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Atmospheric Chemistry of Tetrachloroethene ($Cl_2C{=}CCl_2$): Products of Chlorine Atom Initiated Oxidation

L. P. Thüner, I. Barnes,*,† and K. H. Becker

Bergische Universität GH Wuppertal/FB 9, Physikalische Chemie, Gaussstrasse 20,
D-42097 Wuppertal, Germany

T. J. Wallington*,‡ and L. K. Christensen

Ford Research Laboratory, SRL-3083, Ford Motor Company, P.O. Box 2053, Dearborn, Michigan 48121-2053

J. J. Orlando and B. Ramacher§

Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder Colorado 80303

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The products following Cl atom initiated oxidation of C_2Cl_4 at 700−760 Torr of air and 230−299 K in the presence and absence of NO_x were investigated using three different FTIR smog chamber techniques. There was no measurable effect of temperature on the product yields. $CCl_3C(O)Cl$ and $COCl_2$ were formed with molar yields of 68 ± 6% and 77 ± 12% in the presence of NO_x and 87 ± 11% and 32 ± 4% in the absence of NO_x. These results give branching ratios for the $CCl_3C(O)Cl$ and $COCl_2$ forming channels of 0.64 and 0.36 in the presence of NO_x and 0.84 and 0.16 in the absence of NO_x. Contrary to a recent report by Hasson and Smith (*J. Phys. Chem. A*, **1999**, *103*, 2031), variation of the initial C_2Cl_4 by a factor of 300 over the range $(0.016-5.6) \times 10^{14}$ molecule cm^{-3} had no discernible effect (<10%) on the product distributions. The different product distribution observed in the presence of NO_x may reflect the formation and subsequent decomposition of chemically activated C_2Cl_5O radicals, formed in the exothermic reaction of $C_2Cl_5O_2$ with NO. The kinetics of the reaction of Cl atoms with C_2Cl_4 were measured in 2.0−700 Torr of air at 296 K. The results are in good agreement with the previous study by Nicovich et al. (*J. Phys. Chem.* **1996**, *100*, 680). The combined data can be described using $F_c = 0.6$, $k_o = (1.8 \pm 0.3) \times 10^{-28}$ cm^6 $molecule^{-2}$ s^{-1} and $k_\infty = (4.0 \pm 0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Results are discussed with respect to the atmospheric chemistry of C_2Cl_4.

1. Introduction

Perchloroethene is a widely used chlorinated solvent with an annual global emission rate of 200−300 kt.[1,2] The atmospheric lifetime of C_2Cl_4 is dictated by reaction with OH radicals and is approximately 0.4 years.[1,3,4] Reaction of OH radicals with C_2Cl_4 proceeds via addition leading to the formation of $COCl_2$ as a major product:[5]

$$OH + C_2Cl_4 + M \rightarrow HOCCl_2CCl_2 + M \quad (1)$$

$$HOCCl_2CCl_2 + O_2 + M \rightarrow HOCCl_2CCl_2O_2 + M \quad (2)$$

$$HOCCl_2CCl_2O_2 + NO \rightarrow HOCCl_2CCl_2O + NO_2 \quad (3)$$

$$HOCCl_2CCl_2O + M \rightarrow HOCCl_2 + COCl_2 + M \quad (4)$$

$$HOCCl_2 + O_2 \rightarrow COCl_2 + HO_2 \quad (5)$$

There is a debate concerning the potential importance of Cl atom initiated oxidation of C_2Cl_4 as a source of trichloroacetic acid. The relative importance of Cl atom initiated oxidation depends on the relative reactivity of OH radicals and Cl atoms and their atmospheric abundance. At 298 K in one atmosphere of air, Cl atoms react 235 times faster than OH radicals with C_2Cl_4.[6] The global average tropospheric OH radical concentration is approximately 10^6 cm^{-3}.[7,8] The tropospheric chlorine atom concentration is uncertain. Some estimates suggest typical marine boundary layer Cl atom levels of 10^4 cm^{-3},[9,10,11] others suggest mean tropospheric levels $<10^3$ cm^{-3}.[4,12] Atmospheric concentrations of C_2Cl_4 calculated assuming only loss via OH radical attack reproduce, within the uncertainties of the measurements, the ambient concentrations of C_2Cl_4 in the northern and southern hemispheres.[1] This agreement shows that reaction with OH radicals is the dominant removal mechanism but does not preclude a minor contribution by Cl atoms. Franklin and Sidebottom[13] have estimated that 13% of the global atmospheric loss of C_2Cl_4 is initiated via reaction with Cl atoms.

Reaction of Cl atoms with C_2Cl_4 proceeds via addition leading to the formation of $CCl_3C(O)Cl$ (which can undergo hydrolysis to give $CCl_3C(O)OH$) and $COCl_2$:

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* To whom correspondence should be addressed.

† E-mail: barnes@physchem.uni-wuppertal.de.

‡ E-mail: twalling@ford.com.

§ Permanent Address: Institut für Atmosphärische Chemie, Forschungszentrum Jülich GmbH, D-52425, Jülich, Germany.

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$$\mathrm{Cl + C_2Cl_4 + M \rightarrow CCl_3CCl_2 + M} \qquad (6)$$

$$\mathrm{CCl_3CCl_2 + O_2 + M \rightarrow CCl_3CCl_2O_2 + M} \qquad (7)$$

$$\mathrm{CCl_3CCl_2O_2 + NO \rightarrow CCl_3CCl_2O + NO_2} \qquad (8)$$

$$\mathrm{CCl_3CCl_2O + M \rightarrow CCl_3C(O)Cl + Cl + M} \qquad (9a)$$

$$\mathrm{CCl_3CCl_2O + M \rightarrow CCl_3 + COCl_2 + M} \qquad (9b)$$

$$\mathrm{CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M}$$

$$\mathrm{CCl_3O_2 + NO \rightarrow CCl_3O + NO_2}$$

$$\mathrm{CCl_3O + M \rightarrow COCl_2 + Cl + M}$$

Over the period 1967–1997, five separate studies of the fate of CCl_3CCl_2O radicals[14–18] were conducted using a variety of analytical techniques (GC/IR/FTIR). In all cases, CCl_3CCl_2O radicals were prepared by the self-reaction of the corresponding peroxy radical ($CCl_3CCl_2O_2$) which was produced either via reactions 6–7 or via reaction of Cl atoms with C_2Cl_5H in the presence of O_2. All five studies lead to the same conclusion regarding the atmospheric fate of CCl_3CCl_2O radicals, namely, that this species undergoes decomposition via both elimination of a Cl atom (reaction 9a) and C–C bond scission (reaction 9b) with $k_{9a}/(k_{9a} + k_{9b}) \approx 85\%$ and $k_{9b}/(k_{9a} + k_{9b}) \approx 15\%$. Very recently, Hasson and Smith[19] reported results of a product study of the Cl atom initiated oxidation of C_2Cl_4 in the presence, and absence, of added NO. Hasson and Smith[19] report two very interesting findings.

First, that the product yields of $CCl_3C(O)Cl$ and $COCl_2$ depend on the initial concentration of C_2Cl_4 with the yield of $COCl_2$ increasing with decreasing $[C_2Cl_4]_0$. Extrapolation to the very low atmospheric levels of C_2Cl_4 suggests that $COCl_2$ will be the sole atmospheric degradation product. This is a significant finding as it suggests that C_2Cl_4 may not be a source of $CCl_3C(O)Cl$, and hence $CCl_3C(O)OH$, in the environment.

Second, that for a given $[C_2Cl_4]$ the relative product yields of $CCl_3C(O)Cl$ and $COCl_2$ change when NO is present in the system. As noted by Hasson and Smith,[19] a probable explanation for this observation is that CCl_3CCl_2O radicals formed by the reaction of $CCl_3CCl_2O_2$ with NO contain more initial internal energy than CCl_3CCl_2O radicals formed via self-reaction of $CCl_3CCl_2O_2$ radicals. Such behavior has been reported recently for CF_3CFHO radicals.[20]

In the present study we have used the FTIR smog chamber systems at Wuppertal, Ford, and NCAR to study the products following the Cl atom initiated oxidation of C_2Cl_4. The aims of the present study were two-fold. First, to investigate the effect of initial C_2Cl_4 concentration on the product yields over as wide a range of $[C_2Cl_4]_o$ as possible. Second, to search for the effect of chemical activation in CCl_3CCl_2O radicals by conducting a series of experiments with, and without, added NO.

2. Experimental Section

Experiments were performed using the photoreactors at Wuppertal,[21] Ford,[22] and the National Center for Atmospheric Research.[23] The experimental systems are described in detail elsewhere and are discussed briefly here. In all three laboratories the oxidation of C_2Cl_4 was initiated by reaction with Cl atoms generated by the photolysis of molecular chlorine in synthetic air, with products determined by in situ FTIR spectroscopy.

$$\mathrm{Cl_2} + h\nu \rightarrow 2\,\mathrm{Cl} \qquad (10)$$

$$\mathrm{Cl + C_2Cl_4 \rightarrow products} \qquad (6)$$

2.1 FTIR Photoreactor System in Wuppertal. Experiments were performed at 299 ± 2 K in 1000 mbar total pressure of synthetic air using a 1080-liter photoreactor, equipped with a built-in White mirror system coupled to an FTIR spectrometer to monitor the concentration–time behavior of reactant and products. Photolysis of chlorine with fluorescent lamps (Philips Tl 40W/05, $320 < \lambda < 450$ nm) was used to produce Cl atoms.

The FTIR spectrometer (Bruker IFS-88) was operated with a resolution of 1 cm^{-1} and a path length of 484.7 m. Mixtures of C_2Cl_4, $(0.16-2.2) \times 10^{13}$, Cl_2 $(0.22-1.1) \times 10^{14}$, and NO $(0-1.1) \times 10^{14}$ molecule cm^{-3} in air were irradiated for 10–20 min. During this time 10 spectra were collected, each derived from 64 to 128 co-added interferograms.

2.2 FTIR Smog Chamber System at Ford Motor Company. Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Loss of C_2Cl_4 and formation of products were monitored by Fourier transform infrared spectroscopy using an infrared path length of 27.4 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms.

The products of the atmospheric oxidation of C_2Cl_4 were investigated by irradiating $C_2Cl_4/Cl_2/O_2/N_2$ mixtures with and without added NO at a total pressure of 700 Torr at 296 ± 2 K. Initial concentrations of the gas mixtures were: C_2Cl_4 $(0.96-4.6) \times 10^{14}$, NO $(0-7.1) \times 10^{14}$, Cl_2 $(2.6-6.1) \times 10^{14}$ molecule cm^{-3} in 700 Torr of air diluent.

In smog chamber experiments, unwanted losses of reactants and products via photolysis, dark chemistry, and wall reactions have to be considered. Each experiment lasted 15–25 min with total photolysis times not exceeding 7 min (4–7 irradiations). Control experiments were performed to check for unwanted losses in the chamber. No significant loss (<2%) of C_2Cl_4, $CCl_3C(O)Cl$, or $COCl_2$ was observed when mixtures of these compounds in air were irradiated for 7–10 min or left in the dark for 7–20 min, showing that photolytic and heterogeneous losses of these compounds in the chamber are not important.

2.3 FTIR System at the National Center for Atmospheric Research. The apparatus at NCAR consisted of a 47-liter stainless steel reactor fitted with a quartz window at one end to allow photolysis using a filtered xenon arc lamp. Experiments involved the photolysis of C_2Cl_4 $(0.6-5.6) \times 10^{14}$ molecule cm^{-3}, Cl_2 $(8-80) \times 10^{14}$ molecule cm^{-3}, NO $(0-4) \times 10^{14}$ molecule cm^{-3}, O_2 (140 Torr), and N_2 (560–580 Torr) and were conducted at 230, 250, and 298 K. Typical photolysis times were 5–15 s. A Bomem DA 3.01 FT-IR spectrometer was interfaced to a Hanst-type optical arrangement mounted within the reaction cell, for in situ IR spectroscopic analysis of the gas mixture composition. Reactant loss and product formation were monitored by FTIR absorption spectroscopy, using an optical path length of 32.6 m and a spectral resolution of 1.0 cm^{-1}. Infrared spectra were derived from 50 to 100 co-added interferograms.

3. Results

3.1 Relative Rate Study of $k(Cl + C_2Cl_4)$ in 2.5–700 Torr of Air at 296 K. Prior to investigating the atmospheric oxidation products, relative rate experiments were performed using the experimental system at Ford to investigate the kinetics of the reactions of Cl atoms with C_2Cl_4. Details of the experimental techniques can be found elsewhere.[24] Experiments were per-

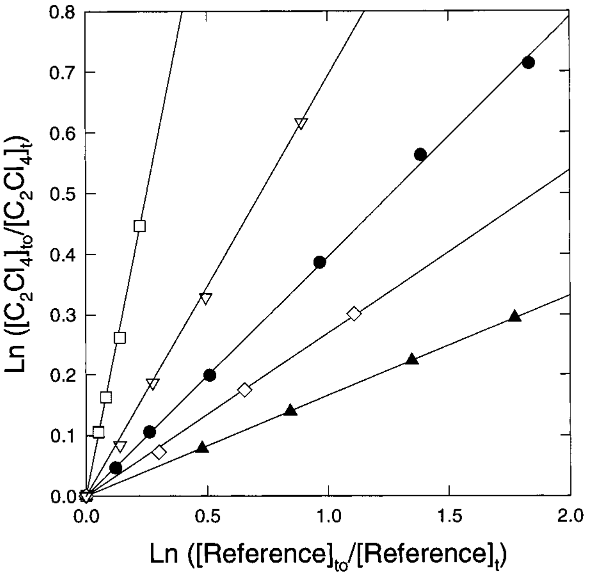

Figure 1. Decay of C_2Cl_4 following exposure to Cl atoms in air diluent at 296 ± 2 K using the following reference compounds and total pressures: open inverse triangles: C_2H_6, 422 Torr; diamonds: C_2H_5OH, 55.8 Torr; squares: C_2H_5F, 11.4 Torr; circles: CH_3OH, 35 Torr; filled triangles: CH_3OH, 2.8 Torr.

TABLE 1: Kinetic Data for $k(Cl + C_2Cl_4)$

total pressure (Torr)	reference	$k(Cl + C_2Cl_4)/k(Cl + \text{reference})$	$k(Cl + C_2Cl_4)$ (cm^3 molecule^{-1} s^{-1})
700	CH_3OH	0.70	3.9×10^{-11}
700	C_2H_6	0.69	4.1×10^{-11}
422	C_2H_6	0.693	4.1×10^{-11}
111	CH_3OH	0.58	3.2×10^{-11}
54.5	CH_3OH	0.494	2.7×10^{-11}
55.8	C_2H_5OH	0.269	2.5×10^{-11}
35	CH_3OH	0.395	2.2×10^{-11}
11.4	C_2H_5F	2.00	1.5×10^{-11}
5.1	CH_3OH	0.220	1.2×10^{-11}
3.7	CH_3OH	0.177	9.7×10^{-12}
2.8	CH_3OH	0.166	9.1×10^{-12}
2.5	C_2H_5F	0.927	6.9×10^{-12}
2.0	C_2H_5F	0.954	7.1×10^{-12}

formed in 2.5–700 Torr (760 Torr = 1013 mbar) of air diluent at 296 K. Photolysis of molecular chlorine was used as a source of Cl atoms.

$$Cl_2 + h\nu \rightarrow 2\,Cl \quad (10)$$

$$Cl + C_2Cl_4 \rightarrow \text{products} \quad (6)$$

$$Cl + CH_3OH \rightarrow \text{products} \quad (11)$$

$$Cl + C_2H_6 \rightarrow \text{products} \quad (12)$$

$$Cl + C_2H_5OH \rightarrow \text{products} \quad (13)$$

$$Cl + C_2H_5F \rightarrow \text{products} \quad (14)$$

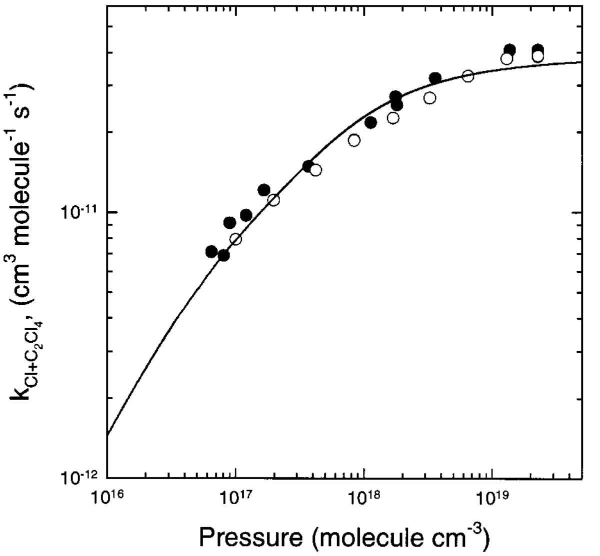

Figure 2. Plot of the effective second-order rate constant $k(Cl + C_2Cl_4)$ at 296 ± 2 K versus total pressure measured in the present work (●) in air and measured by Nicovich et al.[26] (○) in N_2 at 299 K.

The kinetics of reaction 6 were measured relative to reactions 11–14. Figure 1 shows representative data obtained at 2.78, 11.4, 35, 55.8, and 422 Torr (760 Torr = 1013 mbar) total pressure. The lines through the data points in Figure 1 are linear least-squares fits. Rate constant ratios k_6/k_{11}, k_6/k_{12}, k_6/k_{13}, and k_6/k_{14} obtained from the slopes of plots in Figure 1 are given in Table 1. These rate constant ratios can be placed upon an absolute basis using $k_{11} = 5.5 \times 10^{-11}$, $k_{12} = 5.9 \times 10^{-11}$, $k_{13} = 9.4 \times 10^{-11}$, and $k_{14} = 7.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [25] to give the k_6 values in Table 1 and Figure 2. As seen from Figure 2, the results from the present work agree with those measured recently in N_2 diluent by Nicovich et al.[26] The curve in Figure 2 shows the result of a fit of the Troe formula to the combined data set from the present work and Nicovich et al.[26] using F_c fixed at 0.6 which gives $k_o = (1.8 \pm 0.3) \times 10^{-28}$ cm^6 molecule^{-2} s^{-1} and $k_\infty = (4.0 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

3.2 Cl Atom Initiated Oxidation of C_2Cl_4 in Air in the Absence of NO at 298 ± 5 K. The first goal of the present study was to investigate the dependence of the $CCl_3C(O)Cl$ and $COCl_2$ product yields on $[C_2Cl_4]$. Experiments were conducted using the UV irradiation of C_2Cl_4/Cl_2/air mixtures in the FTIR–smog chamber systems at Wuppertal, Ford, and NCAR. The IR path length in the 1080-liter chamber system at Wuppertal is approximately 20 times greater than those in the Ford and NCAR chambers, and this enables the use of much lower initial concentrations of C_2Cl_4 in the experiments at Wuppertal. Typical spectra obtained before (A) and after (B) a 600 s irradiation of a mixture containing 1.2×10^{13} molecule cm^{-3} C_2Cl_4 and 2.2×10^{13} molecule cm^{-3} Cl_2 in 1000 mbar of air diluent in the Wuppertal chamber are shown in Figure 3. Comparison of panel B with reference spectra of $COCl_2$ and $CCl_3C(O)Cl$ given in panels C and D shows the formation of these two products. In all experiments $CCl_3C(O)Cl$ and $COCl_2$ were the only carbon containing products observed. As shown in Figure 4A, the increase in $CCl_3C(O)Cl$ and $COCl_2$ scaled linearly with loss of C_2Cl_4, suggesting that secondary loss of these compounds is insignificant. Linear least-squares analysis of the data in Figure 4A gives molar yields of 79% and 34% for $CCl_3C(O)Cl$ and $COCl_2$, respectively. Individual variation of the following experimental parameters, C_2Cl_4 concentration over the range $(0.016-5.6) \times 10^{14}$ molecule cm^{-3}, Cl_2 over the range $(0.22-1.1) \times 10^{14}$, and light intensity by a factor of 4 (using either 4 or 16 lamps), had no discernible effect (<10%) on the product distributions.

Figure 5A shows the branching ratio for reaction 9 derived from the molar yield of $CCl_3C(O)Cl$ and half the molar yield of $COCl_2$ (channel (9b) leads to the formation of 2 molecules of $COCl_2$) plotted versus the $[C_2Cl_4]$. Data for $[C_2Cl_4]_0 < 3 \times 10^{13}$ were measured using the Wuppertal system while data for $[C_2Cl_4]_0 > 5 \times 10^{13}$ were measured at Ford and NCAR. As

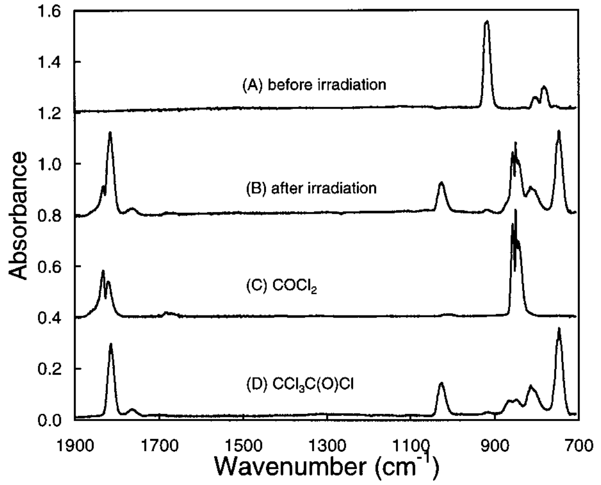

Figure 3. IR spectra acquired before (A) and after (B) a 600 s irradiation of a mixture containing 1.2 × 10^{13} C_2Cl_4 and 2.2 × 10^{13} molecule cm^{-3} Cl_2. During the irradiation about 95% of the C_2Cl_4 was consumed. Panels C and D show reference spectra of $COCl_2$ and $CCl_3C(O)Cl$.

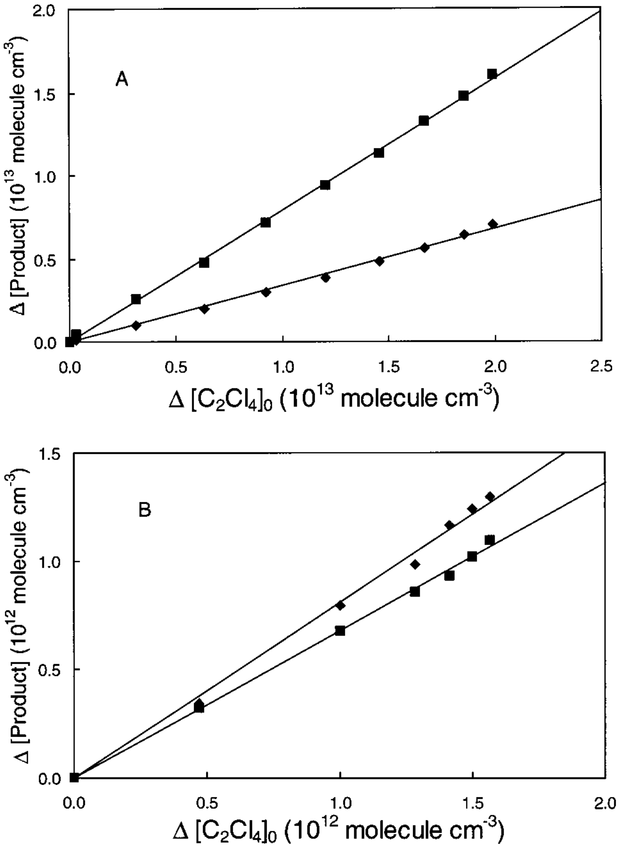

Figure 4. Formation of $CCl_3C(O)Cl$ (■) and $COCl_2$ (◆) versus loss of C_2Cl_4 following UV irradiation of mixtures of either (A) 2.2 × 10^{13} C_2Cl_4 and 2.2 × 10^{13} Cl_2 or (B) 1.64 × 10^{12} C_2Cl_4, 1.1 × 10^{14} Cl_2, and 1.1 × 10^{14} molecule cm^{-3} NO in 1000 mbar of air at 299 K.

seen from Figure 5A there is a small systematic difference between the data sets with the $CCl_3C(O)Cl$ yields measured at Ford and NCAR approximately 10% greater than those at Wuppertal and the $COCl_2$ yield 5−10% lower than measured at Wuppertal. Such differences reflect small differences in the calibration of the reference spectra which we estimate have an accuracy of 5−10%. There is no evidence for any dependence of the product yields on $[C_2Cl_4]_o$ over the range studied. Averaging all the data together gives molar yields of 87 ± 11% and 32 ± 4% for $CCl_3C(O)Cl$ and $COCl_2$ (Table 2) which are indicated by the horizontal lines in Figure 5A.

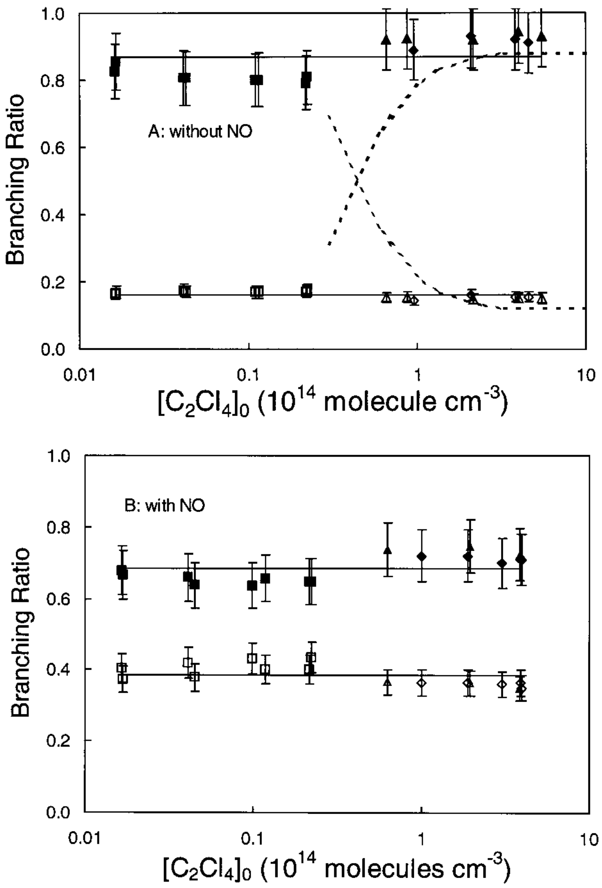

Figure 5. Branching ratios for $CCl_3C(O)Cl$ (filled symbols) and $COCl_2$ (open symbols) producing channels of the Cl atom initiated oxidation of C_2Cl_4 in the absence (A) or presence (B) of NO plotted versus the initial $[C_2Cl_4]$. Squares: Wuppertal; diamonds: Ford; triangles: NCAR. The solid horizontal lines are averages of the Wuppertal/Ford/NCAR data. Dotted lines show the behavior reported by Hasson and Smith[19] (taken from the 700 Torr data in Figure 11).[19]

Hasson and Smith[19] reported a significant change in the observed $CCl_3C(O)Cl$ and $COCl_2$ yields with decreasing $[C_2Cl_4]_o$ as indicated by the dotted lines in Figure 5A (taken from the 700 Torr data in Figure 11 of Hasson and Smith).[19] As seen from Figure 5A, even at much lower values of $[C_2Cl_4]_o$ than those employed by Hasson and Smith,[19] we observe no effect of $[C_2Cl_4]_o$ on the product distribution.

3.3 Cl Atom Initiated Oxidation of C_2Cl_4 in Air in the Presence of NO at 298 ± 5 K. The second goal of the present study was to investigate whether the $CCl_3C(O)Cl$ and $COCl_2$ product yields change if CCl_3CCl_2O radicals are prepared by the reaction of $C_2Cl_5O_2$ with NO rather than the self-reaction of $CCl_3CCl_2O_2$ radicals. Experiments were performed at Wuppertal, Ford, and NCAR using the UV irradiation of $C_2Cl_4/Cl_2/NO$/air mixtures. As with the first set of experiments, only two carbon containing products were observed; $CCl_3C(O)Cl$ and $COCl_2$. Figure 4B, shows typical results following successive irradiations of a mixture containing 1.64 × 10^{12} C_2Cl_4, 1.1 × 10^{14} Cl_2, and 1.1 × 10^{14} molecule cm^{-3} NO in 1000 mbar of air. Linear least-squares analysis of the data in Figure 4B gives molar yields of 68% and 81% for $CCl_3C(O)Cl$ and $COCl_2$, respectively. Individual variation of the following experimental parameters, initial C_2Cl_4 concentration over the range (0.016−4.6) × 10^{14}, Cl_2 over the range (0.022−6.0) × 10^{15}, and light

TABLE 2: Results from Previous Studies of the Fate of C_2Cl_5O Radicals

reactant	primary product	branching ratio		$[\text{reactant}]_0$ molecule cm^{-3}	temp (K)	ref
		without NO_x	with NO_x			
$Cl_2C{=}CCl_2$	$CCl_3C(O)Cl$	0.87 ± 0.11	0.68 ± 0.06	$1.6 \times 10^{12} - 4.6 \times 10^{14}$	230, 250, 298	this work
	$COCl_2$	0.16 ± 0.02	0.39 ± 0.06	$1.6 \times 10^{12} - 4.6 \times 10^{14}$		
$Cl_2C{=}CCl_2$	$CCl_3C(O)Cl$	0.90 [a]	0.75	$> 2 \times 10^{14}$	298, 353, 393	19
	$CCl_3C(O)Cl$	$0.90 \rightarrow 0.30$ [a]		$2 \times 10^{14} \rightarrow 3 \times 10^{13}$		
	$COCl_2$	0.10 [a]		$> 2 \times 10^{14}$		
	$COCl_2$	$0.10 \rightarrow 0.70$ [a]		$2 \times 10^{14} \rightarrow 3 \times 10^{13}$		
$Cl_3C{-}CCl_2H$	$CCl_3C(O)Cl$	0.85 [a]		$> 2 \times 10^{14}$	298, 353, 393	19
	$CCl_3C(O)Cl$	$0.85 \rightarrow 0.60$ [a]		$2 \times 10^{14} \rightarrow 3 \times 10^{13}$		
	$COCl_2$	0.15 [a]		$> 2 \times 10^{14}$		
	$COCl_2$	$0.15 \rightarrow 0.40$ [a]		$2 \times 10^{14} \rightarrow 3 \times 10^{13}$		
$Cl_2C{=}CCl_2$	$CCl_3C(O)Cl$	0.87		1×10^{14}	296	18
	$COCl_2$	0.14				
$Cl_3C{-}CCl_2H$	$CCl_3C(O)Cl$	0.86 ± 0.09		4.2×10^{14}, 4.9×10^{14}	296	17
	$COCl_2$	0.17 ± 0.02				
$Cl_2C{=}CCl_2$	$CCl_3C(O)Cl$	0.85 [b]		$(0.4{-}1.3) \times 10^{17}$	297, 305	15
	$COCl_2$	0.15 [b]				
$Cl_2C{=}CCl_2$	$CCl_3C(O)Cl$	0.85		$(0.8{-}8.0) \times 10^{18}$	354, 373	14
	$COCl_2$	0.15				
$Cl_3C{-}CCl_2H$	$CCl_3C(O)Cl$	0.85		$(0.6{-}1.9) \times 10^{18}$	354, 373	14
	$COCl_2$	0.15				

[a] Yields normalized to sum to 1.0. [b] Only ratio $CCl_3C(O)Cl/COCl_2$ reported as 5.0−6.0.

intensity by a factor of 4 (using either 4 or 16 lamps), had no discernible effect (<10%) on the product distributions.

Figure 5B shows the branching ratio for reaction 8 in the presence of NO derived from the molar yield of $CCl_3C(O)Cl$ and half of the molar yield of $COCl_2$ plotted versus $[C_2Cl_4]_0$. Averaging all the data gives molar yields of 68 ± 6% and 77 ± 12% for $CCl_3C(O)Cl$ and $COCl_2$, which are indicated by the horizontal lines in Figure 5B. Comparison of the data in Figures 5A and 5B shows that the product distribution observed in the presence of NO is significantly different from that observed in the absence of NO. This finding is consistent with the results reported by Hasson and Smith[19] who performed two sets of experiments using a relatively high concentration of $[C_2Cl_4]_0 = 4 \times 10^{14}$ molecule cm^{-3} (with and without) added NO. Hasson and Smith report “the yield of $CCl_3C(O)Cl$ [in the presence of NO] was 75%, about 14% lower than in similar experiments without NO present”.

The different product distribution observed in the presence of NO may reflect the formation and subsequent decomposition of chemically activated C_2Cl_5O radicals formed in the exothermic reaction of $C_2Cl_5O_2$ with NO. Chemical activation effects in the atmospheric chemistry of a number of alkoxy radicals have been reported recently[27−29] and appear to be a phenomenon general to radicals possessing activation barriers to decomposition of about 12 kcal mol^{-1} or less.[30]

3.4 Cl Atom Initiated Oxidation of C_2Cl_4 in Air at 230 and 250 K. Experiments were conducted in the NCAR chamber at 230 K (with and without NO present) and at 250 K (without NO), under conditions similar to the 298 K experiments. At 250 K, in the absence of NO, yields of CCl_3COCl and $COCl_2$ were found to be 97 ± 15% and 30 ± 6%, respectively, while at 230 K these values were 94 ± 15% and 30 ± 6%. Yields were found to be independent of the initial C_2Cl_4 and Cl_2 concentrations. These values are essentially identical to those obtained at room temperature and, coupled with the results of a high-temperature study by Huybrechts et al.,[14] show that the branching ratios to reactions 9a and 9b are independent of temperature over the range 230−357 K. The lack of a temperature dependence indicates that the activation energies to the two pathways are essentially identical. In fact, given that both reactions are quite exothermic (−17 and −20 kcal mol^{-1} for 9a and 9b, respectively,[31] the barriers to their occurrence are likely to be quite small. The fact that the Cl atom elimination channel dominates the fate of the C_2Cl_5O radicals suggests that the A factor for this process is greater than that for C−C bond scission. It is somewhat surprising that chemical activation should favor the lower A factor C−C bond rupture process. There are two possible explanations for this apparent discrepancy. First, dynamical considerations in the reaction of $C_2Cl_5O_2$ radicals with NO could favor C−C bond rupture. Second, it is possible that there is an additional channel of the $C_2Cl_5O_2$ radical self-reaction which yields $CCl_3C(O)Cl + CCl_3CCl_2OCl + O_2$ and that the hypochlorite decomposes to give $CCl_3C(O)Cl + Cl_2$. The $CCl_3C(O)Cl/COCl_2$ product ratio observed in the absence of NO would then not reflect $k_{9a}/k_{9b.}$ In light of the fact that no Cl atom transfer channel has been reported for other peroxy radical reactions, it seems unlikely that such a process is operative here. However, we cannot exclude this possibility. In either case this does not impact the main conclusion from the present work that preparation of C_2Cl_5O radicals via the peroxy radical self-reaction does not provide an accurate picture of the fate of C_2Cl_5O radicals formed via the $C_2Cl_5O_2$ + NO reaction.

In the 230 K experiments conducted in the presence of NO, an absorption centered at 1299 cm^{-1} was observed in addition to those attributable to $COCl_2$ and CCl_3COCl. This new absorption feature is attributed to the formation of a peroxy nitrate species, $CCl_3CCl_2O_2NO_2$, which is likely to be stable at 230 K, but not at 298 K:

$$CCl_3CCl_2O_2 + NO_2 + M \rightarrow CCl_3Cl_2O_2NO_2 + M \quad (15)$$

The peroxy nitrate concentration was estimated using a peak absorption cross-section of 1.5×10^{-18} cm^2 molecule^{-1},[32] and accounted for 10−20% of the C_2Cl_4 consumed. Raw yields of CCl_3COCl and $COCl_2$ were 65 ± 11% and 59 ± 10% which, following correction for peroxynitrate formation, increase to 75 ± 12% and 68 ± 10%, respectivly. These values are identical to those observed at room temperature, within experimental uncertainties.

4. Discussion and Atmospheric Implications

We report the results of three separate product studies of the Cl atom initiated oxidation of C_2Cl_4. Consistent results were obtained in our three laboratories. In contrast to a recent report by Hasson and Smith,[19] we do not observe any change in product yields at low $[C_2Cl_4]_o$ (even at values of $[C_2Cl_4]_o$ at least 1 order of magnitude below that at which Hasson and Smith report a significant effect, see Figure 5). It seems likely that there was some systematic error in the Hasson and Smith measurements at low $[C_2Cl_4]_o$. A slow zeroth order heterogeneous process converting $CCl_3C(O)Cl$ into $COCl_2$ might explain the behavior observed by Hasson and Smith.

Table 2 summarizes the results from previous studies of the fate of C_2Cl_5O radicals. With the exception of the low $[C_2Cl_4]_o$ data from Hasson and Smith,[19] the results from all studies are in excellent agreement. It is clear that C_2Cl_5O radicals formed with little, or no, internal excitation (i.e., via $C_2Cl_5O_2 + RO_2$ reactions) undergo decomposition via both elimination of a Cl atom (reaction 9a) and C−C bond scission (reaction b) with $k_{9a}/(k_{9a} + k_{9b}) \approx 85\%$ and $k_{9b}/(k_{9a} + k_{9b}) \approx 15\%$. Similarly it is clear that C_2Cl_5O radicals formed in the highly exothermic reaction of $C_2Cl_5O_2$ radicals with NO behave differently, with decomposition via Cl atom elimination accounting for ≈70% of the overall loss and with the remainder occurring via C−C bond scission.

Finally, we need to consider the implications of the present results for assessments of the trichloroacetic acid ($CCl_3C(O)OH$)) yield in the atmospheric oxidation of C_2Cl_4. The trichloroacetic acid yield is given by the product of three terms: (i) the fraction of C_2Cl_4 which reacts with Cl atoms to give C_2Cl_5 and hence $C_2Cl_5O_2$ radicals, (ii) the fraction of $C_2Cl_5O_2$ converted into $CCl_3C(O)Cl$, and (iii) the fraction of $CCl_3C(O)Cl$ hydrolyzed (as opposed to other possible loss processes, e.g., photolysis) to give $CCl_3C(O)OH$. Franklin and Sidebottom have evaluated the first and last terms and recommend 0.13 and 0.46, respectively.[13] The present work provides information concerning the second term.

In the atmosphere $C_2Cl_5O_2$ radicals will react with NO, NO_2, and HO_2 radicals. We will consider these reactions in turn. The $CCl_3C(O)Cl$ yield following reaction with NO is ≈70%. Reaction with NO_2 gives a peroxynitrate whose predominant fate will be decomposition to generate $C_2Cl_5O_2$ and NO_2; this reaction is not considered further. While the products of the reaction with HO_2 have not been studied, by analogy to the reaction of CCl_3O_2 and $CHCl_2O_2$ radicals with HO_2,[33] it seems likely that reaction 16 will proceed predominantly, if not exclusively, via channel (16b) giving $CCl_3C(O)Cl$:

$$C_2Cl_5O_2 + HO_2 \rightarrow CCl_3CCl_2OOH + O_2 \qquad (16a)$$

$$C_2Cl_5O_2 + HO_2 \rightarrow CCl_3C(O)Cl + HOCl + O_2 \qquad (16b)$$

Hence, it seems reasonable to estimate that the fraction of $C_2Cl_5O_2$ radicals converted into $CCl_3C(O)Cl$ lies between 0.70 and 1.0 (i.e., 0.85 ± 0.15). It follows that the molar trichloroacetic acid ($CCl_3C(O)OH$)) yield in the atmospheric oxidation of C_2Cl_4 is $0.13 \times 0.85 \times 0.46 = 0.05$. If we assume an annual global C_2Cl_4 emission rate of 170−305 kt (95% confidence range estimated by McCulloch et al. for 1996[2]), it follows that the $CCl_3C(O)OH$ production rate is 8−15 kt year^{-1}.

$CCl_3C(O)OH$ is very soluble and will be removed from the atmosphere by rain-out. The annual global rainfall is 4.9×10^{17} liters.[34] Thus, as a crude global average it might be expected that rainwater will contain 15−30 ng liter^{-1} CCl_3COOH because of atmospheric oxidation of C_2Cl_4. It should be stressed that this estimate is a global average. Industrial emissions of C_2Cl_4 are highly regionalized with the bulk of the emissions occurring in the USA, Europe, and Japan. In regions downwind of C_2Cl_4 emission sources, and in locations with little precipitation, $CCl_3C(O)OH$ concentrations will be greater. In remote sites and in locations with heavy precipitation the $CCl_3C(O)OH$ will be lower than the global average. Concentrations of CCl_3COOH reported in precipitation are 100−300 ng liter^{-1} in Europe (50 °N), 22−348 ng liter^{-1} in the Antarctic (72−75 °S), and < 5−53 ng liter^{-1} in the Arctic (64−77 °N).[13,35−39] The atmospheric oxidation of C_2Cl_4 makes a significant contribution to the environmental CCl_3COOH burden. In addition to man-made sources, recent measurements of significant (5−40 ng liter^{-1}) concentrations of CCl_3COOH in Antarctic firn dating back 190 years[40] point to the exisitence of a significant natural source of this compound.

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