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Chlorine Atom Initiated Oxidation of Chlorinated Ethenes: Results for 1,1-Dichloroethene ($H_2C{=}CCl_2$), 1,2-Dichloroethene ($HClC{=}CClH$), Trichloroethene ($HClC{=}CCl_2$), and Tetrachloroethene ($Cl_2C{=}CCl_2$)

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Experiments have been carried out on the oxidation of the four chlorinated ethenes $H_2C{=}CCl_2$, $HClC{=}CClH$, $HClC{=}CCl_2$, and $Cl_2C{=}CCl_2$. Reaction was initiated by continuous photolysis of Cl_2, and product yields were measured using Fourier transform infrared (FTIR) spectroscopy. In all cases, experiments were performed at different concentrations of the chlorinated ethenes (down to 3×10^{13} molecule cm^{-3}), Cl_2 and O_2. In the cases of $H_2C{=}CCl_2$ and $HClC{=}CCl_2$, the product yields were invariant with these changes, consistent with them being determined by competitive unimolecular dissociations of the chlorinated alkoxy radical; that is, $H_2ClCCCl_2O$ (HCl_2CCCl_2O) (+M) → $H_2ClCCOCl$ (HCl_2CCOCl) + Cl (+M) and $H_2ClCCCl_2O$ (HCl_2CCCl_2O) (+M) → $COCl_2$ + CH_2Cl ($CHCl_2$) (+M), and the subsequent formation of HCOCl and/or $COCl_2$ from CH_2Cl and $CHCl_2$. In the case of $HCl_2CCHClO$ formed from $HClC{=}CClH$, H atom abstraction by O_2 is competitive with CCl and CC bond cleavage, so the yields depended on the concentration of O_2. With C_2Cl_4, the only products observed were CCl_3COCl and $COCl_2$, consistent with competitive dissociations of perchloroethyl radicals: CCl_3CCl_2O (+M) → CCl_3COCl + Cl (+M); CCl_3CCl_2O (+M) → $COCl_2$ + CCl_3 (+M). However, the relative yields of CCl_3COCl and $COCl_2$ were found to depend on the initial concentration of C_2Cl_4 which is incompatible with the simple, and generally accepted, mechanism. To investigate this unexpected result further, experiments were performed on pentachloroethane (C_2Cl_5H). Again, the product yields depended on the initial concentration of the chlorinated compound. In addition, product yields from C_2Cl_4 were measured using two different rates of photolysis of Cl_2, at three temperatures, 298, 353, and 393 K, and in the presence of added NO and added HCl. Although the experimental results could be modeled when bimolecular reactions of perchlorinated methoxy and ethoxy radicals with C_2Cl_4 and HCl were included in the reaction mechanisms, the values of the rate constants which were needed seem unrealistically large if the currently accepted rate for the unimolecular decomposition of CCl_3CCl_2O is correct. This observation on C_2Cl_4 is important since it casts doubt on the current view of the oxidative chemistry of this compound, which is released in significant amounts into the atmosphere.

1. Introduction

Perchloroethene is one of the most widely used chlorinated solvents, with an annual global release of 295 ktons/year in 1992.[1] Its main uses are in dry cleaning and metal degreasing. The atmospheric lifetime of C_2Cl_4 has been estimated to be ca. 0.4 years,[2] on the basis that the major loss is its oxidation initiated by reaction with OH radicals.[3]

$$Cl_2CCCl_2 + OH\ (+M) \rightarrow Cl_2CCCl_2OH\ (+M) \qquad \text{(R0d)}$$

However, because C_2Cl_4 combines with Cl atoms

$$Cl_2CCCl_2 + Cl\ (+M) \rightarrow Cl_3CCCl_2\ (+M) \qquad \text{(R2d)}$$

approximately 300 times faster than with OH radicals,[4] there has been some discussion in the literature as to whether reaction R2d can play a significant role in initiating the tropospheric oxidation of perchloroethene. (Throughout the text of this paper, lower case letters a, b, c, d, and d′ are used to identify elementary reactions in the oxidation of $H_2C{=}CCl_2$, $HClC{=}CClH$, $HClC{=}CCl_2$, $Cl_2C{=}CCl_2$, and CCl_3CCl_2H, respectively.) Oxidation initiated by Cl atoms (as opposed to OH radicals) is known to result in the formation of CCl_3COCl as one of its products,[5] and hydrolysis of CCl_3COCl has been postulated as an atmospheric source of trichloroacetic acid, a chemical that is known to be phytotoxic.[6] Another recognized product of C_2Cl_4 oxidation is $COCl_2$, which is removed from the troposphere by uptake into water droplets followed by hydrolysis,[7,8] probably forming HCl and CO_2.[9] In addition, it has been suggested that CCl_4, a species with a significant ozone depletion potential, might be formed by the degradation of CCl_3COCl in the atmosphere.[10−12]

Cl atoms have never been directly observed in the troposphere, and their concentrations have been the object of much speculation. Clearly, a concentration of more than about 10^2−10^3 molecule cm^{-3} would be required for reaction R2d to occur at a significant fraction of the rate of reaction R0d. Based on atmospheric models and on the finding that the observed abundance of C_2Cl_4 is consistent with its removal only by reaction with OH radicals through reaction R0d, recent estimates have put the average tropospheric concentration of Cl atoms at $<10^3$ molecule cm^{-3} and have therefore cast doubt on the potential significance of Cl atoms as a tropospheric oxidant.[3,13,14] Other estimates, summarized by Graedel and Keene,[15] suggest that concentrations as high as 10^5−10^6 molecule cm^{-3} may occur at least on occasions in the marine boundary layer.

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Although trichloroethene is sometimes used industrially as a solvent for degreasing metals and in dry cleaning whilst 1,1-dichloroethene is employed in the manufacture of polymers and of 1,1,1-trichloroethane, partially chlorinated ethenes only comprise a small fraction of the total atmospheric budget of compounds containing chlorine.[15] Consequently, their atmospheric chemistry is, at most, of slight environmental significance. Nevertheless, understanding their oxidation is of fundamental chemical importance, and should provide insight into the oxidation of tetrachloroethene.

This paper reports a comprehensive study of the Cl atom initiated oxidation of the four chlorinated ethenes $H_2C{=}CCl_2$, $HClC{=}CClH$, $HClC{=}CCl_2$, and $Cl_2C{=}CCl_2$ at a total pressure of 700 Torr with N_2 as the diluent gas. In all cases, the dependence of the product yields on the initial concentration of the chlorinated compound (down to 3×10^{13} molecule cm^{-3}), Cl_2, and O_2 was examined. The generally accepted mechanism, which is described in detail in section 3 below, predicts product distributions which are independent of changes in the initial concentrations of these reagents. Because of unexpected findings in the case of C_2Cl_4, its oxidation was further examined by (a) using two different rates of photolysis of Cl_2; (b) performing experiments at three temperatures, 298, 353, and 393 K, and at 298 K at three different total pressures, 700, 140, and 50 Torr; (c) comparing the results obtained with those from experiments on the Cl atom initiated oxidation of C_2Cl_5H; and (d) observing the effects on the oxidation of C_2Cl_4 of adding HCl and NO.

The experiments on the oxidation of the partially chlorinated ethenes and on tetrachloroethene are reported and discussed in sections 4 and 5 of this paper, respectively. A number of previous laboratory studies have been carried out to identify the product yields of the Cl atom initiated oxidation of $H_2C{=}CCl_2$,[12,16] $HClC{=}CClH$,[17] $HClC{=}CCl_2$,[12,18] $Cl_2C{=}CCl_2$,[12,16,19,20,21] and C_2Cl_5H,[12,22] although several of these studies used partial pressures of Cl_2 and the chlorinated ethene in excess of 1 Torr and much greater than is necessary in modern experiments using FTIR spectroscopy. The results of these studies and the mechanistic aspects which are common to the oxidation of all these species are described in section 3. The mechanisms for all the chlorinated ethenes are closely related and are thought to be well-understood. Although our results confirm previous results and interpretation for $H_2C{=}CCl_2$, $HClC{=}CClH$, and $HClC{=}CCl_2$, our data demonstrate previously undetected complications in the case of C_2Cl_4 and hence challenge the view that the atmospheric chemistry of this compound is well-understood.

2. Experimental Method and Procedures

The experimental apparatus has been described in detail previously.[23] In brief, an FTIR spectrometer (Nicolet Magna 550) is coupled to a 35 L cylindrical reaction cell. Continuous photolysis is provided by two lamps mounted within the cell. Two sets of lamps were employed during the present experiments. "Blacklamps" (Phillips TL40N/08, 35 W output) provided radiation down to 300 nm which overlaps strongly with the absorption spectrum of Cl_2 and results in a relatively rapid rate of photolysis. In some experiments, the blacklamps were replaced by conventional fluorescent tubes (Phillips TLD, 35 W output). Their output is limited to wavelengths greater than 400 nm, and consequently, they provided a much slower rate of Cl_2 photolysis.

The reaction cell is equipped with White cell mirrors enabling most species to be detected at concentrations down to ca. 10^{12} molecule cm^{-3} by long path length infrared absorption. The path length was set at either 20 or 40 m, depending on the concentrations of reactants used, and spectra were recorded by coadding 32 scans at a resolution of 2 cm^{-1}, the data collection taking 16 s. The time scales of most experiments varied from as short as 5 min up to 1.5 h, each mixture being photolyzed until reaction was complete. In experiments on C_2Cl_5H in the presence of NO, the period of photolysis was extended to 15 h.

The chlorinated ethenes were all supplied by Aldridge with stated purities of H_2CCCl_2 (99%), HClCCClH (98%), $HClCCCl_2$ (99%), and Cl_2CCCl_2 (99.5%). They and C_2Cl_5H (Lancaster Synthesis, 95%) were degassed by successive pump−freeze−thaw cycles, impurities in their vapors being spectroscopically undetectable. In the case of $HClC{=}CClH$, a 1:1 mixture of *cis*- and *trans*-1,2-dichloroethenes was used. Initial concentrations of the chlorinated species in the range 3×10^{13} to 1×10^{15} molecule cm^{-3} were used in the experiments. The gas mixture in the cell was made up to a total pressure of 700 Torr using Cl_2 (Matheson, 99%), O_2 (BOC Ltd.), and N_2 (BOC Ltd., "oxygen free"). In addition to these "reagent" chemicals, it was necessary to have samples of a number of other species to calibrate the sensitivity of the FTIR to the product molecules. $COCl_2$ (Argo International Ltd., 99%), CCl_3COCl (Aldrich, 99.5%), and HCl (BDH, 99.99%) were commercially available. Dichloroacetaldehyde, $CHCl_2CHO$, was prepared by the method of Crampton et al.[24] Attempts to prepare formyl chloride, HCOCl, by the method of Staab and Datta[25] were unsuccessful, so yields of this species were determined using the absorption coefficients determined for similar conditions by Libuda et al.,[26] assuming the Beer−Lambert law.

The concentrations of the reagent and product species present in the reaction cell were estimated from the recorded spectra using calibrations of absorption strength with concentration at the following wavenumbers: H_2CCCl_2 (1165−1062 cm^{-1}), HClCCClH (864.5 and 830 cm^{-1}), $HClCCCl_2$ (970−870 cm^{-1}), Cl_2CCCl_2 (940−885 cm^{-1}), C_2Cl_5H (782 cm^{-1}), $CHCl_2COCl$ (1120−1020 cm^{-1}), $CH_2ClCOCl$, (760−690 cm^{-1}), $CHCl_2CHO$ (1761 cm^{-1}), CCl_3COCl (1816 cm^{-1} and 775−710 cm^{-1}), HCOCl (1783 cm^{-1}), $COCl_2$ (1831 cm^{-1} and 885−785 cm^{-1}), HCl (2821 cm^{-1}), and CO (2177 cm^{-1}).

To minimize heterogeneous reactions, the walls of the vessel are coated with Teflon. A thermostated heating tape was wrapped round the cell underneath an insulating jacket enabling experiments to be carried out over the temperature range 298−393 K. The internal temperature of the reactor was monitored using a thermocouple positioned within a glass tube protruding into the cell. Gases were handled in a Pyrex manifold and, to facilitate rapid mixing, were admitted into the reaction cell via a narrow drilled tube which runs the length of the chamber. N_2 was always added last to bring the total pressure up to 700 Torr. Once all of the gases had been introduced, they were left in the dark to ensure complete mixing and equilibration to the temperature of the cell. At higher temperatures, this period was ca. 2 h. During this time, spectra were recorded regularly to confirm that no significant dark reactions were taking place.

For each system $Cl_2/C_2Cl_xH_y/O_2/N_2$, several sets of product yield measurements were taken. Product yields were measured as a function of the initial concentration of the organic species, with the initial concentrations of the other two reactants held constant. This procedure was then repeated for two further sets of experiments with the initial concentrations of Cl_2 and O_2 being varied in turn, and the remaining two reactant concentrations unchanged. In addition, product yields were measured at two different rates of photolysis of Cl_2, corresponding to the two types of photolysis lamps used. Using the fluorescent lamps,

TABLE 1: Previous Measurements of Product Yields from Chlorine Atom Initiated Oxidation of Chlorinated Ethenes

chlorinated ethene	possible primary products	product yields	method[a]	ref
$H_2C{=}CCl_2$	$CH_2ClCOCl$	0.98	UV/IR	16
	$COCl_2$			
	H_2CO			
	HCOCl			
	CH_2ClOH			
$HClC{=}CClH$	$CHCl_2COCl$			
	$CHCl_2CHClOH$			
	CH_2ClCOH			
	HCOCl	1.4 ± 0.05	UV/IR	17
	$COCl_2$	0.06 ± 0.008	(304 K; $p_{O_2} < 85$ Torr	
	$CHCl_2OH$			
		CO: 0.54 ± 0.05		
$HClC{=}CCl_2$	$CHCl_2COCl$	0.90	vis/GC	12
		0.91 ± 0.10	UV/FTIR	18
	$COCl_2$	0.09 ± 0.02		
	HCOCl	0.09 ± 0.02		
	$CHCl_2OH$			
$Cl_2C{=}CCl_2$	CCl_3COCl	0.85 ± 0.05	UV/GC	12
	$COCl_2$	0.30 ± 0.10	(354, 373 K; 590 Torr)	
	CCl_3COCl:	2.5:1 at 297 K	UV/IR	20
	$COCl_2$	3.0:1 at 305 K	(295, 305 K; 6−450 Torr)	
	CCl_3COCl	0.85 ± 0.05	UV/IR	16
	$COCl_2$	0.25 ± 0.10	(298 K; 5−700 Torr)	
		CCl_4: 0.003		
	CCl_3COCl	0.87 ± 0.11	UV/FTIR	21
	$COCl_2$	0.27 ± 0.03	(298 K; 700 Torr)	
C_2Cl_5H	CCl_3COCl	0.85 ± 0.05	UV/GC	12
	$COCl_2$	0.30 ± 0.10	(296 K; 590 Torr)	
		0.85 ± 0.09	UV/FTIR	22
		0.30 ± 0.04	(354, 373 K; 700 Torr)	

[a] UV (vis) denotes continuous ultraviolet (visible) photolysis, IR denotes detection by infrared absorption, FTIR detection by Fourier transform infrared spectroscopy, and GC detection by gas chromatography.

the time dependence of the loss of reactants and formation of products could be observed by recording spectra every few minutes over the course of the entire reaction. With the blacklamps, the yields were determined from pairs of spectra taken before illumination with the lamps and several minutes after reaction was complete.

The product yield dependences on the initial concentrations $[C_2Cl_4]_0$ and $[C_2Cl_5H]_0$ were measured at three temperatures, 298, 353, and 393 K. At 298 K, experiments were carried out at three different total pressure, 700, 140, and 50 Torr. In addition, product yields were measured in the $Cl_2/C_2Cl_4/O_2/N_2$ system in the presence of added NO and HCl. All experiments were repeated at least twice, and the final results represent an average of at least three runs.

3. Primary Reaction Mechanisms and Previous Work

The results of previous laboratory studies designed to determine the product yields from the Cl atom initiated oxidations of chlorinated ethenes and pentachloroethane are summarized in Table 1. The early stages of the oxidative mechanisms are well-established and are similar for all five species. The Cl atoms produced by photolysis of Cl_2 form chlorinated ethyl radicals either by addition in the cases of the chlorinated ethenes or by H-atom abstraction from pentachloroethane

$$Cl_2 + h\nu \rightarrow 2Cl \qquad (R1)$$

$$H_2CCCl_2,\ HClCCClH,\ HClCCCl_2,\ Cl_2CCCl_2 + Cl\ (+M) \rightarrow H_2ClCCCl_2,\ HCl_2CCClH,\ HCl_2CCCl_2,\ Cl_3CCCl_2\ (+M) \qquad (R2a,b,c,d)$$

$$Cl_3CCCl_2H + Cl \rightarrow Cl_3CCCl_2 + HCl \qquad (R2d')$$

At this point the mechanistic pathways for C_2Cl_4 and C_2Cl_5H converge, and the remainder of the chemistry is thought to be identical for both of these systems. Where the two carbon atoms in the chlorinated ethene are not equivalent, Cl adds to the less chlorinated of the two. Oxygen quickly adds to the chlorinated ethyl radicals to form peroxy species, which are converted to chloroethoxy radicals by reaction either with a second peroxy radical or, if NO is present, with NO.

$$H_2ClCCCl_2,\ HCl_2CCClH,\ HCl_2CCCl_2,\ Cl_3CCCl_2 + O_2\ (+M) \rightarrow H_2ClCCCl_2O_2,\ HCl_2CCClHO_2,\ HCl_2CCCl_2O_2,\ Cl_3CCCl_2O_2\ (+M) \qquad (R3a,b,c,d)$$

$$H_2ClCCCl_2O_2,\ HCl_2CCClHO_2,\ HCl_2CCCl_2O_2,\ Cl_3CCCl_2O_2 + RO_2\ (NO) \rightarrow H_2ClCCCl_2O,\ HCl_2CCClHO,\ HCl_2CCCl_2O,\ Cl_3CCCl_2O + RO\ (NO_2) + O_2 \qquad (R4a,b,c,d)$$

The chlorinated ethoxy radicals can then undergo either C−Cl bond scission to produce an acid chloride or an aldehyde or C−C bond scission forming HCOCl or $COCl_2$ and chlorinated methyl radicals.

$$H_2ClCCCl_2O,\ HCl_2CCClHO,\ HCl_2CCCl_2O,\ Cl_3CCCl_2O\ (+M) \rightarrow H_2ClCCOCl,\ HCl_2CCHO,\ HCl_2CCOCl,\ CCl_3COCl + Cl\ (+M) \qquad (R5a,b,c,d)$$

$$H_2ClCCCl_2O,\ HCl_2CCClHO,\ HCl_2CCCl_2O,\ Cl_3CCCl_2O\ (+M) \rightarrow H_2ClC + COCl_2,\ HCl_2C + HCOCl,\ HCl_2C + COCl_2,\ COCl_2 + CCl_3\ (+M) \qquad (R6a,b,c,d)$$

In addition, the $HCl_2CCClHO$ radical from HClCCClH can lose the α-hydrogen atom by reaction with O_2

$$HCl_2CCClHO + O_2 \rightarrow HCl_2CCOCl + HO_2 \qquad (R7b)$$

TABLE 2: Present Measurements of Product Yields from Chlorine Atom Initiated Oxidation of Chlorinated Ethenes and Reaction Enthalpies for Dissociation of Chlorinated Ethoxy Radicals[a]

chlorinated ethenes	product yields	dissociation reactions	$\Delta_r H°$/kJ mol^{-1}
$H_2C{=}CCl_2$	$CH_2ClCOCl$: 0.98 ± 0.03	$CH_2ClCCl_2O \rightarrow CH_2ClCOCl + Cl$	−69
	$COCl_2$: 0.03 ± 0.01	$CH_2ClCCl_2O \rightarrow CH_2Cl + COCl_2$	−42
	HCOCl: 0.03 ± 0.02		
	carbon balance 1.01 ± 0.04		
HClC=CClH	$CHCl_2COCl$: 0.08 ± 0.02	$CHCl_2CHClO \rightarrow CHCl_2COCl + H$	+39
	HCOCl: 1.26 ± 0.32	$CHCl_2CHClO \rightarrow CHCl_2 + HCOCl$	−19
		$CHCl_2CHClO \rightarrow CHCl_2CHO + Cl$	+3
	$COCl_2$: 0.02 ± 0.02		
	CO: 0.96 ± 0.12		
	HCl: 1.15 ± 0.27		
	carbon balance 1.20 ± 0.25		
$HClC{=}CCl_2$	$CHCl_2COCl$: 0.91 ± 0.03	$CHCl_2CCl_2O \rightarrow CH_2ClCOCl + Cl$	−52
	$COCl_2$: 0.09 ± 0.01	$CHCl_2CCl_2O \rightarrow CH_2Cl + COCl_2$	−44
	HCOCl: 0.09 ± 0.02		
	carbon balance 1.00 ± 0.04		
$Cl_2C{=}CCl_2$	dependent on [C_2Cl_4] (see text)	$CCl_3CCl_2O \rightarrow CCl_3 + COCl_2$	−89
		$CCl_3CCl_2O \rightarrow CCl_3COCl + Cl$	−55

[a] Thermodynamic data are taken from: (a) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521. (b) Lias, J. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (suppl 1). (c) Bertrand, L.; Exsteen-Mayer, L.; Franklin, J. A.; Huybrechts, G.; Olbrechts, J. *Int. J. Chem. Kinet.* **1971**, *3*, 89. The data for the substituted ethoxy radicals are estimated by Bertrand et al. using group additivity rules. (d) Finally, the value of $\Delta_r H°$(HOCl) is estimated from the following theoretical work: Francisco, J. S. *J. Chem. Phys.* **1992**, *96*, 7597.

The chlorinated methyl radicals produced in reactions (R6a,b,c,d) are oxidized to produce HOCl or $COCl_2$ in the following reactions:

$$H_2ClC,\ HCl_2C,\ HCl_2C,\ Cl_3C + O_2\ (+M) \rightarrow H_2ClCO_2,\ HCl_2CO_2,\ HCl_2CO_2,\ Cl_3CO_2\ (+M) \quad \text{(R8a,b,c,d)}$$

$$H_2ClCO_2,\ HCl_2CO_2,\ HCl_2CO_2,\ Cl_3CO_2 + RO_2\ (NO) \rightarrow H_2ClCO,\ HCl_2CO,\ HCl_2CO,\ Cl_3CO + RO\ (NO_2) + O_2 \quad \text{(R9a,b,c,d)}$$

$$H_2ClCO,\ HCl_2CO,\ HCl_2CO,\ Cl_3CO\ (+M) \rightarrow H_2CO,\ HCOCl,\ HCOCl,\ COCl_2 + Cl\ (+M) \quad \text{(R10a,b,c,d)}$$

$$H_2ClCO,\ HCl_2CO,\ HCl_2CO + O_2 \rightarrow HCOCl,\ COCl_2,\ COCl_2 + HO_2 \quad \text{(R11a,b,c)}$$

It is these mechanisms which lead to the species identified in Tables 1 and 2 as “primary products”.

4. Cl Atom Initiated Oxidation of $H_2C{=}CCl_2$, ClHC=CHCl, and $ClHC{=}CCl_2$: Results and Discussion

When each of these chlorinated ethenes was mixed with Cl_2 and O_2 and left in the dark, no changes in the reagent concentration nor any products of dark reactions were observed. Initial photochemical experiments were carried out using blacklamps to illuminate gas mixtures containing 4×10^{14} molecule cm^{-3} of the chlorinated ethene, 4×10^{14} molecule cm^{-3} of Cl_2, and 140 Torr of O_2. Typical spectra for such experiments recorded before and after 30 min of photolysis of $HClCCCl_2$ are shown in Figure 1. Concentrations of products derived from experiments on trichloroethene, 1,1-dichloroethene, and 1,2-dichloroethene are plotted in Figure 2 against decrease in the reagent concentration. The product yields derived from the slopes of these lines are listed in Table 2. These data were determined from unweighted linear regressions on plots of the kind shown in Figure 2 which were not forced through the origin. The cited errors correspond to two standard deviations arising from uncertainties in the experimentally determined concentrations. At least three experiments were performed for each of the alkenes under a specific set of reaction conditions, and both the values and the errors stated are the weighted average of these separate experiments.

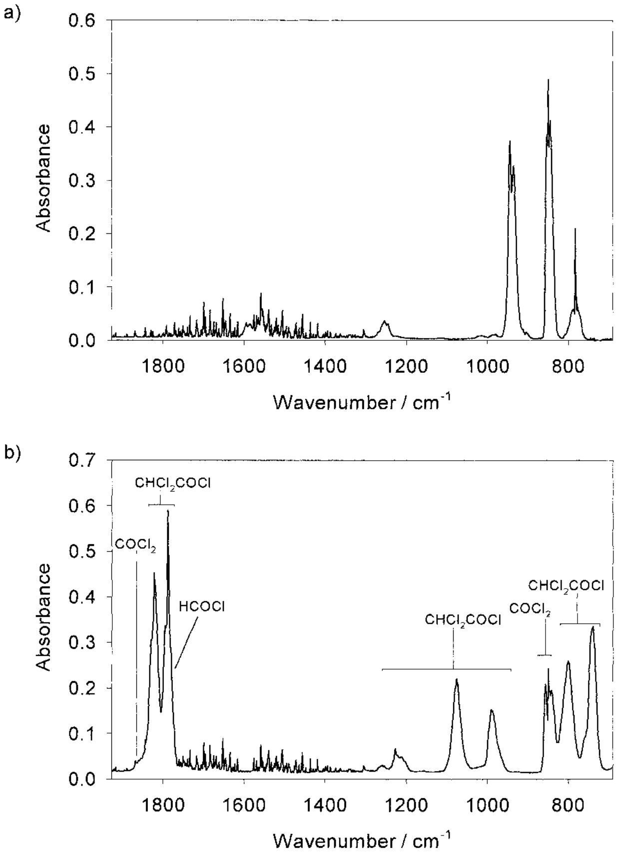

Figure 1. Infrared spectra recorded (a) before and (b) after 30 min photolysis of a mixture initially containing 4×10^{14} molecule cm^{-3} of $HClCCCl_2$, 4×10^{14} molecule cm^{-3} of Cl_2, and 140 Torr of O_2 diluted to a total pressure of 700 Torr with N_2.

According to the mechanisms outlined in section 3, the distribution of product yields from each of the three chlorinated alkenes should be independent of (a) the rate of photolysis, (b)

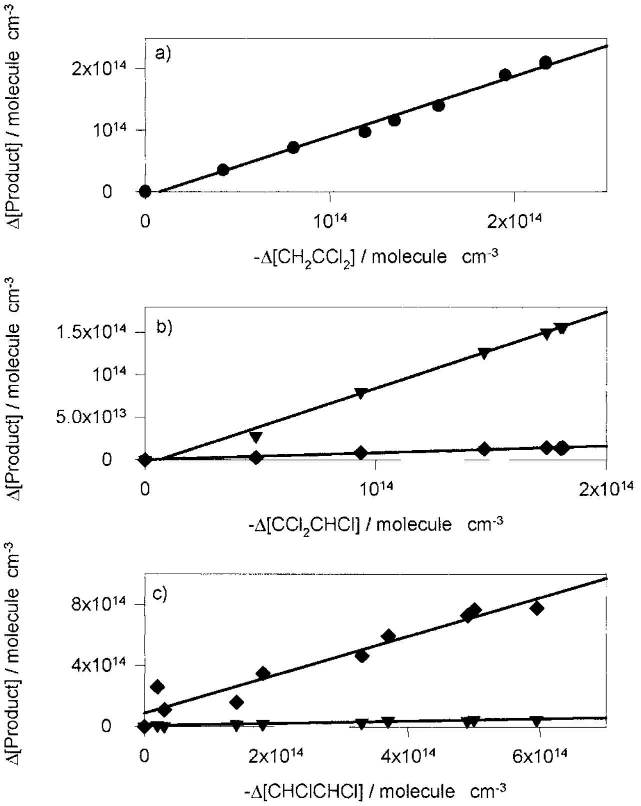

Figure 2. Yields of products plotted against loss of reagents from experiments on (a) H_2CCCl, (b) $HClCCCl_2$, and (c) HClCCClH: (●) $CH_2ClCOCl$; (▼) $CHCl_2COCl$; (◆) HCOCl + CO (see text). In all cases, 140 Torr of O_2 was present in the reaction mixtures.

the initial concentration of the chlorinated ethene, and (c) the initial concentration of Cl_2. Figure 3 displays the results of experiments performed with different initial concentrations of partially chlorinated ethene and of Cl_2, using 3×10^{13} to 4×10^{14} molecule cm^{-3} of chlorinated ethene and 1×10^{14} to 1×10^{15} molecule cm^{-3} of Cl_2, in mixtures containing 140 Torr of O_2 at a total pressure of 700 Torr. Within experimental error, the product yields for all three compounds remained the same as the concentrations of the reagents were varied. The product distributions were also found to be unchanged when the rate of photolysis was reduced by a factor of ca. 100 by replacing the blacklamps with fluorescent lamps.

Figure 4 shows the effect on the product yields of varying the partial pressure of O_2 included in the reaction mixtures from 10 to 700 Torr. As anticipated, in the oxidations of $HClCCCl_2$ and H_2CCCl_2, which contain no α-hydrogen atoms, the yields were found to be independent of [O_2]. Moreover, the product yields from these oxidations both (a) gave excellent carbon balances within tight experimental bounds and (b) agree very well with the limited amount of previous data available for these reactions (cf. Table 1). In the experiments on $HClCCCl_2$, there was no evidence for the unimolecular decomposition products of HCOCl, i.e., HCl + CO, on the time scale of our experiments. In addition, the yields of formyl chloride from all of our experiments were consistent with chlorinated methoxy radicals undergoing only reactions R10a,b,c,d and R11a,b,c. There is some evidence[27] that the elimination of HCl from chloromethoxy radicals may be a minor reaction channel (ca. 20% with 140 Torr of O_2 present), but these radicals are formed in such low yield in the oxidations of 1,2-dichloroethene and trichloroethene that any HCl and CO formed would be below the detection limit in our experiments.

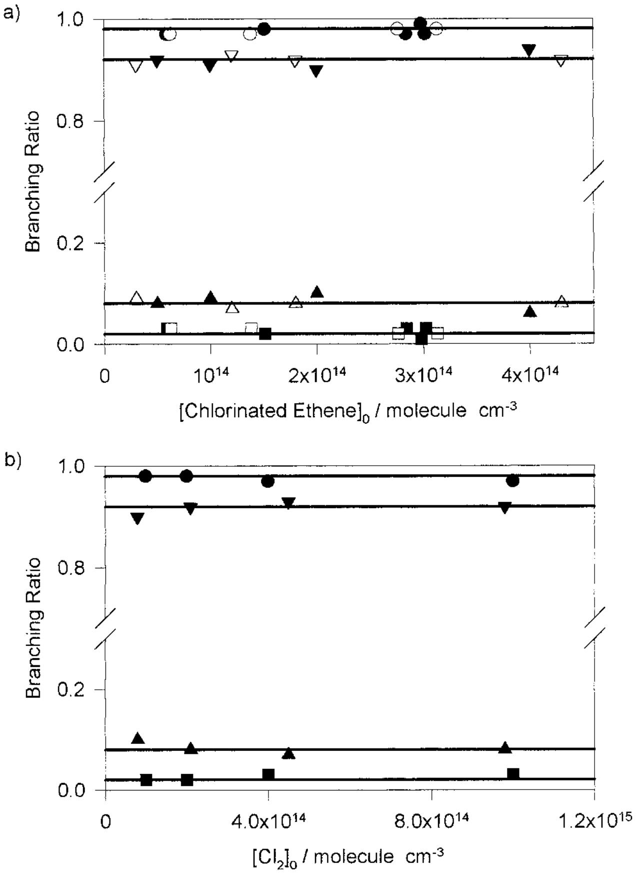

Figure 3. Dependence of product yields on (a) rate of photolysis and [chlorinated ethene]$_0$ with [Cl_2]$_0$ = 4×10^{14} molecule cm^{-3}, and (b) [Cl_2]$_0$ with [chlorinated ethene]$_0$ = 4×10^{14} molecule cm^{-3}: (●), (○) $CH_2ClCOCl$ from H_2CCCl_2; (■), (□) $COCl_2$ from H_2CCCl_2; (▼), (▽) $CHCl_2COCl$ from $HClCCCl_2$; (▲), (△) $COCl_2$ from $HClCCCl_2$. The filled symbols represent data from experiments performed with blacklamps, the open symbols those from experiments performed with fluorescent lamps.

The chlorinated ethoxy radical, $HCl_2CCClHO$, formed in the oxidation of 1,2-dichloroethene does contain an α-hydrogen atom which can be abstracted by reaction with O_2. Consequently, changing the concentration of O_2 alters the rate of reaction R7b, and the product yields from the oxidation of HClCCClH depend on the concentration of O_2 as shown in Figure 4b. The product yields from the oxidation of HClCCClH are in reasonable agreement with the only previous measurement[17] in that the majority of alkoxy radicals decompose via CC bond cleavage, even in the presence of 140 Torr of O_2. No $CHCl_2CHO$ is observed, indicating that carbon−chlorine bond scission does not occur to any appreciable degree in $CHCl_2CHClO$. However, it is necessary to examine the possibility that the concentration of this aldehyde is reduced either because it is photolyzed or because it reacts with Cl atoms. The latter possibility is unlikely since the reaction of Cl atoms with $CHCl_2CHO$ is about 8 times slower than their reaction with HClCCClH.[28,29] In addition, experiments were performed to investigate the possibility of loss of $CHCl_2CHO$ by photolysis. No such loss was observed, so it is concluded that reaction (R5b) was of negligible importance in our experiments.

$CHCl_2COCl$ was observed as a minor product of the oxidation of HClCCClH. The fact that it was not observed by Sanhueza and Heicklen[17] may due to the very different initial partial pressures in their experiments: $p(Cl_2)$ = 0.6−6.6 Torr; p(HClCCClH) = 1.4−9.5 Torr; $p(O_2)$ = 5.8−87.6 Torr. Moreover, the yields of HCOCl and CO observed in the present experi-

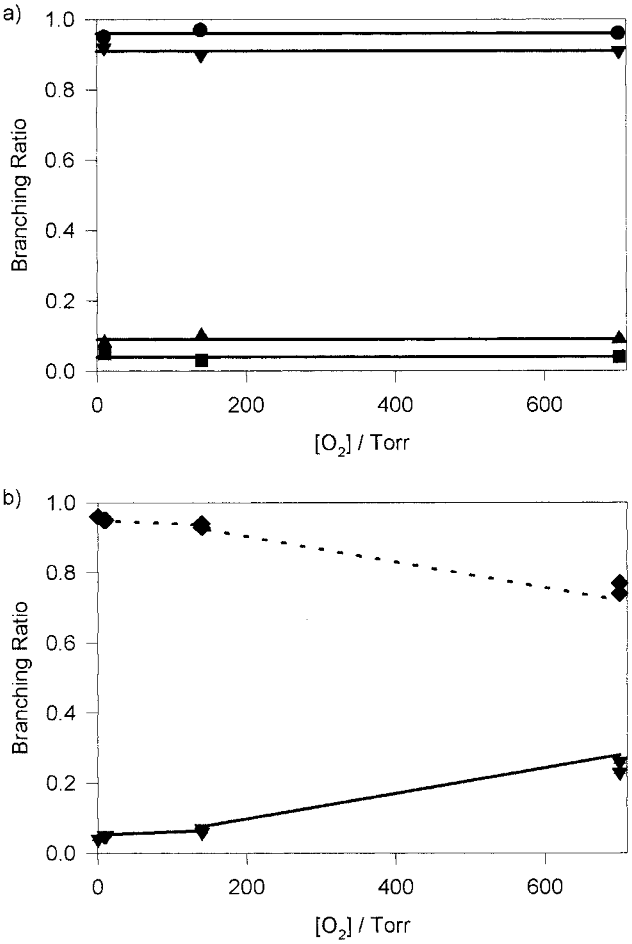

Figure 4. Dependence of product yields on $[O_2]$ with [chlorinated ethene]$_0$ = $[Cl_2]_0$ = 4 × 10^{14} molecule cm^{-3}: (a) for H_2CCCl_2 and $HClCCCl_2$, where (■) represent $COCl_2$ from H_2CCCl_2, (●) $CH_2ClCOCl$ from H_2CCCl_2, (▲) $COCl_2$ from $HClCCCl_2$, (▼) $CH_2ClCOCl$ from $HClCCCl_2$, and (b) for HClCCClH where (▼) represents $CHCl_2COCl$ (— calculated) and (◆) HCOCl (- - - calculated).

TABLE 3: Branching Ratios for Reactions of Chlorinated Ethoxy Radicals Formed in the Cl Atom Initiated Oxidation of H_2CCCl_2, HClCCClH, and $HClCCCl_2$

chlorinated ethene	reaction	branching ratio
H_2CCCl_2	$CH_2ClCCl_2O \rightarrow CH_2ClCOCl + Cl$	0.98 ± 003
	$CH_2ClCCl_2O \rightarrow CH_2Cl + COCl_2$	0.02 ± 0.003
HClCCClH[a]	$CHCl_2CHClO \rightarrow CHCl_2CO + HCl$	0.15 ± 0.08
	$CHCl_2CHClO \rightarrow CHCl_2 + HCOCl$	0.77 ± 0.08
	$CHCl_2CHClO + O_2 \rightarrow CHCl_2COCl + HO_2$	0.08 ± 0.02
$HClCCCl_2$	$CHCl_2CCl_2O \rightarrow CHCl_2COCl + Cl$	0.91 ± 0.03
	$CHCl_2CCl_2O \rightarrow CHCl_2 + COCl_2$	0.09 ± 0.02

[a] The branching ratios are given for 700 Torr total pressure of synthetic air (i.e., 140 Torr O_2). They are determined from the yields measured under these conditions.

ments are different from those measured by Sanhueza and Heicklen, who also deduced that CO is a primary product of the oxidation since its concentration was proportional to the irradiation time. They attributed this behavior to the reaction

$$\mathrm{CHCl_2CHClO \rightarrow CO + HCl + CHCl_2} \tag{R12b}$$

However, the concentrations of CO, HCl, and HCOCl produced in the current set of experiments were found not to be proportional to the consumption of 1,2-dichloroethene. In addition, when the photolysis lamps were switched off, the concentrations of CO and HCl were both observed to increase, whilst that of HCOCl decreased by the same amount. Consequently, CO would appear, at least in part, to be a secondary product formed by the decomposition of HCOCl, and there is no evidence for CO production from (R12b). Studies of the oxidation of 1,2-dichloroethane[30] and 1,1,1,2-tetrachloroethane[31] have shown that reactions analogous to (R12b), i.e.,

$$\mathrm{CCl_3CHClO \rightarrow CCl_3 + CO + HCl} \tag{R13b}$$

$$\mathrm{CH_2ClCHClO \rightarrow CH_2Cl + CO + HCl} \tag{R14b}$$

do not occur. If the CO observed by Sanhueza and Heicklen was a consequence of the decomposition of HCOCl rather than reaction R7b, then the yield of CO at any time would be equal to the amount of HCOCl that had decomposed. Thus the branching ratio of (R6b) would be given by the sum of the product yields of HCOCl and CO. The values 1.1 ± 0.2 and 0.97 ± 0.05 are obtained from the present work and from that of Sanhueza and Heicklen, respectively, the results agreeing within experimental error.

When averaged over all of the experiments on 1,2-dichloroethene, the yield of HCl is 19 ± 10% higher than that of CO. This is clearly not consistent with the formation of these species solely from the decomposition of HCOCl. The partially chlorinated alkoxy radicals CCl_3CHClO and $CH_2ClCHClO$ have been shown to decompose via the three-centered elimination of HCl with branching ratios of 20–25%.[29,30] The corresponding reaction in the 1,2-dichloroethene oxidation is

$$\mathrm{CHCl_2CHClO \rightarrow CHCl_2CO + HCl} \tag{15b}$$

The radical produced would rapidly react with O_2 and would ultimately form CO_2.

$$\mathrm{CHCl_2CO + O_2 + M \rightarrow CHCl_2C(O)O_2 + M} \tag{R16b}$$

$$\mathrm{CHCl_2C(O)O_2 + RO_2 \rightarrow CHCl_2C(O)O + RO + O_2} \tag{R17b}$$

$$\mathrm{CHCl_2C(O)O \rightarrow CHCl_2 + CO_2} \tag{R18b}$$

Unfortunately, due to the interference of CO_2 absorptions outside the reaction cell, it was impossible to obtain an accurate yield for CO_2. However, it seems likely that this is the source of the "extra" HCl observed, leading to the ratio for $k_{R15b}/k_{R6b} = 0.19 \pm 0.1$. This value must be treated with caution because, before the yield of CO_2 is included, the experimental carbon balance from these experiments is in excess of 100%.

Using the yields shown in Figure 4b, the branching ratio $k_{R7b}[O_2]/k_{Rb'}$ could be determined (where $k_{Rb'} = k_{R5b} + k_{R6b} + k_{R12b} + k_{R15b} \approx k_{R6b} + k_{R15b}$, since k_{R5b} and k_{R12b} are much smaller than k_{R6b} and k_{R12b}). An analysis using linear regression led to the value $k_{R7b}/k_{Rb'} = (1.2 \pm 0.5) \times 10^{-20}$ cm^3 molecule^{-1}. This ratio was used to construct the lines shown in Figure 4b. Combining this result with the relative yields of HCl_2CCOCl and HCOCl shown in Table 2 allows the branching ratios for all three reactive channels for the radical $HCl_2CCClHO$ (R6b, R7b, and R15b) to be determined at all concentrations of O_2 (see Table 3).

Table 2 lists the values of $\Delta_rH°$ for the possible dissociations of the chlorinated ethoxy radicals derived from $H_2C{=}CCl_2$, $HClC{=}CClH$, and $HClC{=}CCl_2$. In all three of these cases, it can be seen that the branching ratios between CC, CCl, and where possible, CH bond scission are a reasonable reflection of the thermochemistry. That is, in all cases, the most favored unimolecular process is the most exothermic pathway, although it should be appreciated that the uncertainties in the values of

$\Delta_rH°$ are large since the values of $\Delta_fH°$ for the chlorinated ethoxy radicals are only estimates based on group additivity rules.[34]

5. Cl Atom Initiated Oxidation of $Cl_2C{=}CCl_2$ and Cl_3CCCl_2H: Results

A major objective of the present work was to explore and explain the kinetics and mechanism of the oxidation of C_2Cl_4 and C_2Cl_5H under a range of experimental conditions in order to provide information that would be useful in understanding the fate of C_2Cl_4 in the troposphere. Although there have been several previous studies of the photochemical oxidation of C_2Cl_4, the older studies[12,16,20] used concentrations of Cl_2 and C_2Cl_4 much greater than in the present work, which itself uses concentrations of C_2Cl_4 that are much greater than those present in the atmosphere. As the data in Table 1 shows, these previous studies and that of Ariya et al.[21] measured product distributions that were very similar both to one another and to yields from experiments on C_2Cl_5H, which has been taken as proof that the two mechanisms are identical after reaction R2d or R2d′. Ariya et al.,[21] who used a similar experimental technique to ours, did employ initial partial pressures of Cl_2 and C_2Cl_4 of the order of a few mTorr, but it is not obvious that the product yields were measured as the initial conditions were systematically varied. Likewise, although product yield studies have been carried out previously at different temperatures, no single set of experiments has been performed to investigate whether the yields change over a significant temperature range.

Part of our aim was to compare the rates at which the concentrations of reagents and products changed with those predicted using the modelling program FACSIMILE.[32] In order to do this, it was necessary to determine the first-order rate constant, $k_{p,R1}$, for photolysis of Cl_2 by both the blacklamps and the fluorescent lamps. To estimate $k_{p,R1}$, Cl_2 was photolyzed in the presence of C_2H_6 and O_2 and changes in the concentrations of C_2H_6 and HCl were simultaneously measured. The rates of C_2H_6 loss and HCl formation were found to be the same and were assumed to be twice the rate of photolysis of Cl_2, yielding values of $k_{p,R1}$ of 3×10^{-4} s^{-1} (blacklamps) and 3×10^{-6} s^{-1} (fluorescent lamps).

At room temperature, the time scale for reaction was found to differ quite dramatically between C_2Cl_4 and C_2Cl_5H. For C_2Cl_4, under typical experimental conditions and using blacklamps to photolyze Cl_2, reaction was complete in less than 5 min. However, under identical conditions, complete oxidation of the same concentration of C_2Cl_5H took about 2 h. As the temperature was increased from 298 to 393 K, the rate of reaction of C_2Cl_4 decreased by a factor of 10. The reasons for these observations are discussed later.

In order to follow the kinetics of the C_2Cl_4 oxidation, the fluorescent lamps were used to photolyze Cl_2 and initiate the reaction. With this relatively slow rate of photolysis, C_2Cl_4 was fully consumed in about 30 min. Typical spectra obtained from the reactions of C_2Cl_4 and C_2Cl_5H are shown in Figure 5. The temporal profiles of the reactant and product concentrations in a typical experiment are shown in Figure 6. It is noticeable that the rates of loss of reactant and formation of products are slower initially than at later time intervals. It was also observed that the product concentrations did not increase linearly with the reduction in reagent concentrations. These findings are due to the fact that the concentrations of Cl atoms only slowly approached a limiting steady-state value. Although they are removed rapidly by reaction with C_2Cl_4 and C_2Cl_5H, they are regenerated in subsequent steps of the reaction mechanism and the actual removal of radicals from the system is slow.

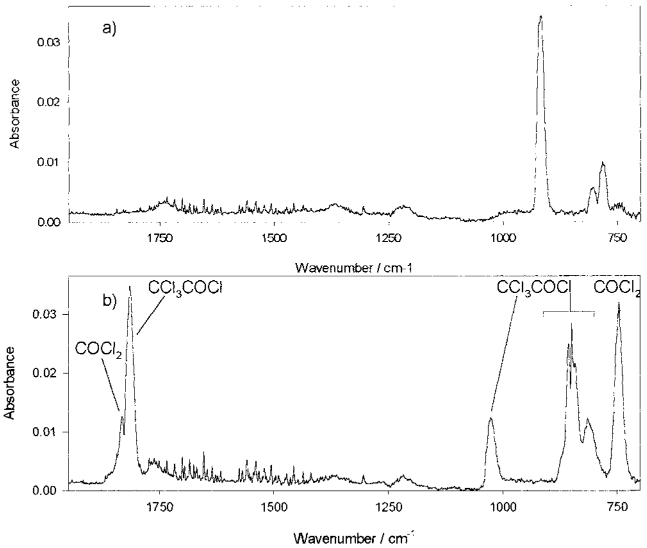

Figure 5. Examples of infrared spectra recorded (a) before and (b) after 20 min of photolysis of a mixture initially containing 4×10^{14} molecule cm^{-3} Cl_2, 4×10^{14} molecule cm^{-3} C_2Cl_4, and 140 Torr O_2, made up to 700 Torr total pressure with N_2, and (c) before and (d) after 2 h of photolysis of a mixture initially containing 4×10^{14} molecule cm^{-3} Cl_2, 4×10^{14} molecule cm^{-3} C_2Cl_5H, and 140 Torr O_2, made up to 700 Torr total pressure with N_2.

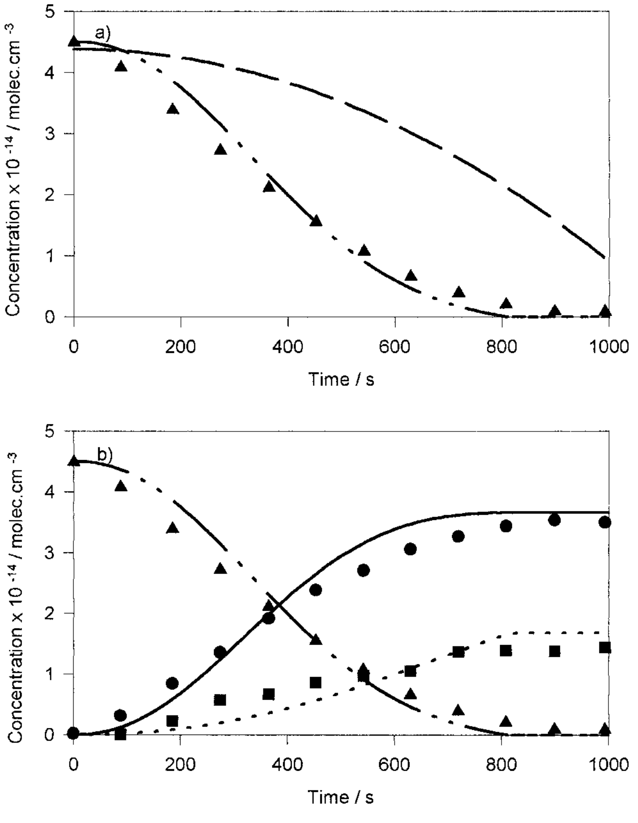

Figure 6. Comparison of the observed concentrations of C_2Cl_4 (▲), CCl_3COCl (●), and $COCl_2$ (■) in a typical experiment using fluorescent lamps ($k_{p,R1} = 3 \times 10^{-6}$ s^{-1}) with those predicted using FACSIMILE and the rate constants listed in Table 4, including reactions R23d and R24d unless otherwise stated: (a) C_2Cl_4 (-•••-), C_2Cl_4 excluding (R26d) and (R27d) (- - -), (b) C_2Cl_4 (-•••-), CCl_3COCl (—), and $COCl_2$ (•••). The reaction mixture was the same as that specified in the caption to Figure 5.

How the final product yields depended on changes in the initial concentrations of Cl_2, O_2, and C_2Cl_4 was investigated in three separate series of experiments. It is important to note that

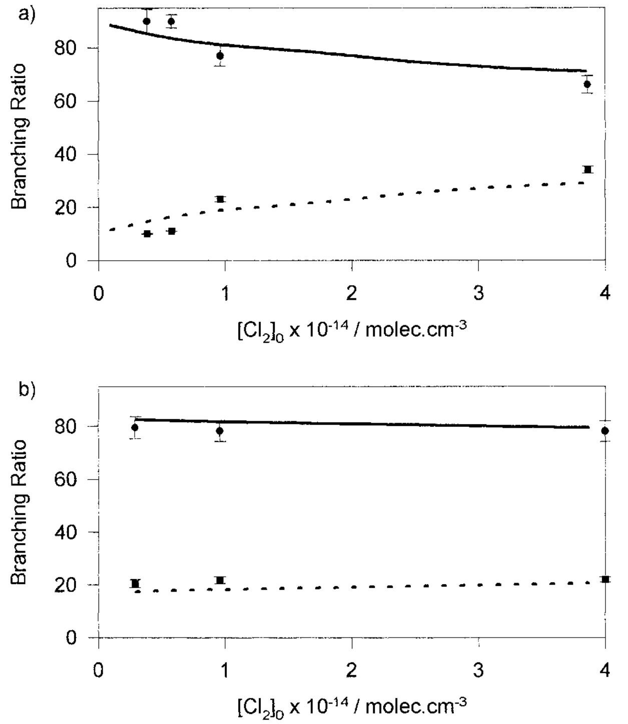

Figure 7. Comparison of the observed yields of CCl_3COCl (●) and $COCl_2$ (■) for different initial concentrations of Cl_2 with those predicted using FACSIMILE and the rate constants listed in Table 4 (including reactions R23d and R24d), CCl_3COCl (—) and $COCl_2$ (•••): (a) using the blacklamps so that $k_{p,R1} = 3 \times 10^{-4}$ s^{-1} and (b) using the fluorescent lamps so that $k_{p,R1} = 3 \times 10^{-6}$ s^{-1} in a reaction mixture initially containing 5.5×10^{13} molecule cm^{-3} C_2Cl_4, and 140 Torr O_2, made up to 700 Torr total pressure with N_2.

the reaction mechanism represented by reactions R1−R10d does not predict any dependence of the product yields on the initial concentrations of any of the reagents involved, since CCl_3COCl and $COCl_2$ are formed only in the unimolecular dissociation reactions R5d, R6d, and R10d. Variations in $[Cl_2]_0$, the initial concentration of Cl_2, in the range 4×10^{13} to 4×10^{14} molecule cm^{-3}, resulted in no significant changes in the product distributions from either C_2Cl_4 or C_2Cl_5H, except at low $[Cl_2]_0$. The results of such experiments using $[C_2Cl_4]_0 = 5.5 \times 10^{13}$ molecule cm^{-3} and with $[O_2] = 140$ Torr are shown in Figure 7. At low photolysis rates, as shown in Figure 7b, the relative yields of CCl_3COCl and $COCl_2$ were independent of the initial concentration of Cl_2, within experimental error. However, at the higher photolysis rates induced by the blacklamps, the yield of CCl_3COCl fell slightly as the amount of Cl_2 present in the reaction mixture was increased. No dependence of the product yields on the O_2 concentration was observed over a range of pressures from 30 mTorr to 700 Torr for any of the initial concentrations of Cl_2 or C_2Cl_4 that were investigated.

To examine if the product yields depended on the initial concentration of the chlorinated hydrocarbon, mixtures of C_2Cl_4 or C_2Cl_5H (3×10^{13} to 1×10^{15} molecule cm^{-3}), O_2 (140 Torr), and Cl_2 (4×10^{14} molecule cm^{-3}) were irradiated using blacklamps for times between 10 min (C_2Cl_4) and 2 h (C_2Cl_5H) with spectra being recorded every few minutes to observe the loss of the reactant and the formation of CCl_3COCl and $COCl_2$. The total yields for each experiment, measured as C atom balances, exceeded 90%, and no products other than CCl_3COCl and $COCl_2$ were detected. The results summarized in Figure 8a represent normalized product distributions from these experiments. It is seen that, at relatively high initial concentrations of C_2Cl_4, CCl_3COCl was the major product with a yield of ca. 90%. This value is in good agreement with previous work[21] carried out on this reaction system under similar conditions with similar initial concentrations (see Table 1). However, and unexpectedly, as $[C_2Cl_4]_0$ was reduced in our experiments, the yield of CCl_3COCl fell and the yield of $COCl_2$ showed a corresponding rise. At the lowest values of $[C_2Cl_4]_0$ that could be used, $COCl_2$ became the dominant product. If this trend were to continue, then at very low C_2Cl_4 concentrations, as in the atmosphere, the yield of CCl_3COCl would become virtually zero.

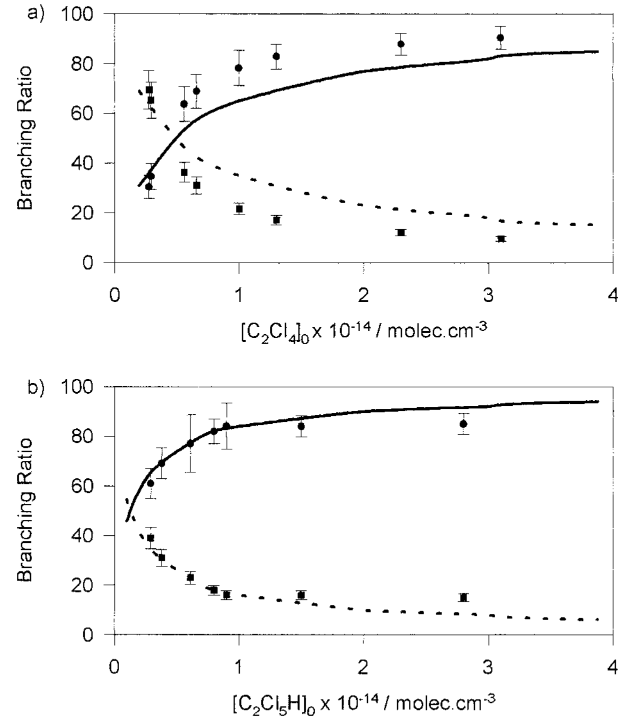

Figure 8. (a) Comparison of the observed yields of CCl_3COCl (●) and $COCl_2$ (■) for different initial concentrations of C_2Cl_4 with those predicted using FACSIMILE and the rate constants listed in Table 4 (including reactions R23d and R24d): CCl_3COCl (—) and $COCl_2$ (•••). (b) Comparison of the dependence of the observed yields of CCl_3COCl (●) and $COCl_2$ (■) on the initial concentration of C_2Cl_5H with those predicted using FACSIMILE and the rate constants listed in Table 4 (including reactions R25d′ and R26d′): CCl_3COCl (—) and $COCl_2$ (•••). The reaction mixtures initially contained 4×10^{14} molecule cm^{-3} Cl_2 and 140 Torr O_2 made up to 700 Torr total pressure with N_2.

Experiments were also performed to check that our results were not affected by wall reactions or by further chemistry or photochemistry of the primary products. To test the latter possibility, samples of CCl_3COCl and $COCl_2$ with 140 Torr O_2 were irradiated, both without and with Cl_2 present. In no case was significant change observed, even with irradiation times well in excess of those used in the main experiments. In our reaction cell (diameter = 7.5 cm) at a total pressure of 700 Torr, molecules would take ca. 100 s to diffuse to the vessel walls which are covered in Teflon to reduce their activity. Leaving both the reagents and products in the dark brought about no discernible change, suggesting that heterogeneous chemistry is also unimportant in our experiments.

The effect of the photolysis rate of Cl_2 on the product distribution was also investigated by measuring the product yields using blacklamps ($k_{p,R1} = 3 \times 10^{-4}$ s^{-1}) and fluorescent lamps ($k_{p,R1} = 3 \times 10^{-6}$ s^{-1}) in two series of experiments. First, gas mixtures containing a low concentration of C_2Cl_4, 140 Torr of O_2, and between 3×10^{13} molecule cm^{-3} and 4×10^{14} molecule cm^{-3} of Cl_2 were photolyzed with the fluorescent

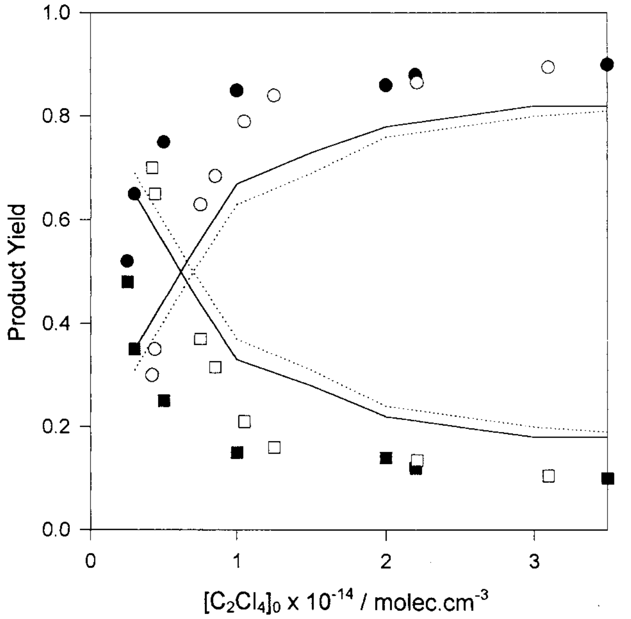

Figure 9. Comparison of the dependence of the observed yields of CCl_3COCl (●,○) and $COCl_2$ (■,□) on the initial concentration of C_2Cl_4 and different rates of photolysis with those predicted using FACSIMILE and the rate constants listed in Table 4 (including reactions R23d and R24d). The data represented by the filled symbols were obtained using fluorescent lamps and those given by the open symbols were obtained using the blacklamps. The line (—) shows the results of calculations using $k_{p,R1} = 3 \times 10^{-6}$ s^{-1}; the line (···) shows the results of calculations using $k_{p,R1} = 3 \times 10^{-4}$ s^{-1}.

lamps. As already discussed, at the slower rate of photolysis, a slightly different product distribution was obtained, and it was found to have a much reduced dependence on $[Cl_2]_0$ (see Figure 7). In addition, a second series of experiments was performed in which a fixed $[Cl_2]_0$ of 4×10^{14} molecule cm^{-3} was photolyzed with the fluorescent lamps, and the initial concentration of C_2Cl_4 was varied as before. The result of these experiments are compared in Figure 9 with those in which photolysis by the blacklamps was used to initiate oxidation of C_2Cl_4. Once again, the yields of CCl_3COCl and $COCl_2$ were found to depend on the initial concentration of C_2Cl_4, although the dependence in this case was slightly less marked than at the higher photolysis rate.

In light of the unanticipated variation of product yields from the oxidation of C_2Cl_4 with initial conditions, especially the initial concentration of C_2Cl_4, it was decided to investigate the effects of temperature and total pressure on these results. Experiments to determine the yields of $COCl_2$ and CCl_3COCl as $[C_2Cl_4]_0$ or $[C_2Cl_5H]_0$ was varied were repeated at 353 and 393 K using the black lamps to photolyze Cl_2. The results for C_2Cl_4 are shown in Figure 10. The temperature dependence of the yields of CCl_3CCOCl and $COCl_2$ was found to be slight, the limit of the yield of CCl_3COCl at high $[C_2Cl_4]_0$ rising from 89.0% at 298 K to 93.5% at 393 K, in agreement with previous measurements[21] carried out using similar concentrations of reactants. At each of the three temperatures which were employed, a similar dependence of product yields on $[C_2Cl_4]_0$ was observed. Figure 11 shows the results of experiments conducted at three different total pressures. Although the dependence of the product yields on $[C_2Cl_4]_0$ persists, it is reduced slightly as the pressure is reduced from 700 to 50 Torr, through the range of $[C_2Cl_4]_0$ which could be used in our experiments.

Experiments on the chlorine atom initiated oxidation of pentachloroethane revealed a similar, and similarly surprising, dependence of the yields of CCl_3COCl and $COCl_2$ on the initial concentration of the reagent, in this case C_2Cl_5H (see Figure 8b), although the dependence of these yields on $[C_2Cl_5H]_0$ was not as great as on $[C_2Cl_4]_0$. In the limit of high $[C_2Cl_5H]_0$ however, the yields of CCl_3COCl and $COCl_2$ were similar to those from C_2Cl_4 under similar conditions, a finding which is in agreement with previous measurements (see Table 1). Suspecting that CCl_3CCl_2O radicals might react with HCl, which is the only product formed in this system that is not present in the experiments on C_2Cl_4, a series of experiments were performed in which HCl was added to $Cl_2/C_2Cl_4/O_2/N_2$ mixtures. $[C_2Cl_4]_0$ was set at 5.5×10^{13} molecule cm^{-3} and the partial pressure of O_2 at 140 Torr, and product yields were studied in the presence of between 3×10^{13} and 4×10^{14} molecule cm^{-3} of HCl. The dependence of the yields on the amount of HCl

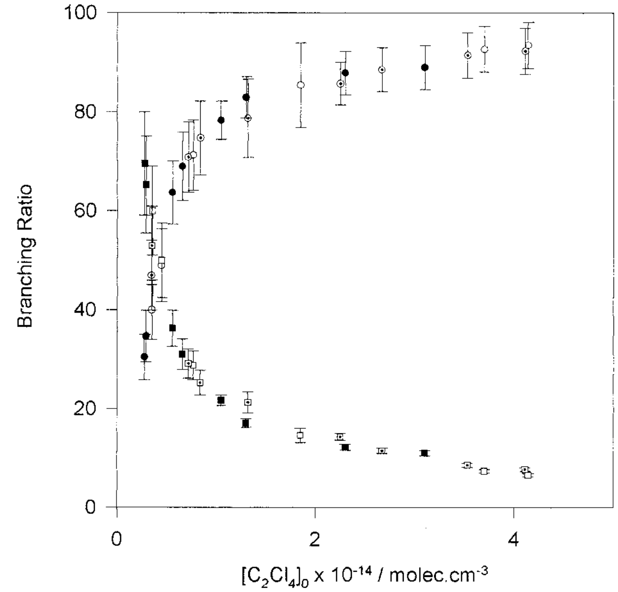

Figure 10. Dependence of the observed yields of CCl_3COCl (●,○,⊙) and $COCl_2$ (■,□,⊡) from the oxidation of C_2Cl_4 on the initial concentration of C_2Cl_4 at different temperatures: 298, 353, and 393 K, under the same experimental conditions as Figure 6.

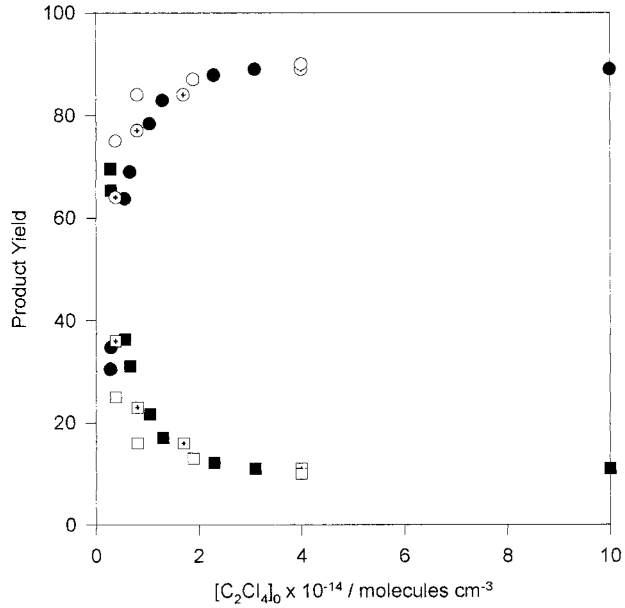

Figure 11. Dependence of the observed yields of CCl_3COCl (●,○,⊙) and $COCl_2$ (■,□,⊡) from the oxidation of C_2Cl_4 on the initial concentration of C_2Cl_4 at different total pressures: 700, 140, and 50 Torr, under the same experimental conditions as Figure 6.

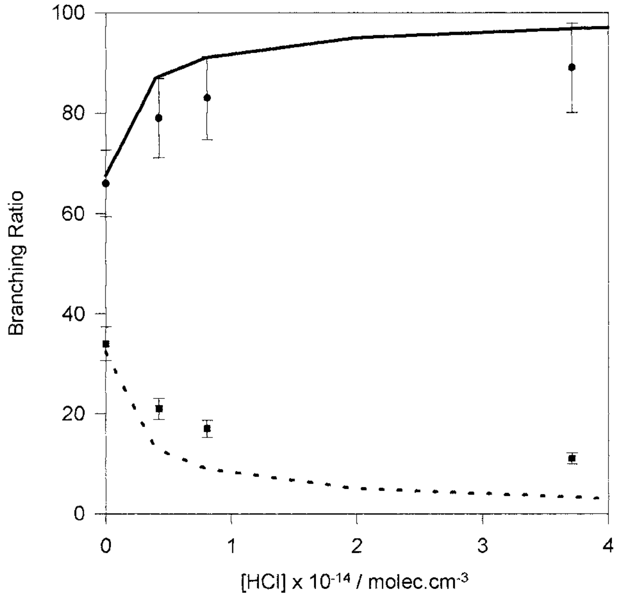

Figure 12. Comparison of the dependence of the observed yields of CCl_3COCl (●) and $COCl_2$ (■) from the Cl atom initiated oxidation of C_2Cl_4 on the initial concentration of HCl with those predicted using FACSIMILE and the rate constants listed in Table 4 (including reactions R23d, R24d, R25d′, and R26d′): CCl_3COCl (—) and $COCl_2$ (···)

present is shown in Figure 12. As the concentration of HCl was increased, the yield of $COCl_2$ fell, a corresponding rise being observed in the concentration of CCl_3COCl.

Finally, as a further attempt to understand our observations on the oxidations of C_2Cl_4 and C_2Cl_5H, we decided to examine the kinetics and product yields in the presence of added NO. It was hoped that it might be possible to determine the rate of unimolecular decomposition of the CCl_3O and C_2Cl_5O radicals by comparison of the yields of $COCl_2$ from reaction R10d and CCl_3COCl and $COCl_2$ from (R5d) and (R6d) with those of CCl_3ONO and C_2Cl_5ONO formed in the association reactions

$$CCl_3O + NO + M \rightarrow CCl_3ONO + M \qquad (R19d)$$

$$C_2Cl_5O + NO + M \rightarrow C_2Cl_5ONO + M \qquad (R20d)$$

although it was also recognized that, with NO present, $C_2Cl_5O_2$ radicals would be converted to C_2Cl_5O radicals by reaction with NO, rather than with another peroxy radical (see R5d).

To generate CCl_3O and C_2Cl_5O radicals fairly directly, experiments were performed on the Cl atom initiated oxidations of $CHCl_3$ and C_2Cl_5H. Mixtures of 4×10^{14} molecule cm^{-3} of the chlorinated alkane, 4×10^{14} molecule cm^{-3} Cl_2, 1×10^{15} molecule cm^{-3} NO, and 140 Torr O_2 were diluted to 700 Torr in N_2 and irradiated with the fluorescent lamps. In both cases, $COCl_2$ was the only product observed but the yield could not be quantified as its formation was extremely slow. Almost certainly this was due to the NO-catalyzed recombination of Cl atoms,

$$Cl + NO + M \rightarrow ClNO + M \qquad (R21)$$

$$Cl + ClNO \rightarrow Cl_2 + NO \qquad (R22)$$

drastically reducing the concentration of Cl atoms present in the system. Even after several hours of the irradiation with the blacklamps, only 2% of the $CHCl_3$ had reacted. Varying the initial concentration of NO altered the overall rate of reaction, but $COCl_2$ remained the only observed product.

Some experiments were also performed on the oxidation of C_2Cl_4 in the presence of NO. The time scale for reaction was much shorter. Mixtures of 4×10^{14} molecule cm^{-3} C_2Cl_4, 4×10^{14} molecule cm^{-3} Cl_2, 1×10^{15} molecule cm^{-3} NO, and 140 Torr O_2, diluted to 700 Torr in N_2 were converted completely to products in about 2 h. Again, no evidence was found for the formation of CCl_3ONO or C_2Cl_5ONO. The yield of CCl_3COCl from this mixture was 75%, about 14% lower than in similar experiments without NO present. A possible explanation for this difference is that the C_2Cl_5O radicals formed by reaction of $C_2Cl_5O_2$ with NO contain more initial internal energy than when the same radicals are formed from two peroxy radicals and this accelerates their rate of unimolecular dissociation by CC bond scission thereby increasing the yield of $COCl_2$. Behavior of this kind has been observed for CF_3CFHO.[33]

6. Cl Atom Initiated Oxidation of $Cl_2C{=}CCl_2$ and Cl_3CCCl_2H: Discussion

The observations reported in the previous section cannot be explained simply in terms of the mechanism which was outlined in section 3 and which is sufficient to explain our results for the three partially chlorinated ethenes. If this mechanism held for the oxidations of C_2Cl_4 and C_2Cl_5H, then the ratio of products, $[CCl_3COCl]/[COCl_2]$, should be determined only by the relative rates of the unimolecular decompositions of the C_2Cl_5O radical in reactions R5d and R6d. To explain the observed chemistry, especially the dependence of the product yields on the initial concentrations, $[C_2Cl_4]_0$ and $[C_2Cl_5H]_0$, it seems that at least one bimolecular reaction forming product must be included in the mechanisms for the oxidation of these compounds.

In the case of the oxidation of C_2Cl_4, it seemed reasonable to suppose that this species might be involved in this additional reaction and one possible step that would influence the yields of products in the manner that is observed is

$$C_2Cl_4 + C_2Cl_5O \rightarrow CCl_3COCl + C_2Cl_5 \qquad (R23d)$$

This reaction is thermodynamically allowed,[34] being exothermic by -128 kJ mol^{-1}, and, if it were fast enough to compete with the unimolecular decompositions R5d and R6d, its occurrence would explain why higher initial concentrations of C_2Cl_4 result in higher yields of CCl_3COCl and decreased yields of $COCl_2$. The reaction

$$C_2Cl_4 + CCl_3O \rightarrow CCl_3COCl + CCl_3 \qquad (R24d)$$

is also exothermic, although reaction to produce $C_2Cl_5 + COCl_2$ is possible.

To examine the potential importance of these reactions, we employed the modeling program FACSIMILE.[32] In Figure 6a, we compare the observed decrease in $[C_2Cl_4]$ with time with predictions of the model using the rate constants given in Table 4, both excluding and including reactions R23d and R24d. In the absence of these reactions, the model failed to reproduce the experimental results, particularly the decrease in the rate of loss of C_2Cl_4 which is observed towards the end of the reaction. In these calculations, the concentration of Cl atoms continued to rise at long times causing the rate of loss of C_2Cl_4 to accelerate. On the other hand, addition of reactions R23d and R24d to the model resulted in good agreement with experiment, both in regard to the consumption of C_2Cl_4 and the rates of formation of the major products, as shown in Figure 6. Using the values of the first-order rate constants for the unimolecular dissociations of C_2Cl_5O and CCl_3O, i.e., for reactions R5d, R6d,

TABLE 4: Reactions and Rate Constants Used in Modeling Calculations at 298 K

	reaction	k/cm^3 molecule^{-1} s^{-1} or k/s^{-1} ^{a}	ref
(R1)	$Cl_2 + h\nu \rightarrow 2Cl$	3×10^{-4} or 3×10^{-6}	fitted (see text)
(R-1)	$2Cl \rightarrow Cl_2$	2.5×10^{-13}	39
	$Cl + O_2 \rightarrow ClO_2$	1.18×10^{-14}	38
	$ClO_2 \rightarrow Cl + O_2$	4.7×10^{6}	38
(R2d)	$Cl + C_2Cl_4 \rightarrow C_2Cl_5$	3×10^{-11}	4
(R2d′)	$Cl + C_2Cl_5H \rightarrow C_2Cl_5 + HCl$	1.2×10^{-14}	22
(R3d)	$C_2Cl_5 + O_2 \rightarrow C_2Cl_5O_2$	8.6×10^{-13}	11
(R4d)	$2C_2Cl_5O_2 \rightarrow 2C_2Cl_5O + O_2$	6×10^{-11}	11
(R5d)	$C_2Cl_5O \rightarrow CCl_3COCl + Cl$	1×10^{3}	fitted (see text)
(R6d)	$C_2Cl_5O \rightarrow COCl_2 + CCl_3$	1×10^{4}	fitted (see text)
(R8d)	$CCl_3 + O_2 \rightarrow CCl_3O_2$	2.5×10^{-12}	40
(R9d)	$2CCl_3O_2 \rightarrow 2CCl_3O + O_2$	1.5×10^{-12}	35
(R10d)	$CCl_3O \rightarrow COCl_2 + Cl$	1×10^{5}	37
(R23d)	$C_2Cl_5O + C_2Cl_4 \rightarrow CCl_3COCl + C_2Cl_5$	5×10^{-10}	fitted (see text)
(R24d)	$CCl_3O + C_2Cl_4 \rightarrow CCl_3COCl + CCl_3$	5×10^{-10}	fitted (see text)
(R25d′)	$C_2Cl_5O + HCl \rightarrow C_2Cl_5OH + Cl$	9×10^{-10}	fitted (see text)
	$CCl_3O + HCl \rightarrow CCl_3OH + Cl$	9×10^{-10}	fitted (see text)
(R26d′)	$C_2Cl_5OH \rightarrow CCl_3COCl + HCl$	1×10^{6}	fitted (see text)
	$CCl_3OH \rightarrow COCl_2 + HCl$	1×10^{6}	fitted (see text)

and R10d, agreement with experiment was given by choosing the values of k_{R23d} and k_{R24d} to be 5×10^{-10} cm^3 molecule^{-1} s^{-1}. Although these rate constants seem unreasonably high, we point out that such values are needed in order for the bimolecular reactions R23d and R24d to compete with unimolecular decomposition of the chlorinated ethoxy radicals. Similar agreement can be obtained by lowering the values for both groups of rate constants by the same amount.

Having obtained reasonably good agreement with the experimentally determined profiles of [C_2Cl_4] versus time, using the extended model, attempts were made to reproduce the measured product yields and how they depended on experimental conditions. The addition of reactions R23d and R24d also resulted in good agreement with the sets of experiments where the initial concentrations of Cl_2 (Figure 7) and of C_2Cl_4 (Figure 8a), and the photolysis rate of Cl_2 (Figure 7) were varied. Then, according to the model and using the rate constants listed in Table 4, with high [C_2Cl_4]$_0$ products are formed principally through the bimolecular reactions R23d and R24d. Hence the major product is CCl_3COCl. However, at low concentrations of C_2Cl_4, this reaction becomes slower and the product distribution is largely determined by the two unimolecular reactions R5d and R6d. Our results therefore suggest that (R6d) is faster than (R5d), a result which is consistent with the finding that fission of the C−C bond in the pentachloroethoxy radical is more exothermic than fission of a C−Cl bond in the CCl_2O group (see Table 2).

The small effects on the product yields from C_2Cl_4 of varying [Cl_2]$_0$ is well matched by the model calculations for both fast and slow rates of photolysis. With reactions R23d and R24d included, the relative rates of formation of CCl_3COCl and $COCl_2$ are given by the ratio of (a) the sum of the rates of reactions R5d, R23d, and R24d to (b) the rate of reaction R6d, i.e.,

$$(\text{rate} \rightarrow CCl_3COCl)/(\text{rate} \rightarrow COCl_2) = \{k_{R5d}[C_2Cl_5O] + k_{R23d}[C_2Cl_5O][C_2Cl_4] + k_{R24d}[C_2Cl_4][CCl_3O]\}/k_{R6d}[C_2Cl_5O] \quad (1)$$

and the ratio of the observed yields corresponds to an integration of this expression over the duration of an experiment. Effects of changing the rate of photolysis, by exchanging blacklamps for fluorescent lamps, are also shown as a function of [C_2Cl_4]$_0$ in Figure 9. Once again, the effect of the higher rate of photolysis is seen to be an increase in the yield of $COCl_2$ and a decrease in that of CCl_3COCl. The effect is strongest at low [C_2Cl_4]$_0$. It appears that the decrease in CCl_3COCl produced, and the corresponding increase in $COCl_2$, at high [Cl_2]$_0$ and with the fast photolysis rate must be associated with the very rapid consumption of C_2Cl_4 under these conditions. Although the results of the calculations using FACSIMILE only fit the experimental data on Figure 8a moderately well, they do reproduce quite well the smaller effects of changing the rate of photolysis.

At first sight, our tentative explanation for the results of our experiments on C_2Cl_4, particularly the variation of product yields with [C_2Cl_4]$_0$, appears to conflict with the finding that in similar experiments with C_2Cl_5H the major product is again CCl_3COCl (see Figure 7b). Since there is no C_2Cl_4 present in these experiments and the C_2Cl_5 radicals formed by abstraction of the H atom from C_2Cl_5H by Cl atoms should be rapidly converted to C_2Cl_5O radicals by reactions R3d and R4d, one might expect the products to be the same as those found in the experiments with low [C_2Cl_4]$_0$. The reason why this discrepancy might arise is given by the experiments on the oxidation of C_2Cl_4 in the presence of HCl, the results of which are shown in Figure 12. As the HCl concentration is increased, the yield of $COCl_2$ falls. We ascribe this observation to the reaction of C_2Cl_5O radicals with HCl:

$$C_2Cl_5O + HCl \rightarrow C_2Cl_5OH + Cl \quad (R25d')$$

Perchloroethanol is not observed among the products and presumably decomposes

$$C_2Cl_5OH\ (+M) \rightarrow CCl_3COCl + HCl\ (+M) \quad (R26d')$$

so that HCl can act catalytically to convert C_2Cl_5O radicals to CCl_3COCl via reactions R25d′ and R26d′. Although a similar sequence of reactions can occur for CCl_3O radicals yielding $COCl_2$, it will not increase the yield of $COCl_2$ since any CCl_3O radicals that are formed are converted to $COCl_2$ in unit yield in any case. Once again, FACSIMILE[32] was used to examine the validity of these proposals. Using the values $k_{R25d'} = 9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $k_{R26d'} = 1 \times 10^{6}$ s^{-1}, good agreement was obtained for the variation of product yields with [C_2Cl_5H]$_0$ in experiments on $Cl_2/C_2Cl_5H/O_2/N_2$ mixture (see Figure 7b) and fair agreement was obtained for the variation of product yields when HCl was added to $Cl_2/C_2Cl_4/O_2/N_2$ mixtures (see Figure 12).

At this point, we consider the magnitude of the rate constants k_{R23d}, k_{R24d}, k_{R25d}, and k_{R26d} that have been used in the modelling calculations. For the oxidation of C_2Cl_5H, we note that the model results were insensitive to the value chosen for $k_{R26d'}$ (it was reduced by several orders of magnitude without significant change in the computed results, since it is only needed to explain the absence of any CCl_3CCl_2OH in the reaction products), and that $k_{R25d'}$ could be reduced as long as k_{R5d} and k_{R6d} were reduced by the same amount. Similarly, the calculated results for the oxidation of C_2Cl_4 were insensitive to the *absolute* values of the rate constants for the bimolecular and unimolecular reactions of the chlorinated alkoxy radicals, C_2Cl_5O and CCl_3O, but were sensitive to their *relative* values. The values of k_{R23d}, k_{R24d}, and $k_{R25d'}$ that are referred to above and given in Table 4, and which may seem unreasonably large, are the result of taking the values of the rate constants for unimolecular decomposition of these radicals that are listed in Table 4.

As the temperature was increased, the most obvious effect on the reaction of C_2Cl_4 was that the time for complete reaction, with the illumination by the blacklamps, increased from a few minutes to ca. 1 h. This can be attributed to the fact that, at 330 K and below, the addition of Cl atoms to C_2Cl_4, i.e., reaction R2d, is essentially irreversible.[4] However, at higher temperatures, especially above 330 K, the reaction becomes reversible and the equilibrium starts to favor Cl + C_2Cl_4 under the conditions of our experiments. As a result, the concentration of C_2Cl_5 radicals is reduced and the overall reaction slows down.

Figure 10 shows the CCl_3COCl and $COCl_2$ yields from the oxidation of C_2Cl_4 at three temperatures, 298, 353, and 393 K. They are surprisingly insensitive to temperature. Whatever the rate constants for the unimolecular dissociations of the C_2Cl_5O radicals via reactions R5d and R6d, it is reasonable to suppose that they have larger activation energies than the bimolecular reactions R23d and R24d, which must have rather large rate constants at room temperature if they are responsible for the dependence of product yields on the initial concentration of C_2Cl_4. A partial explanation for the fact that the dependence of product yields on $[C_2Cl_4]_0$ scarcely depends on temperature may be the difference in the temperature dependence of the rate constants for (R5d) and (R6d). Reaction R5d which, like (R23d) and (R24d), produces CCl_3COCl, is apparently slower at room temperature than (R6d), consistent with the fact that the C−Cl bond is stronger than the C−C bond in CCl_3CCl_2O (see Table 2). Consequently, the rate of (R5d) will increase more rapidly with temperature than (R6d), thereby compensating to some extent for the diminishing effect of reactions R23d and R24d.

The mild dependence of the product yields on total pressure which is shown in Figure 11 is consistent with the product yields depending on bimolecular as well as unimolecular reactions. Thus, the rates of reactions R5d, R6d, and R10d may all fall as the total pressure is lowered, whereas the rates of the bimolecular reactions R23d and R24d would be unaffected. As a result, the influence of the bimolecular reactions would extend to lower total pressures resulting in a reduced dependence of the product yields on $[C_2Cl_4]_0$.

It has to be said that the hypothesis that reactions R23d and R24d may be predominantly responsible for the formation of products in the Cl atom initiated oxidation of C_2Cl_4 at relatively high initial concentrations of C_2Cl_4 is not entirely satisfactory. Unfortunately, there have been no direct studies of reactions R23d and R24d. CH_3O radicals have been reported to react slowly with ethene and substituted ethenes,[35] whilst the reaction of CF_3O radicals with C_2H_4 is reported to have a rate constant of about 10^{-11} cm^3 molecule^{-1} s^{-1}.[36] It would seem that the most likely mechanism for rapid reactions giving the products shown in (R23d) and (R24d) would be the initial formation of an energized adduct

$$CCl_3CCl_2O + C_2Cl_4 \rightarrow (CCl_3CCl_2OCCl_2CCl_2)^{\dagger} \qquad \text{(R27d)}$$

followed by intramolecular transfer of a Cl atom and fragmentation to CCl_3COCl + CCl_3CCl_2. For the latter process to be effective, it would seem that its rate would have to compete with addition of O_2 to the radical and possibly with collisional removal of the excess internal energy released as the $(RCCl_2\text{-}OCCl_2CCl_2)^{\dagger}$ radicals are formed in reaction (R27d). Lifetimes with regard to both these processes can be estimated. Assuming a rate constant for addition of O_2 of 10^{-13} cm^3 molecule^{-1} s^{-1}, with 140 Torr of O_2 decomposition of the $RCCl_2OCCl_2CCl_2$ radical would have to occur in less than ca. 1 μs to compete favorably with addition of O_2. If production of CCl_3COCl + $RCCl_2$ can only occur from the energized adduct formed in reaction (R27d), then it would have to rearrange and decompose even more rapidly, since the average time between collisions at 700 Torr total pressure is only ca. 0.1 ns.

Finally, we reemphasise that the rate constants for (R23d) and (R24d) which are required to match the model predictions to our experimental results depend on the rate constants assumed for (R5d), (R6d), and (R10d). The latter are very uncertain. The only attempt to measure any of these rate constants was in an indirect study of reaction R10d by Lesclaux et al.[37] who concluded that, at 7.5 Torr, $k_{R10d} > 1 \times 10^5$ s^{-1}. Atkinson et al.[38] suggest a value of 8×10^6 s^{-1} for atmospheric conditions. However, in order to keep the rate constants for the bimolecular reactions R23d and R24d within anything like reasonable bounds, k_{R10d} was set at the lower limit set by Lesclaux et al. and k_{R5d} and k_{R6d} were given the values shown in Table 4. If these rate constants are actually smaller, then those for reactions R23d and R24d could be lowered in proportion. Perhaps the least satisfactory aspect of the *tentative* proposal that is made here is that one would expect the variation of product yields from the oxidation of C_2Cl_4 to show a quite marked temperature dependence in contrast to what is found experimentally. Whatever the absolute values of k_{R5d}, k_{R6d}, and k_{R10d}, it seems impossible that they have a similar temperature dependence to k_{23d}.

7. Summary and Conclusions

A comprehensive study of the Cl atom initiated oxidations of four chlorinated ethenes has been carried out. For the first time, experiments have been performed using initial concentrations of the organic species below 10^{14} molecule cm^{-3}. For the three partially chlorinated ethenes, $H_2C{=}CCl_2$, $HClC{=}CHCl$, and $HClC{=}CCl_2$, the product yields show no dependence on the initial concentrations of either Cl_2 or the chlorinated ethene and only in the case of $HClC{=}CHCl$, as expected, do they show any variation with the concentration of O_2 included in the reaction mixture.

However, under similar conditions, the product yields of $COCl_2$ and CCl_3COCl from $Cl_2C{=}CCl_2$ (and from C_2Cl_5H) depend on the initial concentration of the chlorinated species and less strongly on $[Cl_2]_0$ and on the rate of photolysis of Cl_2. This is inconsistent with the accepted reaction mechanism. Incorporation of the steps

$$CCl_3CCl_2O, CCl_3O + C_2Cl_4 \rightarrow C_2Cl_5, CCl_3 + CCl_3COCl \qquad \text{(R23d,24d)}$$

$$CCl_3CCl_2O + HCl \rightarrow CCl_3COCl + HCl + Cl \qquad \text{(R25d')}$$

into the reaction mechanisms enabled the experimental results to be modelled reasonably well, although the values of the rate constants that had to be assumed conflict with present indirect evidence about the rates of these reactions. Whilst our results provide some evidence for the above reactions, direct kinetic studies of these processes are required to confirm their importance. Such measurements are at present beyond the capabilities of our apparatus.

The tropospheric concentration of C_2Cl_4 is around 15 pptv. This is several orders of magnitude below the lowest concentration used in our experiments. As a result of this, $COCl_2$ and not CCl_3COCl may be the major product of Cl atom initiated oxidation of C_2Cl_4 in the troposphere. If this is true, then tetrachloroethene is unlikely to be a source of trichloroacetic acid in the environment.

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