Cl$	2.7×10^{-11}	this work
$Cl + Cl \rightarrow Cl_2$	2.5 × 10 ^{-13 b}	31
$CH_2OH + O_2 \rightarrow HO_2 + HCHO$	1.0×10^{-11}	
$Cl + HO_2 \rightarrow HCl + O_2$	4.0×10^{-11}	
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	3.0×10^{-12}	
$Cl + H_2O_2 \rightarrow HCl + HO_2$	4.1×10^{-13}	
$CH_2OH + CI \rightarrow HCI + HCHO$	2.0×10^{-10}	7
$CH_2OH + CH_2OH \rightarrow HOCH_2CH_2OH$	2.4×10^{-11}	7
$CH_2OH + HO_2 \rightarrow CH_3OH + O_2$	6.0 × 10 ⁻¹¹	6
$HCO + O_2 \rightarrow HO_2 + CO$	5.5 × 10 ⁻¹²	
$ClCH_2OH \rightarrow HCl + HCHO$	1.6 × 10 ⁻³ c	this work
$Cl + HCHO \rightarrow HCO + HCl$	7.3 × 10 ⁻¹¹	
$HCO + Cl_2 \rightarrow HCOCl + Cl$	1.0×10^{-11}	17

^a Units of cm³ molecule⁻¹ s⁻¹. ^b Pseudo-second-order rate constant, value appropriate for 700 Torr. ^c Units of s⁻¹. ^d From ref 3 unless stated.

decompose to produce HCHO. A small correction to our observed HCHO yield was applied to account for decomposition of $ClCH_2$ -OH.

To assess the importance of reaction 9 in our system, simulations of our experiments were performed using the Acuchem chemical kinetics modeling program²⁴ with the chemical mechanism given in Table II. Simulations were performed for each of our experiments with, and without, the inclusion of reaction 9. Corrections to account for the consumption of HCHO via reaction 9 were computed from the ratio of the predicted HCHO concentration when reaction 9 was omitted from the mechanism to that obtained with reaction 9 included. Because reaction of Cl atoms with HCHO is rapid, and significant consumptions of methanol occurred in this work, these corrections were between 20% and 40%. However, we feel justified in making the correction, since the simulations showed that its magnitude was not dependent on the value of k_3 used in the model.

Finally, we must consider the potential loss of HCHO from its reaction with HO₂, which ultimately produces formic acid.²⁵ No evidence for formic acid production was observed in the present experiments, the production always being less than 1% of the observed CH₃OH loss. Thus, no correction to the observed HCHO concentration was necessary.

In Figure 4 we have plotted Δ [CH₃OH]/ Δ [HCHO] versus [Cl₂]/[O₂] (with Δ [HCHO] points corrected as described above). We have included a data point at [Cl₂]/[O₂] = 0 with Δ [CH₃-OH]/ Δ [HCHO] = 1 since in the presence of a large excess of O₂, HCHO is formed in 100% yield. The solid line in Figure 4, the result of an unweighted linear least-squares analysis of the data, has a slope $k_3/k_1 = 2.8 \pm 0.4$ and an intercept 0.98 \pm 0.20; uncertainties are 2σ . Each data point has been corrected for HCHO formation by reaction 4 and loss by reaction 9. In light of the inherent uncertainties in these corrections (most signifi-



Figure 4. Plot of Δ [CH₃OH]/ Δ [HCHO] versus [Cl₂]/[O₂]; see text for details.

cantly in the rate constant ratio k_2/k_2), we choose to add an additional 10% uncertainty to our determination, i.e., $k_3/k_1 = 2.8 \pm 0.7$.

Experiments To Determine k_3 at NCAR. Due to the rapid decay of ClCH₂OH in these experiments, the ratio of methanol loss to HCHO formation could not be used to determine k_3/k_1 . Instead, the absolute loss of methanol was calibrated relative to the chlorine photolysis rate. This was determined at least once per day from the photolysis of Cl₂-CH₃OH-O₂ mixtures. If a large excess of O₂ is used, all the CH₂OH radicals are converted to HCHO and HO₂. The HO₂ radicals combine to form H₂O₂.

$$Cl_2 + h\nu \rightarrow Cl + Cl$$
 (5)

$$Cl + CH_3OH \rightarrow HCl + CH_2OH$$
 (2)

$$CH_2OH + O_2 \rightarrow HO_2 + HCHO$$
(1)

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
(10)

Thus, two molecules of methanol should be consumed for every Cl_2 molecule photolyzed. Infrared analysis of the mixtures showed that a small amount of CO was also produced, so a small correction was made for secondary consumption of HCHO by reaction with Cl atoms.

$$Cl + HCHO \rightarrow HCl + HCO$$
 (9)

$$HCO + O_2 \rightarrow HO_2 + CO$$
 (11)

The derived photolysis rates were in the range $(3.0-3.3) \times 10^{-4}$ s⁻¹.

For the experiments to measure k_3 , quantitative measurements were made of CH₃OH, HCHO, CO, and HCOCl.

$$HCO + Cl_2 \rightarrow HCOCl + Cl$$
 (12)

The mixtures were photolyzed for an appropriate time and then allowed to stand in the dark, until all of the ClCH₂OH had decomposed to HCHO. The chemistry occurring during the irradiation period was simulated using the Acuchem program, using the measured chlorine photolysis rate and the set of reactions given in Table II. The measured amount of HCHO at the end of the dark period was compared to the combined yield of HCHO + $ClCH_2OH$ obtained in the simulation. This approach was more realistic than allowing ClCH₂OH to decay instantaneously to HCHO + HCl in the model, since chlorine atoms are much more reactive toward HCHO than ClCH₂OH, and the methanol depletion can be underestimated if HCHO is allowed to build up in the model. Again, no significant buildup of HCOOH was observed (<3% of the methanol removed). Experiments were carried out using $0.25 < [Cl_2]/[O_2] < 3.1$. A summary of the experimental conditions and derived values for the ratio k_3/k_1 is given in Table III. The measured depletions of CH₃OH and yields of the carbon-containing products could be reproduced with $k_3/k_1 = 2.5 \pm 0.5$. We add an extra 10% to account for uncertainty in the value of the ratio k_2/k_9 and uncertainty in the measurement of the chlorine photolysis rate, leading to $k_3/k_1 =$ 2.5 ± 0.8 . This value is in excellent agreement with that obtained by the graphical method at Ford (2.8 \pm 0.7). We combine the two determinations to obtain $k_3/k_1 = 2.7 \pm 0.7$.

Discussion

We have shown that chloromethanol and dichloromethanol have lifetimes of at least 660 and 110 s, with respect to homogeneous gas-phase decomposition. This is in contrast to the very short lifetime of chloroformic acid, HO(CO)Cl, which is formed in the chain reaction of COOH with Cl_2^{26} and which decays by a similar mechanism.

$$HO(CO)Cl \rightarrow HCl + CO$$
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Grotheer et al.^{6,7} observed no chloromethanol in their mass spectrometer studies of reaction 3; this indicates that it either decomposed heterogeneously in their flow tube or fragmented in the mass spectrometer.

To the best of our knowledge, the spectra of $ClCH_2OH$ and $CHCl_2OH$ are the first published gas-phase spectra of these molecules. The fundamentals observed at 1083 and 1105 cm⁻¹ correspond to the C-O stretching modes, while the other bands correspond to various C-H and O-H deformations. Although no rotational structure is observable at the resolution used here, the band envelopes change from mainly perpendicular-type (prominent multiple Q-branches) in $ClCH_2OH$ to parallel-type in $CHCl_2OH$, corresponding to a shift in the dipole axis on substitution of a second chlorine atom.

The rate coefficient ratio $k_3/k_1 = 2.7 \pm 0.7$ is in good agreement with that derived by Jenkin et al., ${}^{14}k_3/k_1 = 3.4 \pm 0.3$ (precision only), who followed the initial change in optical density attributed to Cl_2 in the photolysis of Cl_2 -CH₃OH-O₂ mixtures. From the ratio $k_3/k_1 = 2.7 \pm 0.7$, an absolute value for k_3 can be derived using the mean of current values for $k_1 (1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1})$ s⁻¹). Our rate coefficient is approximately a factor of 2 higher than that measured by Grotheer et al.^{6,7} It appears that CH_2OH reacts with Cl₂ much faster than any of the halogenated methyl radicals studied by Gutman and co-workers,17 for which the rate coefficients range between 1.4×10^{-16} for CCl₃ and 2.0×10^{-12} cm³ molecule⁻¹ s⁻¹ for CH₃ at 298 K. Gutman and co-workers¹⁷ looked for various structure-reactivity relationships to explain the rate coefficients they measured. Of these, the electronegativity of the substituent provided the best degree of correlation, with increasing electronegativity leading to a slower rate coefficient. Substitution of OH quite clearly goes against this trend. However, in the case of CH₂OH, a larger effect is probably exerted by π -bonding from the oxygen atom back into the singly-occupied orbital on the carbon atom, thus increasing the electron density available for bonding. This picture is supported by the structure for CH₂OH calculated by Jacox and Milligan,²⁷ in which it can be thought of as a hydrogen atom bonded to formaldehyde rather than methanol with one methyl hydrogen missing.

Our experiments show that $ClCH_2OH$ and $CHCl_2OH$ decompose readily in the gas phase to HCHO + HCl and HCOCl

TABLE III: Summary of Experimental Conditions for Determination of k_3/k_1 at NCAR

[CH ₃ OH] (mTorr)	[Cl ₂] (mTorr)	[O ₂] (mTorr)	[Cl ₂]/[O ₂]	time (s)	Δ[CH ₃ OH] (mTorr)	k_{3}/k_{1}
23	34	33	1.0	35	2.9	2.9
26	66	33	2.0	60	11	2.0
21	33	11	3.1	50	6.0	2.5
21	31	124	0.25	120	3.1	2.5
25	61	62	1.0	80	7.9	2.3

TABLE IV: Calculated RHF/6-31G**//RHF/6-31G** and MP2/6-311G(2d,p)//RHF/6-31G** Electronic Energies, Along with Zero-Point Energies, Translational, Rotational, and Vibrational Corrections to 298.15 K, and Entropy at 298.15 K, Calculated from RHF/6-31G** Results (All Energies in au)

<u></u>	HCI	HC(O)H	CIC(O)H	CICH ₂ OH	CHCl ₂ OH
		6-310	;**		
SCF energy	-460.066 214	-113.869 743	-572.783 337	-573.953 185	-1032.847 786
ZPE	0.007 244	0.028 981	0.020 979	0.047 035	0.037 211
$\Delta E^{298.15}$ trans+rot+bib	0.002 360	0.002 853	0.003 154	0.003 578	0.002 040
E ^{298.15} tot	-460.056 610	-113.837 909	-572.759 204	-573.902 572	-1032.808 535
S (cal/(mol K))	44.539	52.106	61.522	63.822	70.299
		6-311G	(2d,p)		
SCF energy	-460.096 270	-113.903 115	-572.844 596	-574.013 072	-1032.934 992
MP2 energy	-460.324 887	-114.298 534	-573.454 478	-574.644 137	-1033.779 903

TABLE V: Energy (ΔE), Enthalpy ($\Delta H = \Delta E + RT$), and Free Energy ($\Delta G = \Delta H - T\Delta S$) of Decomposition of Monoand Dichloromethanol, Evaluated from MP2/6-311G(2d,p)// RHF/6-31G** Electronic Energies and RHF/6-31G**

Zero-Point and Thermal Corrections (All Values in kcal/mol)

	CiCH20H	
ΔΕ		
SCF	8.59	-3.69
MP2	13.00	0.34
MP2 + ZPE	6.22	-5.30
MP2 + ZPE + 298.15 K corrections	7.24	-3.12
$\Delta H(298.15)$	7.83	-2.53
$\Delta G(298.15)$	-1.95	13.19

+ HCl, respectively. To determine the enthalpy of these processes, values of $\Delta H_f(\text{ClCH}_2\text{OH})$ and $\Delta H_f(\text{CHCl}_2\text{OH})$ are needed. We have used two different approaches to estimate these values. First, $\Delta H_f(\text{ClCH}_2\text{OH})$ can be estimated from the enthalpies of formation of chloromethanes and chlorinated methyl radicals given by Seetula et al.¹⁷ and Russell et al.²⁸ Simple additivity considerations imply $\Delta H_f(\text{ClCH}_2\text{OH}) = -50.4$ kcal mol⁻¹ and $\Delta H_f(\text{Cl}_2\text{CHOH}) = -52.6$ kcal mol⁻¹. The decomposition reaction for chloromethanol is then 2.3 ± 3 kcal mol⁻¹ endothermic and that for dichloromethanol 8.8 kcal mol⁻¹ exothermic (using heats of formation for HCHO and HCl of -26.0 and -22.1 kcal mol⁻¹, the mean of HCHO and COCl₂).³

In the second approach we used ab initio MP2/6-311G(2d,p)electronic energies in conjunction with zero-point and translational, rotational, and vibrational temperature corrections obtained from the RHF/6-31G** optimized geometry and vibrational frequencies to estimate the thermochemistry associated with the decomposition of the chlorinated methanols. The raw computational results are presented in Table IV, and the energetics of the two decomposition reactions (4 and 6) are presented in Table V. From Table V, decomposition of CHCl₂OH is roughly 11 kcal/mol more exothermic than decomposition of ClCH₂OH, and this result also holds when RHF and MP2/6-31G** electronic energies are used. For chloromethanol and dichloromethanol. the decompositions at 298.15 K are predicted to be endothermic by nearly 8 kcal/mol and exothermic by about 2.5 kcal/mol, respectively. These results are consistent with the bond additivity approach used above. We observe both decomposition reactions to occur spontaneously in our chambers. The more favorable thermochemistry associated with the decomposition of dichloromethanol may be reflected in our experimental observation of a more rapid decay of this species, although we consider both decompositions to be predominantly heterogeneous.

Finally, we consider the formation of chloromethanol in the oxidation of methyl chloride. The occurrence of a molecular channel in the self- or cross-reaction of alkyl- and acylperoxy radicals has recently received a certain amount of interest in terms of the formation of organic acids and alcohols in the troposphere.²⁹

$$RCH_2O_2 + R'O_2 \rightarrow RCHO + R'OH + O_2$$

Here, R' can be an alkyl or acyl group. The atmospheric degradation of methyl chloride leads to the production of chloromethyl radicals, which add oxygen to form chloromethylperoxy. The occurrence of this mechanism, either in the atmosphere or in laboratory reactors, could thus lead to the formation of chloromethanol.

$$ClCH_2O_2 + ClCH_2O_2 \rightarrow ClCH_2O + ClCH_2O + O_2 \quad (13a)$$
$$ClCH_2O_2 + ClCH_2O_2 \rightarrow ClCH_2OH + HCOCl + O_2 \quad (13b)$$

Niki et al.³⁰ studied the products arising from the self-reaction of ClCH₂O₂ radicals in air. Two carbon-containing products were reported (yield in parentheses): HCOCl (90%) and an unknown species tentatively identified as the hydroperoxide ClCH₂OOH (<10%). The reaction of Cl atoms with CH₃Cl in the presence of O₂ was used as the source of the ClCH₂O₂ radicals. In the majority of the experiments reported by Niki et al. significant conversions of CH₃Cl were employed (typically $\approx 20\%$). In the present work we report a rate constant for the reaction of Cl atoms with ClCH₂OH of (4 ± 2) × 10⁻¹² cm³ molecule⁻¹ s⁻¹. This is an order of magnitude larger than the reaction of Cl atoms with CH₃Cl.³ Hence, the possibility exists for significant loss of ClCH₂OH, which would result in formation of HCOCl, thus masking the identification of this pathway.

$$CI + CICH_2OH \rightarrow HCI + CICHOH$$

$$CICHOH + O_2 \rightarrow HO_2 + HCOCI$$

Niki et al.³⁰ were aware of potential complications caused by the low reactivity of Cl atoms toward CH₃Cl. For example, they conducted an experiment using a high initial CH₃Cl concentration (and hence a low conversion) to look for HCHO; none was seen. However, it is unclear as to whether features other than HCHO were searched for or whether the reaction mixture was allowed to age in the dark to check for the formation of HCHO by reaction 4 under such conditions. To resolve this point, we repeated the experiment described by Niki et al.³⁰ and used our reference spectrum for ClCH₂OH to look for this product. The conditions used were as follows: $[CH_3Cl]_0 = 2$ Torr, $[Cl_2] = 0.1$ Torr in 700 Torr of ultrapure synthetic air diluent, UV irradiation for 1-3 min, the conversion of CH₃Cl was 0.5-2.0%. Following irradiation we observed the same carbon-containing products reported by Niki et al. in the same yields. There was no evidence for ClCH₂OH (<1.5% of the yield of HCl) immediately after irradiation or for its decomposition product HCHO (<1% of the yield of HCl) after the mixtures were allowed to stand for 20 min in the dark. We conclude that the molecular channel of the self-reaction of ClCH₂O₂ radicals (reaction 13b) is of negligible importance.

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