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Kinetic and Product Study of the Cl-Initiated Oxidation of 1,2,3-Trichloropropane ($CH_2ClCHClCH_2Cl$)

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The kinetics and products of the Cl atom initiated oxidation of $CH_2ClCHClCH_2Cl$ (1,2,3-trichloropropane) have been investigated at (295 ± 2) K in 700−760 Torr of air in a 405 L reaction chamber. The major oxidation product (in terms of carbon balance) was $CH_2ClC(O)CH_2Cl$ with smaller amounts of HC(O)Cl and $CH_2ClC(O)Cl$. It was observed that chemical activation effects play a significant role in the atmospheric fate of $CH_2ClCHClO(\cdot)$ and $CH_2ClCO(\cdot)ClCH_2Cl$ radicals. Relative rate techniques were used to measure the following: $k(Cl + CH_2ClCHClCH_2Cl) = (1.86 \pm 0.32) \times 10^{-12}$, $k(Cl + CHCl{=}CHCH_2Cl) = (1.67 \pm 0.18) \times 10^{-10}$, $k(Cl + CH_2{=}CClCH_2Cl) = (1.46 \pm 0.15) \times 10^{-10}$, and $k(Cl + CH_2ClC(O)CH_2Cl) = (5.53 \pm 0.63) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. The UV−visible spectrum of $CH_2ClC(O)CH_2Cl$ was measured over the range 270−385 nm and has a maximum at 305 nm where $\sigma = (1.6 \pm 0.2) \times 10^{-19}$ cm^2 $molecule^{-1}$ (base e). Assuming a photolysis quantum yield of 1.00−0.04, the lifetime of $CH_2ClC(O)CH_2Cl$ with respect to photolysis on a summer day at 40° latitude is calculated to be 0.5−12 h. Photolysis is likely to be the dominant atmospheric loss mechanism of $CH_2ClC(O)CH_2Cl$. The results are discussed in the context of the atmospheric chemistry of 1,2,3-trichloropropane.

1. Introduction

1,2,3-Trichloropropane is a volatile (bp 156 °C) chlorinated solvent used in paint removal and degreasing operations. Assessment of the environmental impact of organic compounds such as trichloropropane released into the atmosphere requires a detailed understanding of their atmospheric degradation pathways. Little is currently known about the atmospheric oxidation mechanism of trichloropropane.

Alkoxy radicals are important intermediates in the atmospheric oxidation of all organic compounds. At the present time there are significant uncertainties in our understanding of the atmospheric chemistry of alkoxy radicals. Reaction of alkyl peroxy radicals with NO can produce alkoxy radicals possessing internal excitation that is comparable to, or greater than, the barrier to decomposition. These “hot” alkoxy radicals (e.g., $CF_3CFHO(\cdot)$,[1] $CH_2ClO(\cdot)$,[2] and $HOC_2H_4O(\cdot)$[3]) can decompose immediately and play an important role in dictating the nature of the atmospheric oxidation products. Alkoxy radicals formed in the oxidation of compounds such as trichloropropane possess a variety of potentially accessible decomposition pathways (elimination of Cl atoms, HCl) and may be prone to chemical activation effects not recognized previously.

Experimental studies have demonstrated the importance of a novel decomposition pathway for the α-monochloroalkoxy radicals derived from CH_3Cl and C_2H_5Cl; three-center intramolecular elimination of HCl.[4−8] However, it is unclear as to whether three-center intramolecular elimination of HCl is of general importance in the atmospheric oxidation of chlorinated organic compounds. To improve the technical basis for predictions of the environmental impact of industrial solvents we have conducted a study of the atmospheric chemistry of 1,2,3-trichloropropane.

The atmospheric oxidation of $CH_2ClCHClCH_2Cl$ is initiated by reaction with OH radicals producing alkyl radicals that will, in turn, react with O_2 to give peroxy radicals:

$$CH_2Cl{-}CHCl{-}CH_2Cl + OH \rightarrow CH_2Cl{-}CHCl{-}C(\cdot)HCl + H_2O \quad (1a)$$

$$CH_2Cl{-}CHCl{-}CH_2Cl + OH \rightarrow CH_2Cl{-}C(\cdot)Cl{-}CH_2Cl + H_2O \quad (1b)$$

$$CH_2Cl{-}CHCl{-}C(\cdot)HCl + O_2 + M \rightarrow CH_2Cl{-}CHCl{-}CHClO_2(\cdot) + M \quad (2a)$$

$$CH_2Cl{-}C(\cdot)Cl{-}CH_2Cl + O_2 + M \rightarrow CH_2Cl{-}CClO_2(\cdot)\text{-}CH_2Cl + M \quad (2b)$$

In urban air masses, the peroxy radicals will react with NO to generate the alkoxy radicals $CH_2Cl{-}CHCl{-}CHClO(\cdot)$ and CH_2-

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Cl−CClO(•)−CH_2Cl which will react further to give a diverse array of halogenated products.

In the initial stages of this work a relative kinetic and product study of the reaction of $CH_2ClCHClCH_2Cl$ with OH radicals was attempted; however, with the source of OH radicals employed (the photolysis of methyl nitrite) the reaction was too slow to produce accurate results. Thus, in the present work, reaction with Cl was substituted for reaction with OH. Although reaction of volatile organic compounds (VOCs) with Cl atoms is, in general, not as selective as with OH radicals the subsequent chemistry is the same and thus it is a convenient method to emulate OH radical initiated chemistry.

We present here the results of a kinetic and mechanistic study of the Cl atom initiated oxidation of $CH_2ClCHClCH_2Cl$ using FTIR-smog chamber systems at the Bergische Universität GH Wuppertal and Ford Motor Company.

$$\mathrm{Cl} + \mathrm{CH_2ClCHClCH_2Cl} \rightarrow \text{products} \tag{3}$$

2. Experimental Section

The majority of experiments were performed at Wuppertal using a 405 L Pyrex cylindrical glass reactor (1.5 m length, 0.6 m diameter) with Teflon coated metal end flanges described elsewhere.[9] A White mirror system (base path length 1.4 m) mounted inside the reactor and coupled by an external mirror system to a Fourier Transform-Spectrometer (Nicolet 7199) enables the in-situ monitoring of both reactants and products by long path infrared absorption, using a total path length 50.4 m. The reactor is equipped with 18 fluorescent lamps (Philips TLA 40 W/ 05: $320 < \lambda < 480$ nm, $\lambda_{max} = 365$ nm) arranged concentrically around the chamber. Experiments were performed in 700−760 Torr total pressure of synthetic air at 295 ± 2 K.

Rate constants for reactions of Cl atoms with trichloropropane, 1,3-dichloropropene, 2,3-dichloropropene, and 1,3-dichloroacetone were determined at Wuppertal using the relative rate method in which the reactant and reference are exposed to attack by Cl atoms.

$$\mathrm{Cl} + \text{reactant organic} \rightarrow \text{products} \tag{4}$$

$$\mathrm{Cl} + \text{reference compound} \rightarrow \text{products} \tag{5}$$

Provided that the reactant and reference compounds are removed solely by reaction with Cl atoms and are not formed in any process, then it can be shown that

$$\ln\left(\frac{[\text{reactant}]_{t0}}{[\text{reactant}]_{t}}\right) = \frac{k_4}{k_5} \ln\left(\frac{[\text{reference}]_{t0}}{[\text{reference}]_{t}}\right) \tag{i}$$

Plots of $\ln([\text{reactant}]_{t0}/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_{t0}/[\text{reference}]_t)$ yield slopes of k_4/k_5.

Reactants were injected into the reactor in a stream of synthetic air or nitrogen using microliter syringes for liquids and gastight syringes for gases. Concentrations of the organic reactants were in the range (19−26) ppm (1 ppm = 2.48×10^{13} molecule cm^{-3} at 298 K). The photolysis of Cl_2 (70−100 ppm) was used to generate Cl atoms. The Cl atom concentrations were typically $(4-9) \times 10^9$ cm^{-3}.

The UV-absorption spectrum of $CH_2ClC(O)CH_2Cl$ was measured in a 480 L volume reactor at Wuppertal equipped with multiple reflection mirror optics for simultaneous in situ measurement in the UV and IR. The UV spectrometer consists of a modified 22-cm monochromator (SPEX) and a diode array detector (EG & G PAR 1412). A spectral resolution of 0.6 nm was achieved with a grating of 1200 lines/mm covering a spectral range of 70 nm on the diode array detector. The wavelength scale was calibrated using atomic emission lines from a low-pressure mercury lamp. The UV absorbance increased linearly with $CH_2ClC(O)CH_2Cl$ concentration in accordance with Lambert-Beer's law, $\ln(I_o/I) = \sigma cl$. The products of the Cl atom initiated oxidation of trichloropropane in the present and absence of NO_x were investigated at Ford using a 140 L Pyrex reactor[10] surrounded by 22 fluorescent blacklamps (GTE F40BLB, $\lambda > 300$ nm). All experiments were performed at 700−760 Torr total pressure ($N_2 + O_2$) and 296 ± 3 K.

3. Results and Discussion

3.1. Relative Rate Kinetic Studies of Cl Atoms with Halogenated Organics. Prior to investigating the oxidation products of 1,2,3-trichloropropane, relative rate experiments were performed to study the kinetics of reactions of Cl with 1,2,3-trichloropropane ($CH_2ClCHClCH_2Cl$), 1,3-dichloropropene ($CHCl{=}CHCH_2Cl$), 2,3-dichloropropene ($CH_2{=}CClCH_2Cl$), and 1,3-dichloroacetone ($CH_2ClC(O)CH_2Cl$). Reaction 3 was measured relative to (9) and (10), reactions 6 and 7 were measured relative to (11) and (12), and reaction 8 was studied relative to (9, 13, and 14).

$$\mathrm{Cl} + \mathrm{CH_2ClCHClCH_2Cl} \rightarrow \text{products} \tag{3}$$

$$\mathrm{Cl} + \mathrm{CHCl{=}CHCH_2Cl} \rightarrow \text{products} \tag{6}$$

$$\mathrm{Cl} + \mathrm{CH_2{=}CClCH_2Cl} \rightarrow \text{products} \tag{7}$$

$$\mathrm{Cl} + \mathrm{CH_2ClC(O)CH_2Cl} \rightarrow \text{products} \tag{8}$$

$$\mathrm{Cl} + \mathrm{CH_3OCHO} \rightarrow \text{products} \tag{9}$$

$$\mathrm{Cl} + \mathrm{CH_3CH_2Cl} \rightarrow \text{products} \tag{10}$$

$$\mathrm{Cl} + \mathrm{C_2H_6} \rightarrow \text{products} \tag{11}$$

$$\mathrm{Cl} + \mathrm{C_3H_6} \rightarrow \text{products} \tag{12}$$

$$\mathrm{Cl} + \mathrm{CH_3Cl} \rightarrow \text{products} \tag{13}$$

$$\mathrm{Cl} + \mathrm{CH_4} \rightarrow \text{products} \tag{14}$$

Figures 1 and 2 show plots of the loss of reactants versus reference compounds following exposure to Cl atoms in 700−760 Torr of air. Rate constant ratios, k_{compd}/k_{ref}, derived from linear least-squares analysis of the data in Figures 1 and 2 are given in Table 1. Quoted errors for k_{compd}/k_{ref} in Table 1 are two standard deviations from the least squares analyses. The relative rate data can be placed upon an absolute basis using $k_9 = 1.4 \times 10^{-12}$,[11] $k_{10} = 8.04 \times 10^{-12}$,[12] $k_{11} = 5.7 \times 10^{-11}$,[13] $k_{12} = 2.48 \times 10^{-10}$,[14] $k_{13} = 4.9 \times 10^{-13}$,[15] and $k_{14} = 1.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.[14] As seen in Table 1, consistent values of k_{compd} were obtained using multiple reference compounds suggesting the absence of substantial systematic errors associated with the use of individual reference reactions. We chose to quote final values of k_3, k_6, k_7, and k_8 which are averages of the individual measurements, together with error limits which encompass the extremes of the individual determinations. Hence, $k_3 = (1.86 \pm 0.32) \times 10^{-12}$, $k_6 = (1.67 \pm 0.18) \times 10^{-10}$, $k_7 = (1.46 \pm 0.15) \times 10^{-10}$, $k_8 = (5.53 \pm 0.63) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. We estimate that potential systematic errors associated with uncertainties in the reference rate constants contribute an additional 10% to the uncertainty

TABLE 1: Kinetic Data for Cl Atom Reactions Investigated in This Study

compound (compd)	reference (ref)	rate coefficient ratio k_{compd}/k_{ref}	rate coefficient k_{compd} (cm^3 molecule^{-1} s^{-1})	recommended value k_{compd} (cm^3 molecule^{-1} s^{-1})
$CH_2ClCHClCH_2Cl$	CH_3OCHO	1.22 ± 0.12	$(1.71 \pm 0.17) \times 10^{-12}$	$(1.86 \pm 0.32) \times 10^{-12}$
(1,2,3-trichloropropane)	C_2H_5Cl	0.25 ± 0.02	$(2.01 \pm 0.16) \times 10^{-12}$	
$CH_2Cl{-}CH{=}CHCl$	CH_3CH_3	3.06 ± 0.20	$(1.74 \pm 0.11) \times 10^{-10}$	$(1.67 \pm 0.18) \times 10^{-10}$
(1,3-dichloropropene)	$CH_3CH{=}CH_2$	0.65 ± 0.04	$(1.61 \pm 0.10) \times 10^{-10}$	
$CH_2Cl{-}CCl{=}CH_2$	CH_3CH_3	2.41 ± 0.07	$(1.36 \pm 0.05) \times 10^{-10}$	$(1.46 \pm 0.15) \times 10^{-10}$
(2,3-dichloropropene)	$CH_3CH{=}CH_2$	0.63 ± 0.01	$(1.57 \pm 0.02) \times 10^{-10}$	
$CH_2ClC(O)CH_2Cl$	CH_4	5.7 ± 0.5	$(5.7 \pm 0.5) \times 10^{-13}$	$(5.53 \pm 0.63) \times 10^{-13}$
(1,3-dichloroacetone)	CH_3Cl	1.04 ± 0.08	$(5.0 \pm 0.4) \times 10^{-13}$	
	CH_3OCHO	0.42 ± 0.05	$(5.9 \pm 0.7) \times 10^{-13}$	
$CHCl_2CHClCH_2Cl$				$(9.3 \pm 2.0) \times 10^{-13}$
(1,1,2,3-tetrachloropropane)				
$CH_2ClCCl_2CH_2Cl$				$(1.7 \pm 1.0) \times 10^{-13}$
(1,2,2,3-tetrachloropropane)				

range. There are no previous studies of these reactions with which to compare our results.

3.2. Reaction Site Selectivity for Cl + 1,2,3-Trichloropropane. To ascertain the relative importance of Cl atom attack at the terminal and central H atoms in 1,2,3-trichloropropane, experiments were performed in which mixtures of $CH_2ClCHClCH_2Cl$ and Cl_2 in 760 Torr of N_2 diluent were subjected to UV irradiation. The alkyl radicals formed following H atom abstraction react with Cl_2 to give either 1,1,2,3-tetrachloropropane (terminal H abstraction) or 1,2,2,3-tetrachloropropane (central H abstraction)

$$CH_2Cl{-}CHCl{-}CH_2Cl + Cl \rightarrow CH_2Cl{-}CHCl{-}C(\cdot)HCl + HCl \tag{3a}$$

$$CH_2Cl{-}CHCl{-}CH_2Cl + Cl \rightarrow CH_2Cl{-}C(\cdot)Cl{-}CH_2Cl + HCl \tag{3b}$$

$$CH_2Cl{-}CHCl{-}C(\cdot)HCl + Cl_2 \rightarrow CH_2Cl{-}CHCl{-}CHCl_2 + Cl \tag{15a}$$

$$CH_2Cl{-}C(\cdot)Cl{-}CH_2Cl + Cl_2 \rightarrow CH_2Cl{-}CCl_2{-}CH_2Cl + Cl \tag{15b}$$

The yields of 1,1,2,3- and 1,2,2,3-tetrachloropropane provide information on the importance of Cl attack at the central and terminal H atoms, respectively. Unfortunately, neither of the tetrachloropropanes are commercially available. To obtain calibrated infrared spectra of these compounds they were produced in-situ from 1,3-dichloropropene and 2,3-dichloropropene (which are commercially available) by UV irradiation of dichloropropene/Cl_2 mixtures in 760 Torr of N_2. By analogy to the reaction with propene,[16] it is reasonable to assume that the reaction of Cl atoms with dichloropropene proceeds predominately via addition to the double bond and that the fate of the resulting chloroalkyl radical is reaction with Cl_2.

$$\underset{\text{(1,3-dichloropropene)}}{CH_2Cl{-}CH{=}CHCl} + Cl_2 + hv \rightarrow\rightarrow \underset{\text{(1,1,2,3-tetrachloropropane)}}{CH_2Cl{-}CHCl{-}CHCl_2} \tag{16}$$

$$\underset{\text{(2,3-dichloropropene)}}{CH_2Cl{-}CCl{=}CH_2} + Cl_2 + hv \rightarrow\rightarrow \underset{\text{(1,2,2,3-tetrachloropropane)}}{CH_2Cl{-}CCl_2{-}CH_2Cl} \tag{17}$$

Calibration of the spectra was achieved by assuming 100% conversion of dichloropropene into tetrachloropropane.

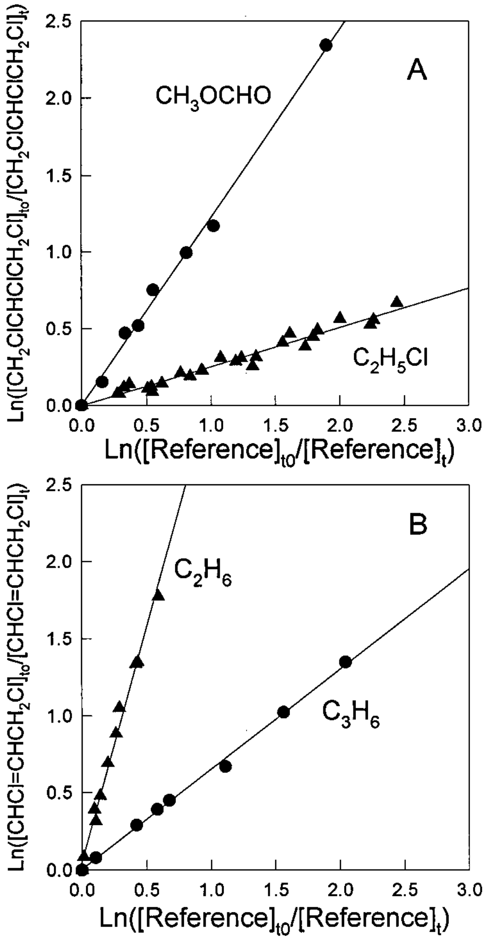

Figure 1. Loss of trichloropropane (A) and 1,3-dichloropropene (B) versus reference compounds following exposure to Cl atoms in 760 Torr of air at 296 K.

The filled symbols in Figure 3 show the observed formation of 1,1,2,3- and 1,2,2,3-tetrachloropropane versus consumption of 1,2,3-trichloropropane following UV irradiation of trichloropropane/Cl_2/N_2 mixtures. The dotted lines are second-order fits to the data to aid visual inspection of the data trends. We attribute the curvature of the plot to secondary loss of tetrachloropropane via reaction with Cl atoms. Control experiments in which reaction mixtures were allowed to stand in the chamber in the dark revealed no evidence for heterogeneous loss of tetrachloro- or trichloropropanes. To derive values for the yields of the tetrachloropropanes and their reactivity with Cl atoms

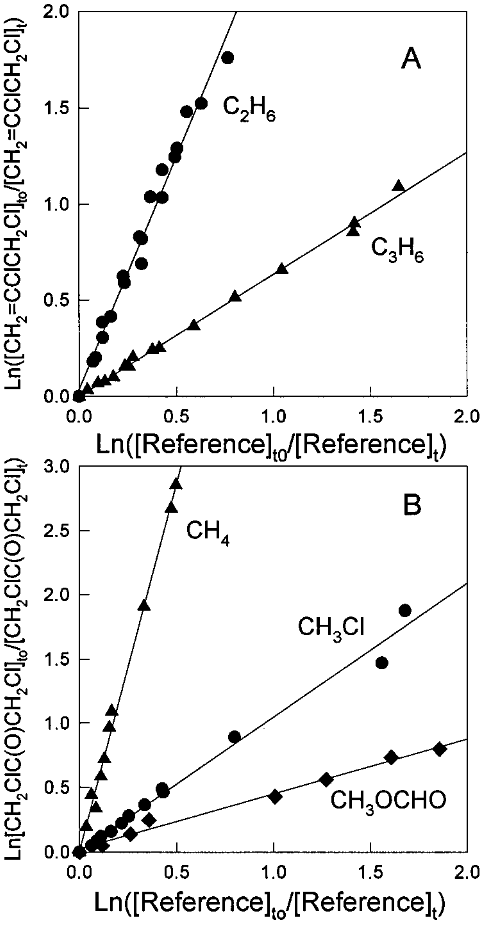

Figure 2. Loss of 2,3-dichloropropene (A) and dichloroacetone (B) versus reference compounds following exposure to Cl atoms in 760 Torr of air at 296 K.

the following expression[17] was fit to the data in Figure 3

$$\frac{[\text{tetrachloropropane}]_t}{[\text{1,2,3-trichloropropane}]_{t0}} = \frac{\alpha}{1-\frac{k_{18}}{k_3}}(1-x)[(1-x)\{k_{18}/k_3\}-1] \quad \text{(I)}$$

where x is the conversion of 1,2,3-trichloropropane, defined as

$$x \equiv 1 - \frac{[\text{1,2,3-trichloropropane}]_t}{[\text{1,2,3]trichloropropane}_{t_0}}$$

α is the molar yield of the tetrachloropropane, and k_3 and k_{18} are the rate constants for reactions 3 and 18.

$$\text{tetrachloropropane} + \text{Cl} \rightarrow \text{products} \quad (18)$$

A fit of expression I to the data in Figure 3 gives $\alpha = 0.70 \pm 0.09$ and 0.44 ± 0.05 and $k_{18}/k_3 = 0.09 \pm 0.05$ and 0.50 ± 0.06 for 1,2,2,3- and 1,1,2,3-tetrachloropropane, respectively. Corrections to account for loss of the tetrachloropropanes can be calculated using the values of k_{18}/k_3 derived above to give the data indicated by the open symbols in Figure 3. Normalizing the combined product yield to 100% gives $k_{3a}/(k_{3a}+k_{3b}) = 0.39 \pm 0.04$ and $k_{3b}/(k_{3a}+k_{3b}) = 0.61 \pm 0.08$. Quoted errors include our estimate of uncertainties associated with the tetrachloropropane calibrations and corrections for their reaction with Cl. Combination of the k_{18}/k_3 rate constant ratios with $k_3 = (1.86 \pm 0.32) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (see section 3.1) results in the values for k_{18} given in Table 1.

Combining the branching ratios above with $k_3 = (1.86 \pm 0.32) \times 10^{-12}$ gives $k_{3a} = (7.3 \pm 1.5) \times 10^{-13}$ and $k_{3b} = (1.1 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The reactivity of each $-CH_2Cl$ group in trichloropropane is $k_{3a}/2 = (3.6 \pm 0.7) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. As might be expected from such structurally similar molecules, this result is comparable to the reactivity of a $-CH_2Cl$ group in CH_2ClCH_2Cl: $(6.5 \pm 1.0) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[18]

3.3. Is Chemical Activation Important for $CH_2ClCHClO$(·) Radicals? Prior to the investigation of the Cl-initiated oxidation of 1,2,3-trichloropropane a limited set of experiments were conducted to determine if chemical activation is an important factor in the fate of $CH_2ClCHClO$(·) radicals. Experiments were first conducted using a mixture containing 26 mTorr of CH_2ClCH_2Cl and 160 mTorr of Cl_2 in 700 Torr of air. UV irradiation led to the formation of HC(O)Cl and $CH_2ClC(O)Cl$ in molar yields of 53 ± 6% and 15 ± 2%, respectively. These results are in excellent agreement with yields of 56 ± 4% and 16 ± 2% for these species reported previously.[18] Experiments were then performed in the presence of NO using mixtures containing 26 mTorr of CH_2ClCH_2Cl, 160 mTorr of Cl_2, 30 mTorr of NO, and either 126 or 401 Torr of O_2 in 700 Torr total pressure with N_2 diluent. HC(O)Cl was observed in a yield comparable to that observed in the absence of NO. Interestingly, in the presence of NO there was no observable formation of $CH_2ClC(O)Cl$ (<3% yield).

Reaction of Cl atoms with 1,2-dichloroethane gives CH_2ClC(·)HCl radicals which add O_2 to give peroxy radicals, $CH_2ClCHClO_2$(·), which are then converted into alkoxy radicals, $CH_2ClCHClO$(·), either via self-reaction or, when NO is present, via reaction with NO.

$$CH_2ClC(\cdot)HCl + O_2 + M \rightarrow CH_2ClCHClO_2(\cdot) + M \quad (19)$$

$$CH_2ClCHClO_2(\cdot) + CH_2ClCHClO_2(\cdot) \rightarrow CH_2ClCHClO(\cdot) + CH_2ClCHClO(\cdot) + O_2 \quad (20a)$$

$$CH_2ClCHClO_2(\cdot) + CH_2ClCHClO_2(\cdot) \rightarrow CH_2ClC(O)Cl + CH_2ClCHClOH + O_2 \quad (20b)$$

$$CH_2ClCHClO_2(\cdot) + NO \rightarrow CH_2ClCHClO(\cdot) + NO_2 \quad (21)$$

$CH_2ClCHClO$(·) radicals formed in reaction 20a undergo reaction with O_2 and intramolecular HCl elimination.[18]

$$CH_2ClCHClO(\cdot) + M \rightarrow CH_2ClC(\cdot)O + HCl + M \quad (22)$$

$$CH_2ClCHClO(\cdot) + O_2 \rightarrow CH_2ClC(O)Cl + HO_2 \quad (23)$$

Using experiments employing reaction 20a as a source of $CH_2ClCHClO$(·), it has been reported that $k_{23}/k_{22} = 2.3 \times 10^{-20}$ cm^3 molecule^{-1}.[18] Hence, in the presence of 401 Torr O_2 the yield of $CH_2ClC(O)Cl$ is expected to be 22%. The absence of $CH_2ClC(O)Cl$ can be explained by the fact that reaction 21 is more exothermic than reaction 20a. Reaction 21 may produce $CH_2ClCHClO$(·) radicals possessing significant internal excitation which undergo decomposition on a time scale too short for the bimolecular reaction 23 to compete. It appears that chemical activation plays a significant role in the atmospheric chemistry of $CH_2ClCHClO$(·) radicals.

3.4. Product Study of Cl-Initiated Oxidation of 1,2,3-Trichloropropane with/without NO Present. The products of

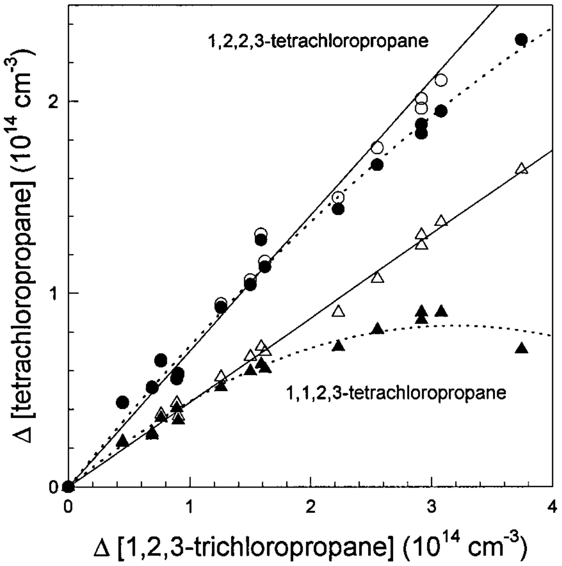

Figure 3. Formation of 1,2,2,3- and 1,1,2,3-tetrachloropropane versus loss of trichloropropane following UV irradiation of trichloropropane/Cl_2/N_2 mixtures. Filled symbols are observed data; open symbols have been corrected for secondary reaction with Cl atoms.

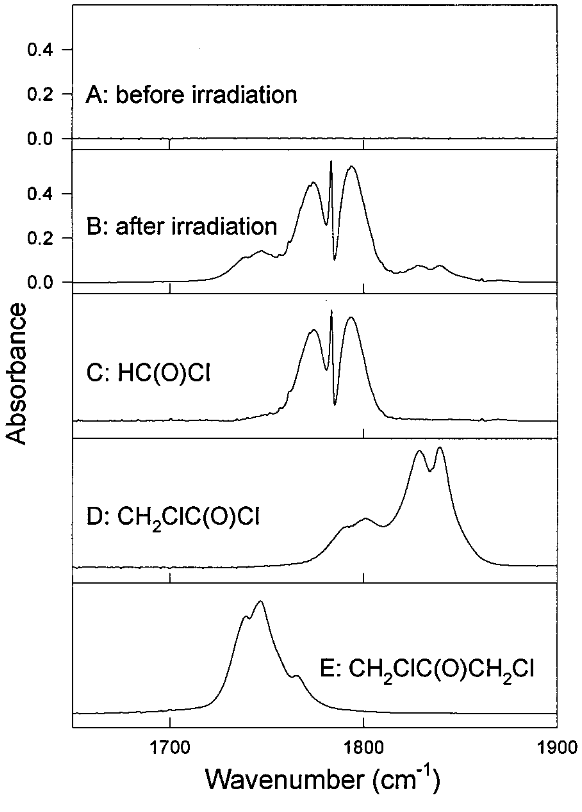

Figure 4. Spectra acquired before (A) and after (B) a 470 s irradiation of a mixture containing 20 ppm $CH_2ClCHClCH_2Cl$ and 73 ppm Cl_2 in 760 Torr of synthetic air. Reference spectra of HC(O)Cl (C), $CH_2ClC(O)Cl$ (D), and $CH_2ClC(O)CH_2Cl$ (E) are shown for comparison.

the Cl atom initiated oxidation of trichloropropane in 700 Torr of synthetic air were studied using the UV irradiation of mixtures of 15−30 mTorr trichloropropane, 50−200 mTorr Cl_2, 0−30 mTorr NO, and either 16−700 Torr of O_2 in 700 Torr total pressure using N_2 diluent. Figure 4 shows typical infrared spectra in the wavenumber region (2200−1700) cm^{-1} obtained before (A) and after (B) UV irradiation of a mixture of 15 mTorr $CH_2ClCHClCH_2Cl$ and 50 mTorr Cl_2 in 700 Torr of synthetic air.

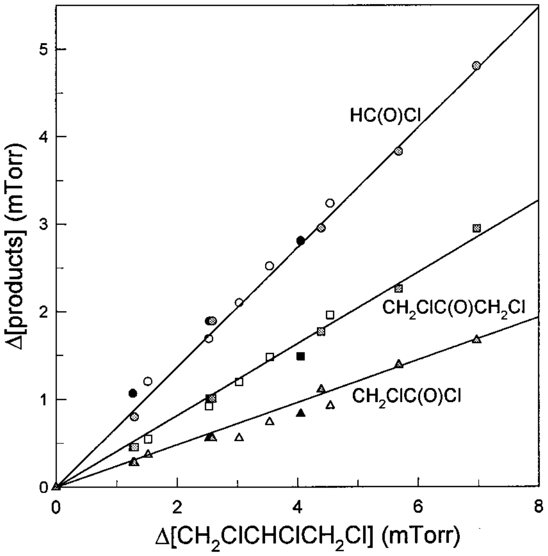

Figure 5. Formation of $CH_2ClC(O)CH_2Cl$ (squares), HC(O)Cl (circles), and $CH_2ClC(O)Cl$ (triangles) versus loss of trichloropropane following the Cl atom initiated oxidation of trichloropropane in the presence of NO_x. Experiments were conducted in 700 Torr total pressure of N_2 at 296 K with $[O_2]$ = 17 (open), 147 (gray), or 554 Torr (filled symbols).

Comparison of panel B with reference spectra of HC(O)Cl, $CH_2ClC(O)CH_2Cl$, and $CH_2ClC(O)Cl$ in panels C−E shows these species are products. In the Cl atom initiated oxidation of $CH_2ClCHClCH_2Cl$, three carbon-containing products were readily identified: HC(O)Cl, $CH_2ClC(O)Cl$, and $CH_2ClC(O)CH_2Cl$. In addition, a small unidentified product feature was observed at 1802 cm^{-1}. The unknown increased with increasing $[O_2]$ and was not present in experiments conducted in the presence of NO. We tentatively assign the unknown to $CH_2ClCHClC(O)Cl$. Features attributable to CO and CO_2 were observed. The molar CO_2 yield was approximately 40%. The molar CO yield was inversely dependent on the O_2 partial pressure and varied from ≈10% in experiments conducted in 700 Torr of O_2 in the absence of NO to ≈55% in experiments with an O_2 partial pressure of 16 Torr in the presence of NO. Figure 5 shows the formation of HC(O)Cl, $CH_2ClC(O)Cl$, and $CH_2ClC(O)CH_2Cl$ versus loss of trichloropropane following irradiation of trichloropropane/Cl_2/NO/O_2/N_2 mixtures. Small corrections (<10%) were applied to the HC(O)Cl and $CH_2ClC(O)CH_2Cl$ data to account for loss of these species via reaction with Cl atoms. Corrections were computed using the kinetic data reported in section 3.1 and $k(\mathrm{Cl}+\mathrm{HC(O)Cl}) = 7.8 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}[19] using the expression[17]

$$\text{correction factor} = \left[\frac{x}{\left(\dfrac{1}{1-\dfrac{k_{\mathrm{prod}}}{k_3}}\right)(1-x)[(1-x)\{k_{\mathrm{prod}}/k_3 - 1\} - 1]}\right)$$

The "correction factor" is the factor by which the observed product yield needs to be mulitiplied to account for secondary loss via reaction with Cl atoms, "x" is the fractional consumption of trichloropropane, and k_3 and k_{prod} are the bimolecular rate constants for reaction of Cl atoms with trichloropropane and the product. To facilitate accurate corrections for secondary reactions a product study of the Cl atom initiated oxidation of dichloroacetone in air was performed. UV irradiation of dichloroacetone/Cl_2/air mixtures produced HC(O)Cl in a molar yield indistinguishable from 200%. This finding is consistent

TABLE 2: Product Data for the Cl Atom Initiated Oxidation of 1,2,3-Trichloropropane in 700 Torr of N_2/O_2 Diluent at 298 K

	molar yield (%) (without NO_x)			molar yield (%) (with NO_x)
product	$[O_2]$ = 16 Torr	$[O_2]$ = 147 Torr	$[O_2]$ = 700 Torr	$[O_2]$ = 16−554 Torr
HC(O)Cl	55 ± 4	57 ± 5	47 ± 5	68 ± 7
$CH_2ClC(O)Cl$	13 ± 1	13 ± 1	18 ± 2	24 ± 3
$CH_2ClC(O)CH_2Cl$	36 ± 3	36 ± 3	35 ± 3	39 ± 5
carbon balance	63 ± 5	64 ± 6	63 ± 6	78 ± 9

with the atmospheric oxidation mechanism of acetone[20] and butadione.[21] Reaction of Cl atoms with $CH_2ClC(O)Cl$ is $1.9 \times 10^{-12}/6.4 \times 10^{-14}$ [18] = 30 times slower than with trichloropropane; no correction of the $CH_2ClC(O)Cl$ data is required. As seen from Figure 5, there was no discernible effect of $[O_2]$ on the product yields observed in the presence of NO. Linear least-squares analysis of the data in Figure 5 gives molar yields (%) for HC(O)Cl, $CH_2ClC(O)Cl$, and $CH_2ClC(O)CH_2Cl$ of 68 ± 7, 24 ± 3, and 39 ± 5 for the Cl atom initiated oxidation of 1,2,3-trichloropropane in the presence of NO. Results obtained in the presence and absence of NO_x are given in Table 2. As shown in Table 2, there was a small but significant effect of $[O_2]$ on the yields of HC(O)Cl and $CH_2ClC(O)Cl$ observed in experiments in the absence of NO. The increased $CH_2ClC(O)Cl$ and decreased HC(O)Cl yields observed in the experiment conducted in 700 Torr of O_2 presumably reflect the competition of reactions 22 and 23 for the available $CH_2ClCHClO(\cdot)$ radicals.

At this point it is germane to consider possible additional losses of these products in the chamber. None of the products are expected to be photolyzed significantly by the UV blacklamps for the 10−60 s irradiation periods used in this work. To check for possible heterogeneous losses, reaction mixtures were allowed to stand in the dark; there were no significant losses (<2%) of any of these compounds over the time scale of the experiments.

3.5. UV−Visible Absorption Spectrum of $CH_2ClC(O)CH_2Cl$. Eight separate injections of $CH_2ClC(O)CH_2Cl$ were made into the 480-L chamber in Wuppertal of 4−25 ppm of $CH_2ClC(O)CH_2Cl$. The resulting UV and IR spectra scaled linearly (to within ±5%) with the $CH_2ClC(O)CH_2Cl$ concentration. The UV spectrum had a maximum at 305 nm. Values of σ (305 nm) = $(1.6 \pm 0.2) \times 10^{-19}$ cm^2 $molecule^{-1}$ and σ (1750 cm^{-1}) = 5.8×10^{-19} cm^2 $molecule^{-1}$ (both base *e*) were obtained. The quoted errors reflect uncertainties associated with the reproducibility of the measurements and our estimate of possible systematic errors associated with uncertainties in the UV and IR path length, calibration of the $CH_2ClC(O)CH_2Cl$ concentration, and sample purity. Figure 6 shows the UV−visible absorption spectrum of $CH_2ClC(O)CH_2Cl$ measured in the present work together with spectra of acetone (average from refs 22 and 23) and chloroacetone.[24] As seen from Figure 6, chlorination of acetone results in a red shift and increase of the UV absorption spectrum. Prolonged exposure of $CH_2ClC(O)CH_2Cl$/air mixtures in the reaction chamber to UV irradiation led to the formation of two products: HC(O)Cl and CO_2. Formation of these products suggests that photolysis proceeds to give $CH_2ClC(O)$ and CH_2Cl radicals which add O_2 to give the corresponding peroxy radicals which are then converted into HC(O)Cl.[2]

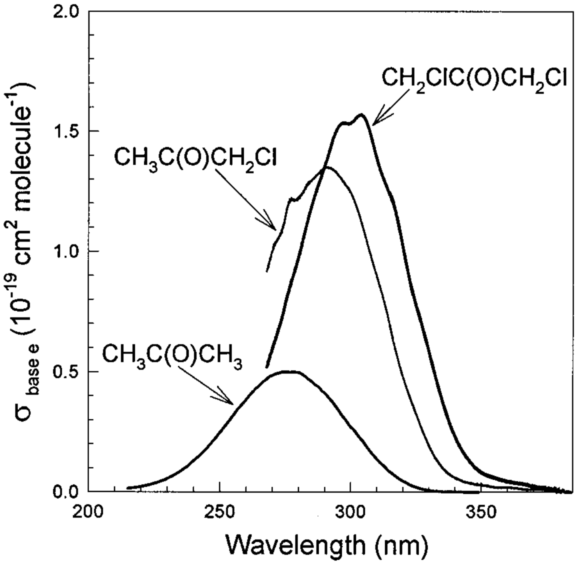

Figure 6. UV spectra of $CH_2ClC(O)CH_2Cl$ (this work), $CH_3C(O)CH_2Cl$,[24] and $CH_3C(O)CH_3$.[22]

To determine a first-order photolysis rate (*j*) for $CH_2ClC(O)CH_2Cl$ in the atmosphere, wavelength-dependent cross section, $\sigma(\lambda)$, quantum yield, $\phi(\lambda)$, and actinic flux, $I(\lambda)$, data are required:

$$j = \int_\lambda \sigma(\lambda)\phi(\lambda)I(\lambda)d\lambda$$

While no gas-phase photolysis quantum yield data are available for $CH_2ClC(O)CH_2Cl$ (to the best of our knowledge) such data are available for acetone. At the maximum of the UV absorption (278 nm) the photodissociation quantum yield for acetone is close to unity, at 300 nm the quantum yield is approximately 0.2, and at 330 nm the quantum yield drops to approximately 0.04.[25] For simplicity we will assume that the quantum yield at all wavelengths for $CH_2ClC(O)CH_2Cl$ photolysis is less than unity and greater than 0.04. Using actinic flux data from Finlayson-Pitts and Pitts,[26] the photolysis rate of $CH_2ClC(O)CH_2Cl$ is calculated to lie in the range $(0.2-5.6) \times 10^{-4}$ s^{-1} for a solar zenith angle of 25 degrees (representative of a typical summer day at 40°N), corresponding to a photolysis lifetime of between 30 min and 12 h.

We can compare this result with the expected atmospheric lifetime of $CH_2ClC(O)CH_2Cl$ with respect to reaction with OH radicals. Using $k(OH+CH_2ClC(O)CH_2Cl) = 5 \times 10^{-13}$,[27] an atmospheric lifetime for methane of 9 years,[28] and $k(OH+CH_4) = 6.3 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} gives an atmospheric lifetime of $CH_2ClC(O)CH_2Cl$ with respect to reaction with OH radicals of 40 days. We conclude that photolysis is the atmospheric fate of $CH_2ClC(O)CH_2Cl$.

4. Discussion

4.1. Atmospheric Oxidation Mechanism of 1,2,3-Trichloropropane. The data in Table 2 provide insight into the atmospheric oxidation mechanism of 1,2,3-trichloropropane. As discussed above, the reaction of Cl atoms with 1,2,3-trichloropropane gives two different alkyl radicals which are expected to rapidly (within 1 μs in an atmosphere of air) add O_2 to give alkyl peroxy radicals. Alkyl peroxy radicals (RO_2) react rapidly with NO via two pathways giving alkoxy radicals (RO) as major products and organic nitrates ($RONO_2$) as minor products.

$$RO_2 + NO \rightarrow RO + NO_2 \tag{24a}$$

$$RO_2 + NO + M \rightarrow RONO_2 + M \tag{24b}$$

The database concerning nitrate yields for reactions of alkyl peroxy radicals with NO shows that the organic nitrate yield, $k_{19b}/(k_{19a}+k_{19b})$, increases with the size of the peroxy radical from <0.005 for methylperoxy,[29] 0.036 for 1- and 2-propylperoxy radicals,[30] to 0.20−0.30 for heptyl- and octylperoxy radicals.[30] Organic nitrates have a characteristic IR feature at 1660−1670 cm^{-1} (asymmetric NO_2 stretch).[31] The product spectra in the present work were examined for features which could be assigned to organic nitrates; none were found. Using an integrated absorption cross section of $(2.5 \pm 0.2) \times 10^{-17}$ cm $\mathrm{molecule}^{-1}$ (base 10) for the asymmetric NO_2 stretch[31] an upperlimit of 10% for the sum of the yields of $CH_2ClCHClCHClONO_2$ and $CH_2ClCCl(ONO_2)CH_2Cl$ was established. The chlorinated peroxy radicals generated from trichloropropane generate far less organic nitrate than unsubstituted alkyl peroxy radicals of comparable molecular weight. Hydroxy-[32] and fluoro-[33] substituted peroxy radicals also give lower nitrate yields in their reactions with NO than comparable alkyl peroxy radicals. At the present time the factors which dictate the nitrate yield in reactions of peroxy radicals with NO are unclear. However, in light of the similar effect of −OH, −F, and −Cl substituents it seems reasonable to speculate that electron withdrawing groups decrease the nitrate yield in reactions of peroxy radicals with NO. In the following discussion we will not consider nitrate formation further.

As stated in the Introduction a major goal of the present study was to investigate the atmospheric fate of the two different alkoxy radicals formed from 1,2,3-trichloropropane. To this end it is useful to consider first the product data obtained from the Cl-initiated oxidation in the presence of NO. In such experiments the peroxy radicals derived from trichloropropane react with NO to give two alkoxy radicals:

$$CH_2ClCHClCHClO_2(\cdot) + NO \rightarrow CH_2ClCHClCHClO(\cdot) + NO_2 \quad (25)$$

$$CH_2ClCO_2(\cdot)ClCH_2Cl + NO \rightarrow CH_2ClCO(\cdot)ClCH_2Cl + NO_2 \quad (26)$$

Two reaction channels are open to the $CH_2Cl{-}CO(\cdot)Cl{-}CH_2Cl$ radical, ejection of a Cl atom, or C−C bond scission:

$$CH_2ClCO(\cdot)ClCH_2Cl + M \rightarrow CH_2ClCOCH_2Cl + Cl + M \quad (27)$$

$$CH_2ClCO(\cdot)Cl{-}CH_2Cl + M \rightarrow CH_2ClC(O)Cl + CH_2Cl(\cdot) + M \quad (28)$$

$CH_2ClCOCH_2Cl$ product provides a marker for the importance of reaction 27. $CH_2ClC(O)Cl$ product provides a marker for the importance of reaction 28. It should be noted that in the presence of NO there are no complications caused by $CH_2ClC(O)Cl$ formation following decomposition of $CH_2ClCHClCHClO(\cdot)$ radicals (see section 3.3). As seen from Table 2, the combined yield of dichloroacetone and $CH_2ClC(O)Cl$ in the presence of NO_x (63 ± 6%) was indistinguishable from the yield of $CH_2Cl{-}CO(\cdot)Cl{-}CH_2Cl$ radicals in the system; $k_{3b}/(k_{3a}+k_{3b}) = (61 \pm 8\%)$. We conclude that reactions 27 and 28 are competing fates of $CH_2ClCO(\cdot)ClCH_2Cl$ radicals formed in reaction 26.

Peroxy radical self-and cross reactions are the source of $CH_2ClCO(\cdot)ClCH_2Cl$ radicals in the absence of NO_x, e.g.,

$$CH_2ClCOO(\cdot)ClCH_2Cl + CH_2ClCOO(\cdot)ClCH_2Cl \rightarrow 2CH_2ClCO(\cdot)ClCH_2Cl + O_2 \quad (29)$$

As seen from Table 2 the combined yield of dichloroacetone and $CH_2ClC(O)Cl$ in the absence of NO_x is smaller than that in the presence of NO_x, and the relative importance of the two different products is different. By analogy to other peroxy radical reactions,[14] reaction 26 is expected to be 14 kcal mol^{-1} more exothermic than reaction 29. Alkoxy radicals formed in reaction 26 may possess significant internal excitation. It appears that chemical excitation of $CH_2ClCO(\cdot)ClCH_2Cl$ radicals produced in reaction 26 results in a greater fraction of these radicals undergoing decomposition via C−C bond scission. As discussed in the Introduction, such chemical activation effects have been reported for several atmospherically relevant alkoxy radicals.

Let us now consider the fate of the alkoxy radical formed following H-atom abstraction from the end of the trichloropropane molecule. The $CH_2ClCHClCHClO(\cdot)$ radical can either react with O_2, decompose via intramolecular HCl elimination, undergo C−C bond scission, or elimate a Cl atom.

$$CH_2ClCHClCHClO(\cdot) + O_2 \rightarrow CH_2ClCHClC(O)Cl + HO_2 \quad (30)$$

$$CH_2ClCHClCHClO(\cdot) + M \rightarrow CH_2ClCHClC(\cdot)(O) + HCl + M \quad (31)$$

$$CH_2ClCHClCHClO(\cdot) + M \rightarrow CH_2ClC(\cdot)HCl + HC(O)Cl + M \quad (32)$$

$$CH_2ClCHClCHClO(\cdot) + M \rightarrow CH_2ClCHClC(O)H + Cl + M \quad (22)$$

The observation of a substantial HC(O)Cl yield shows that reaction 30 does not dominate the fate of $CH_2ClCHClCHClO(\cdot)$ radicals. The $CH_2ClCHClC(\cdot)(O)$ radicals formed in reaction 31 will be converted into $CH_2ClC(\cdot)HCl$ radicals via

$$CH_2ClCHClC(\cdot)(O) + O_2 + M \rightarrow CH_2ClCHClC(O)O_2(\cdot) + M \quad (34)$$

$$CH_2ClCHClC(O)O_2(\cdot) + RO_2 \rightarrow CH_2ClCHClC(O)O(\cdot) + RO + O_2 \quad (35)$$

$$CH_2ClCHClC(O)O(\cdot) + M \rightarrow CH_2ClC(\cdot)HCl + CO_2 + M \quad (36)$$

The observation of a significant yield of CO_2 suggests, but does not prove, that reaction 31 is an important loss fate of $CH_2ClCHClCHClO(\cdot)$. At present we are unable to deduce the atmospheric fate of $CH_2ClCHClCHClO(\cdot)$ radicals.

4.2. Implications for Atmospheric Chemistry. We present here the results of the first study of the atmospheric oxidation mechanism of 1,2,3-trichloropropane. Atmospheric oxidation will be initiated by reaction with OH radicals which is calculated to proceed with a rate constant of 3.5×10^{-13} cm^3 $\mathrm{molecule}^{-1}$ s^{-1} at 298 K.[27] Assuming an atmospheric lifetime for methane of 9 years[34] and a rate constant for the CH_4 + OH reaction of 6.3×10^{-15} cm^3 $\mathrm{molecule}^{-1}$ s^{-1} leads to an atmospheric lifetime for 1,2,3-trichloropropane against reaction with OH of 2 months. Dichloroacetone is the major oxidation product with smaller amounts of $CH_2ClC(O)Cl$, HC(O)Cl, and $CH_2ClCHClC(O)Cl$. The atmospheric fate of dichloroacetone is photolysis which is estimated to proceed at a rate of $(5.6 \pm 0.7) \times 10^{-4}$ s^{-1} in the sunlit atmosphere to produce HC(O)Cl. The atmospheric fate of the acid chlorides $CH_2ClC(O)Cl$, $CH_2ClCHClC(O)Cl$, and HC(O)Cl is expected to be incorporation into rain-cloudfogwater followed by hydrolysis and removal by wet deposition within probably 5−15 days.[35] Hydrolysis of HC(O)Cl gives formic acid which is a ubiquitous component of the environment and is of no concern. Hydrolysis of $CH_2ClC(O)Cl$ and $CH_2ClCHClC(O)Cl$ gives monochloroacetic and 1,2-dichloropropionic acids. In spiked river water, biodegradation of monochloroacetic acid was complete within 30 days,[36] and it is likely that degradation of 1,2-dichloropropionic acids will be equally rapid. The atmospheric degradation of 1,2,3-trichloropropane is unlikely to produce persistent organic pollutants.

Finally, the present work shows that chemical activation plays a role in the atmospheric fate of $CH_2ClCHClO(\cdot)$ and $CH_2ClCO(\cdot)ClCH_2Cl$ radicals. Activation effects have now been demonstrated for several atmospherically important alkoxy radicals and should be considered when assessing the atmospheric oxidation mechanism of organic compounds.

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