Time-Resolved Experiments on the Chlorine Atom Initiated Oxidation of Tetrachloroethene ($Cl_2C{=}CCl_2$)

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We report time-resolved measurements relevant to the atmospheric oxidation of tetrachloroethene ($Cl_2C{=}CCl_2$) and pentachloroethane (CCl_3CCl_2H). Cl atoms were produced by photolysis of Cl_2 at 351 nm, using the output from a pulsed excimer laser, in the presence of C_2Cl_4 and a large excess of O_2. Experiments were performed with and without NO present. The formation of the reaction products $C(O)Cl_2$ and $CCl_3C(O)Cl$ was followed, in real time, via absorption of infrared radiation provided by tunable diode lasers. Contrary to the finding of Hasson and Smith (*J. Phys. Chem. A* **1999**, *103*, 2031) but in agreement with the results of Thüner et al. (*J. Phys. Chem. A* **1999**, *103*, 8657), the relative yields of $C(O)Cl_2$ and $CCl_3C(O)Cl$ were found to be independent of the concentration of C_2Cl_4. However, as found in both previous studies, the relative yields were sensitive to whether the CCl_3CCl_2O radical was formed by the reaction between $CCl_3CCl_2O_2$ and NO or by the mutual reaction of two $CCl_3CCl_2O_2$ radicals. From the results it was possible to estimate the branching ratio $k_{5a}/(k_{5a} + k_{5b})$ for decomposition of the CCl_3CCl_2O radical by the pathways $CCl_3CCl_2O\ (+M) \rightarrow CCl_3C(O)Cl + Cl\ (+M)$ and $CCl_3CCl_2O\ (+M) \rightarrow CCl_3 + C(O)Cl_2\ (+M)$. With CCl_3CCl_2O formed from $CCl_3CCl_2O_2 + NO$, $(k_{5a}/[k_{5a} + k_{5b}]) = 0.69 \pm 0.13$, whereas with $2CCl_3CCl_2O$ formed from $2CCl_3CCl_2O_2$, $(k_{5a}/[k_{5a} + k_{5b}]) = 0.91 \pm 0.21$. Attempts to use literature values of the rate constants in modeling, (a) how the concentration of $CCl_3C(O)Cl$ varied with time following the initiation of reaction and (b) how the yield of $CCl_3C(O)Cl$ depended on the initial concentration of tetrachloroethene, were not successful. Agreement between the experimental results and the calculations could only be obtained using rate constants for the reactions between $CCl_3CCl_2O_2$ and NO and between $CCl_3CCl_2O_2$ and NO_2 that were appreciably larger than previous values.

1. Introduction

Tetrachloroethene, $Cl_2C{=}CCl_2$, is one of the most widely used chlorinated solvents having an annual release, from anthropogenic and natural sources, estimated recently as 432 ktonnes/year in 1992,[1] with its main uses being in dry cleaning and metal degreasing. The atmospheric lifetime of C_2Cl_4 is 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]

$$Cl_2C{=}CCl_2 + OH\ (+M) \rightarrow CCl_2OHCCl_2\ (+M)$$

However, because Cl atoms associate with C_2Cl_4 ca. 300 times faster than OH,[4] the reaction

$$Cl_2C{=}CCl_2 + Cl\ (+M) \rightarrow CCl_3CCl_2\ (+M) \qquad (1)$$

may also play a significant role in initiating the atmospheric oxidation of C_2Cl_4. Oxidation initiated by Cl atoms is known[5] to yield $CCl_3C(O)Cl$ as one of its products and the hydrolysis of this species has been postulated as a source of trichloroacetic acid, $CCl_3C(O)OH$, which is known to be phytotoxic.[6]

Under atmospheric, or simulated atmospheric, conditions, the oxidation of both the R = CCl_2OHCCl_2 and R = CCl_3CCl_2 radicals is expected to proceed by the reactions common to the oxidation of ethyl and halogenated ethyl radicals, namely the creation of the peroxy radicals (RO_2) by the addition of O_2 and then the conversion of these peroxy radicals to alkoxy radicals (RO), in either the reaction with NO or reactions with other peroxy radicals. (In experiments, reaction 4 will generally be between two identical peroxy radicals, RO_2. In the atmosphere, any given peroxy radical, RO_2, is most likely to react with HO_2 or some other alkyl peroxy radical, $R'O_2$. Both possibilities are represented by reaction 4. We omit the possibility that such reactions lead to products other than those given, as it is not relevant to the present experiments.) For the case of the pentachloroethyl radicals formed in reaction 1, these reactions would be

$$CCl_3CCl_2 + O_2\ (+M) \rightarrow CCl_3CCl_2O_2\ (+M) \qquad (2)$$

$$CCl_3CCl_2O_2 + NO \rightarrow CCl_3CCl_2O + NO_2 \qquad (3)$$

$$CCl_3CCl_2O_2 + R'O_2\ (\text{or } HO_2) \rightarrow CCl_3CCl_2O + O_2 + R'O\ (\text{or } OH) \qquad (4)$$

In the case of CCl_2OHCCl_2 radicals, the corresponding reactions would occur with the CCl_3 moiety replaced by CCl_2OH.

In general, ethoxy and substituted ethoxy radicals can undergo three reactions: abstraction by O_2 of a H-atom from the methylene group, or decomposition, either by cleavage of the C−C bond or loss of one of the atoms in the methylene group. In the case of the radicals of interest here, reaction with O_2 is not possible and loss of RO must be by one or other of the dissociation channels; for example

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$$CCl_3CCl_2O\ (+M) \rightarrow CCl_3C(O)Cl + Cl\ (+M) \quad (5a)$$

$$CCl_3CCl_2O\ (+M) \rightarrow CCl_3 + C(O)Cl_2\ (+M) \quad (5b)$$

Recent laboratory measurements on the oxidation of $Cl_2C{=}CCl_2$,[7−9] and of the related compounds, the partially chlorinated ethenes ($H_2C{=}CCl_2$,[8] $HClC{=}CClH$,[8] and $HClC{=}CCl_2$[8,10]) and pentachloroethane (CCl_3CCl_2H[11]), which yields CCl_3CCl_2 radicals via H-atom abstraction by OH or Cl atoms, have mainly been carried out using the continuous photolysis, Fourier transform infrared (FTIR) spectroscopy method.[12] Most of these studies have yielded results in satisfactory agreement, both with one another and with earlier experiments[13,14] on the oxidation of these compounds. However, this is not the case in one instance. In 1999, Hasson and Smith[8] reported results that called into question previous conclusions about the Cl-atom initiated oxidation of $Cl_2C{=}CCl_2$. Like others before them, they found that $CCl_3C(O)Cl$ and $C(O)Cl_2$ were the main reaction products. However, they reported that the relative yields of these compounds depended on the initial concentration of $Cl_2C{=}CCl_2$, i.e., $[C_2Cl_4]_0$. With $[C_2Cl_4]_0 \geq 2 \times 10^{14}$ molecule cm^{-3}, the relative product yields were approximately constant with $CCl_3C(O)Cl$ being the major product. However, as $[C_2Cl_4]_0$ was lowered, the relative yield of $CCl_3C(O)Cl$ fell and that of $C(O)Cl_2$ increased.

Following the paper by Hasson and Smith, which included studies of partially chlorinated ethenes that showed no similar effects on the product yields to those found for tetrachloroethene, Thüner et al.[9] described the results of extensive experiments in three different laboratories on the Cl-atom initiated oxidation of $Cl_2C{=}CCl_2$. The method used in all these experiments was similar to that employed by Hasson and Smith, but they found no similar effect on the product yields of the initial concentration of $Cl_2C{=}CCl_2$.

In the experiments reported here, we have performed time-resolved measurements on the formation of $CCl_3C(O)Cl$ and $C(O)Cl_2$ created by decomposition of CCl_3CCl_2O radicals, employing time-resolved IR absorption using tunable IR diode laser radiation. Reaction has been initiated by pulsed laser photolysis of Cl_2 to generate Cl atoms in the presence of $Cl_2C{=}CCl_2$ and a large excess of O_2. Experiments have been performed both in the presence of NO, so that CCl_3CCl_2O radicals were formed in reaction 3 between $CCl_3CCl_2O_2$ and NO, and in the absence of NO, so that CCl_3CCl_2O radicals were created by the slower mutual reaction of two $CCl_3CCl_2O_2$ radicals; i.e., reaction 4 with $R'O_2 = CCl_3CCl_2O_2$.

2. Experimental Method

The general experimental method has been described previously[15,16] and is only summarized here. A schematic diagram of the apparatus is shown in Figure 1 of ref 14.

In the present experiments, a pulsed excimer laser (Lambda Physik, Compex 102), operating on XeF and therefore providing radiation at 351 nm, was used to photolyze Cl_2. Gas mixtures containing Cl_2, ca. 1.5×10^{15} molecule cm^{-3}, C_2Cl_4, varied in the range ca. $(0.3-12) \times 10^{14}$ molecule cm^{-3}, NO, either zero or 9.4×10^{14} molecule cm^{-3}, and O_2 to a total pressure of 30 Torr were passed through a tubular Pyrex vessel, which was ca. 1 m long and 40 mm in diameter and fitted with Herriott cell mirrors. The output from the excimer laser entered this reaction vessel through one of the mirrors, which has a central hole, and irradiated a cylindrical volume around the longitudinal axis with a fluence of ca. 7.6 mJ cm^{-2}. On the basis of the known absorption cross-sections of Cl_2,[17] we estimate that, within the path of the laser beam, the laser photodissociated ca. 0.26% of Cl_2. The excimer laser was fired at 0.2 Hz, so that the gas mixture in the cell was refreshed between successive laser shots.

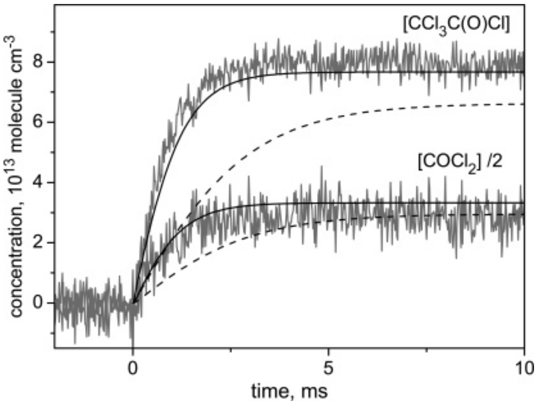

Figure 1. Traces with "noise" represent the concentration of $CCl_3C(O)Cl$ and half the concentration of $C(O)Cl_2$ inferred from traces of time-resolved infrared absorption. In this experiment, the initial partial pressures of the component of the reaction mixture were (mTorr) Cl_2, 46.0; C_2Cl_4, 35.3; and NO, 28.8. The total pressure was 30 Torr, the remainder of the gas being O_2. The smooth dashed curves show the model results using the rate constants listed in Table 1; the full curves were obtained when the rate constants for reactions 3 and 16 (and reaction 15) were increased to $k_3 = 3.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and k_{16} $(=k_{15}) = 1.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

Variations in the concentration of $C(O)Cl_2$ and $CCl_3C(O)Cl$ were monitored by time-resolved infrared absorption at 1808.2 and 1808.4 cm^{-1}, respectively. Although these frequencies are close, we could discriminate between the two products by using relatively sharp features in the spectrum of $C(O)Cl_2$. Tunable continuous wave (cw) infrared radiation was provided by a liquid nitrogen cooled diode laser system (Mutek GmbH, MDS 1150). The direction of the beam and the mirrors of the Herriott cell were arranged so that the single mode beam made 2 passes through the cell. The total path length over which the ultraviolet photolysis and infrared probe beams overlapped was estimated as ca. 1.25 m. The intensity of the emerging infrared beam was measured by a fast (20 MHz) HgCdTe infrared detector coupled to a dc amplifier, then collected in the desired time window by the digital oscilloscope, and ultimately transferred to a PC for further analysis. Generally 64 traces were averaged before subsequent processing. The time response of the detector−amplifier combination was about 10 μs.

Calibration measurements were performed on samples of $C(O)Cl_2$ (99% pure, Argo International Ltd.) and $CCl_3C(O)Cl$ (98.5% pure, Fluorochem) diluted in He to a total pressure of 30 Torr; that is, separate experiments were carried out in which the optical density of absorption at the appropriate frequency was measured with different concentration of the gas in the reaction cell. Making allowance for the difference in path length in these experiments (in which the absorbing gas was present in all of the cell) and in the time-resolved experiments (in which reaction products were only produced in the volume irradiated by the output from the excimer laser), these calibrations were used to estimate absolute concentrations of $C(O)Cl_2$ and $CCl_3C(O)Cl$ in the time-resolved experiments.

A Pyrex vacuum system, consisting of several flow lines fitted with 20 L storage bulbs, greaseless stopcocks, and electronic mass flow controllers, was used to handle the gases. The flows from different lines were mixed immediately before entering the reaction vessel. The experiments reported here were all performed at room temperature (298 ± 3 K).

TABLE 1: Assumed Reaction Mechanism of the Cl Atom Initiated Oxidation of Tetrachloroethene

	reaction	k/cm^3 molecules^{-1} s^{-1} or s^{-1}	reference
	$Cl_2 + h\nu$ (351 nm) $\rightarrow 2Cl$	taken as instantaneous	
1	$C_2Cl_4 + Cl\ (+M) \rightarrow C_2Cl_5\ (+M)$	2.2×10^{-11}	Wine et al.[20]
2	$C_2Cl_5 + O_2\ (+M) \rightarrow C_2Cl_5O_2\ (+M)$	1.66×10^{-13}	Huybrechts et al.[21]
3	$C_2Cl_5O_2 + NO \rightarrow C_2Cl_5O + NO_2$	6.2×10^{-12}	Møgelberg et al.[11]
4	$C_2Cl_5O_2 + C_2Cl_5O_2 \rightarrow C_2Cl_5O + C_2Cl_5O + O_2$	1.3×10^{-11}	Huybrechts et al.[22]
5a	$C_2Cl_5O\ (+M) \rightarrow CCl_3C(O)Cl + Cl\ (+M)$	2×10^{6}	Czarnowski[23]
5b	$C_2Cl_5O\ (+M) \rightarrow CCl_3 + COCl_2\ (+M)$	$0.1 \times k_{5(a)}$ or $0.45 \times k_{5(a)}$	using branching ratios from the present work
6[a]	$CCl_3 + O_2\ (+M) \rightarrow CCl_3O_2\ (+M)$	3.7×10^{-13}	17, 19
7	$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2$	1.8×10^{-11}	17, 19
8	$CCl_3O \rightarrow COCl_2 + Cl$	8.8×10^{6}	17, 19
9	$CCl_3O_2 + CCl_3O_2 \rightarrow CCl_3O + CCl_3O + O_2$	4.0×10^{-12}	17, 19
10	$Cl + Cl\ (+M) \rightarrow Cl_2\ (+M)$	5.5×10^{-14}	17, 19
11	$Cl + NO\ (+M) \rightarrow ClNO\ (+M)$	8.8×10^{-14}	17, 19
12	$Cl + ClNO \rightarrow Cl_2 + NO$	8.1×10^{-11}	17, 19
13[b]	$Cl + NO_2\ (+M) \rightarrow ClNO_2\ (+M)$	1.3×10^{-12}	17, 19
14[b]	$Cl + ClNO_2 \rightarrow Cl_2 + NO_2$	1.0×10^{-11}	17, 19
15[a]	$CCl_3O_2 + NO_2\ (+M) \rightarrow CCl_3O_2NO_2\ (+M)$	$4.0 \times 10\text{-}^{12}$	5
16	$C_2Cl_5O_2 + NO_2\ (+M) \rightarrow C_2Cl_5O_2NO_2\ (+M)$	$6 \times 10\text{-}^{12}$	Møgelberg et al.[11]

[a] For these association reactions occurring in the falloff regime, correction for falloff is made using the simple formula in the JPL evaluation. [b] In the case of these reactions, $ClNO_2$ is taken to include both isomers, $ClNO_2$ and ClONO.

3. Results and Discussion

Our experiments had two main aims: (a) to observe whether the relative yields of $C(O)Cl_2$ and $CCl_3C(O)Cl$ in the Cl atom initiated oxidation of C_2Cl_4 does, or does not, depend on the concentration of C_2Cl_4 present in laboratory experiments, and (b) to observe if the branching ratio for these products depends on whether the pentachloroethoxy radicals, CCl_3CCl_2O, are formed in reaction 4 of two peroxy radicals, $CCl_3CCl_2O_2$, or in reaction 3 of $CCl_3CCl_2O_2$ with NO, as has been found by Thüner et al.,[9] and also, for example, in the oxidation of CF_3CFH_2.[16,18]

Figure 1 shows an example of the measured variation in concentrations of $C(O)Cl_2$ and $CCl_3C(O)Cl$ inferred from measurements of the time-resolved IR absorption by these species in mixtures containing NO. To interpret the measurements of the relative yields of $CCl_3C(O)Cl$ and $C(O)Cl_2$, it is necessary to describe the mechanism of the overall reaction that occurs in our experimental mixtures. Table 1 lists all the reactions that, we believe, play any significant role. According to this mechanism, in the presence of NO, the production of Cl atoms initiates two consecutive chain reactions. The first, and main, branch of this chain reaction is propagated by reactions 1−3 and 5a and produces *one* molecule of $CCl_3C(O)Cl$. The other branch consists of reactions 1−3 and 5b, followed by reactions 6−8, and produces *two* molecules of $C(O)Cl_2$. In the absence of NO, reactions 3 and 7 do not occur. Rather, the chain is propagated by reactions 4 and 9. Otherwise the mechanism is the same. In both cases, the chains are terminated by reactions 10−16.

This qualitative discussion is sufficient to show that to find the fraction of the CCl_3Cl_2O radicals that decompose via reaction 5a, i.e., the branching ratio $k_{5a}/(k_{5a} + k_{5b})$, it is necessary to calculate the ratio $[CCl_3C(O)Cl]/\{0.5[C(O)Cl_2] + [CCl_3C(O)Cl]\}$ from the traces of IR absorption like those shown in Figure 1. Figure 2 shows an example of the results of one such calculation. The early data show a great deal of scatter, but it is clear that the branching ratio $k_{5a}/(k_{5a} + k_{5b})$ can be determined by averaging the calculated values after about 1 ms.

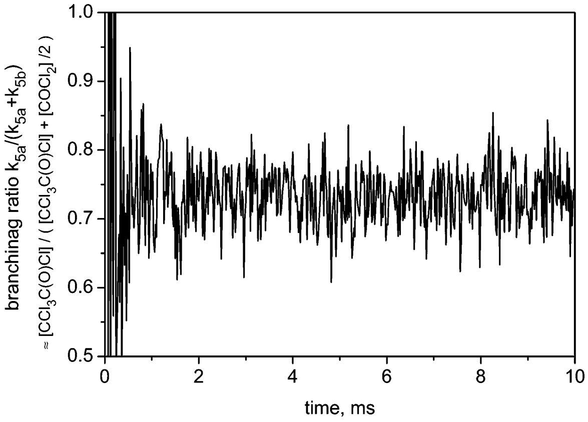

Figure 2. Approximate branching ratio $k_{5a}/(k_{5a} + k_{5b})$ derived from the data shown in Figure 1. Averaging the values after 1 ms leads to the value of 0.73 ± 0.05 shown in Figure 3 at a C_2Cl_4 concentration of 11.4×10^{14} molecule cm^{-3}.

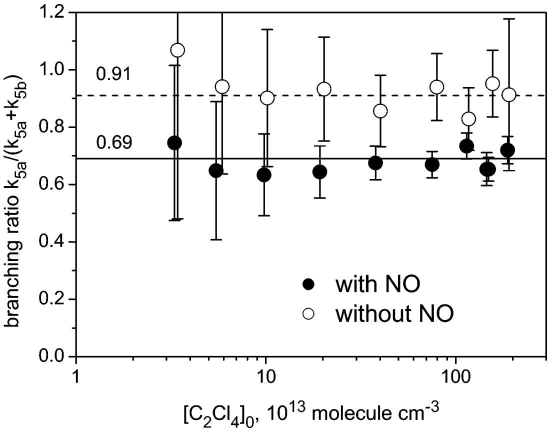

Figure 3. Branching ratio $k_{5a}/(k_{5a} + k_{5b})$ determined with different initial concentrations of $[C_2Cl_4]$ in the reaction mixture. Filled and open symbols correspond to measurements with NO present and without NO present, respectively. Lines show weighed average for the two data sets, assuming that the branching ratios are independent of $[C_2Cl_4]_0$.

Experiments designed to determine the branching ratio, $k_{5a}/(k_{5a} + k_{5b})$, have been carried out on mixtures containing between 0.3×10^{14} and 19.1×10^{14} molecule cm^{-3} of C_2Cl_4, both with no NO present and with 9.4×10^{14} molecule cm^{-3} of NO in the gas mixture. The results of these two series of experiments are presented in Figure 3. Two conclusions emerge clearly. First, the branching ratio *does* depend on whether the CCl_3CCl_2O radicals are produced by the mutual reaction (4) of two $CCl_3CCl_2O_2$ radicals or by reaction 3 of one $CCl_3CCl_2O_2$ radical with NO. This finding agrees with the results reported by Thüner et al.[9] and by Hasson and Smith[8] and has been attributed[9] to differences in the energies of the chemically activated $CCl_3CCl_2O_2$ radicals formed in reactions 3 and 4. The second conclusion to be drawn from the results summarized in Figure 3 is that the branching ratio, $k_{5a}/(k_{5a} + k_{5b})$, *does not* depend on $[C_2Cl_4]_0$, the concentration of C_2Cl_4 included in the reaction mixture. This result agrees with those reported by Thüner et al.[9] but disagrees with the findings of Hasson and Smith.[8]

Because the data in Figure 3 show no discernible dependence on $[C_2Cl_4]_0$, to calculate the best values of $k_{5a}/(k_{5a} + k_{5b})$, we took weighted averages of the two sets of data shown in Figure 3. This procedure yielded $k_{5a}/(k_{5a} + k_{5b}) = 0.69 \pm 0.13$ for the branching ratio when CCl_3CCl_2O radicals were formed from reaction 3 between $CCl_3CCl_2O_2$ and NO and $k_{5a}/(k_{5a} + k_{5b}) = 0.91 \pm 0.21$ when CCl_3CCl_2O radicals were formed from reaction 4 between two $CCl_3CCl_2O_2$ radicals. The errors cited here correspond to 95% confidence limits. These values are in excellent agreement with those of 0.68 ± 0.06 and 0.87 ± 0.11 determined by Thüner et al.[9]

Although the principal objective of our experiments was not to determine rate constants for individual steps in the reaction mechanism, we have attempted to model (a) how the observed concentrations of $C(O)Cl_2$ and $CCl_3C(O)Cl$ vary with time, and (b) how the yield of $CCl_3C(O)Cl$ varies with the concentration of C_2Cl_4 included in the reaction mixture, first by using the reactions and literature rate constants listed in Table 1. For the most part, the rate constants listed in Table 1 are taken from the evaluations by the IUPAC[17] and JPL[19] panels. The relative importance of these reactions will vary as the reaction proceeds and, for example, NO_2 is formed as a product of the propagation steps (3) and (7). In the absence of NO, reactions 4 and 9 rather than reactions 3 and 7 are responsible for forming the perchloroethyl and perchloromethyl radicals and hence the products, $CCl_3C(O)Cl$ and $C(O)Cl_2$.

On the time scale of our measurements, reactions 2, 5, 6, and 8 are very fast. In the presence of NO and relatively high initial concentrations of C_2Cl_4, the initial *rate* of formation of $CCl_3C(O)Cl$ is largely determined by the rate of reaction 3 and the *yield* of $CCl_3C(O)Cl$ depends principally on the chain length, which is, in turn, mainly dependent on the relative rates of reactions 3 and 16.

Figure 1 compares how the concentrations of $CCl_3C(O)Cl$ and $C(O)Cl_2$ vary with time following the initiation of reaction, according to experiment and two sets of modeling calculations, whereas Figure 4 shows similar comparisons for the variation in the amount of $CCl_3C(O)Cl$ formed with different concentrations of C_2Cl_4 included in the initial reaction mixture. The dashed lines in these two diagrams show the results of modeling calculations carried out with the rate constants listed in Table 1. Despite possible errors in the estimate of the initial concentration of Cl atoms (estimated at ±25%) and in the inferred concentrations of $CCl_3C(O)Cl$, arising from uncertainty in the calculation of the absorption path (again estimated at ±25%), it is clear from Figure 1 that the calculated and observed curves are significantly different, when the model uses the rate constants listed in Table 1. In particular, the initial rate of formation of $CCl_3C(O)Cl$ that is observed is appreciably greater than the calculated rate and the final yield of $CCl_3C(O)Cl$ is also not well matched by the calculations. Figure 4 also shows modest differences in how the experimental and calculated yields of $CCl_3C(O)Cl$ vary with $[C_2Cl_4]_0$ when literature values of the rate constants for reactions in the mechanism are used in the model.

The initial rate of formation of $CCl_3C(O)Cl$ depends chiefly on the rates of reactions 2 and 3. The rate constant for reaction 1 has been determined in direct experiments using laser pulsed photolysis to generate Cl atoms and resonance fluorescence to detect Cl atoms.[20] The rate of reaction is dependent on the total pressure, and the value given in Table 1 is directly interpolated from the result obtained by Nicovich et al.[20] The rate constant of reaction 3 between $CCl_3CCl_2O_2$ radicals and NO has been determined only once, in pulsed radiolysis experiments.[11] Extraction of the rate constant k_3 required considerable modeling. We decided to vary the rate constants k_3 and k_{16} in the model until we obtained a better fit to experimental data of the kind shown in Figures 1 and 4. In these calculations, k_{15} was assumed to be equal to k_{16}. The continuous curves on these two diagrams show the results of these calculations using $k_3 = 3.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and k_{16} $(=k_{15}) = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

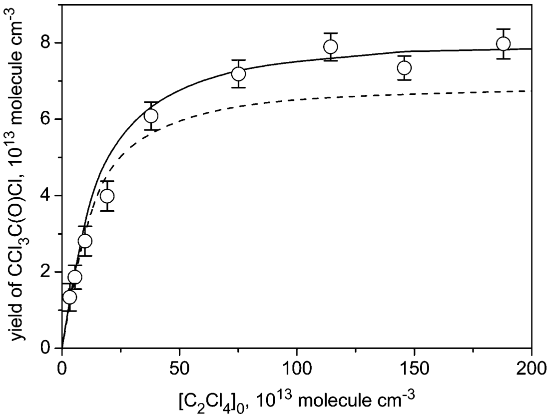

Figure 4. Comparison between the experimental and calculated absolute yields of $CCl_3C(O)Cl$ and their dependence on the initial concentration of C_2Cl_4. In the experiments, the mixtures contained 15 × 10^{14} molecule cm^{-3} of Cl_2, 9.4 × 10^{14} molecule cm^{-3} of NO, 9.8 × 10^{17} molecule cm^{-3} of O_2, and variable amounts of C_2Cl_4. The dashed curves show the model results using the rate constants listed in Table 1. The full traces were obtained when the rate constants for reactions 3 and 16 were increased to $k_3 = 3.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and k_{16} $(= k_{15}) = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The values of k_3 and k_{16}, which are required to match the experimental data like those shown in Figures 1 and 4, are significantly larger than the rate constants given in Table 1. These latter values are derived from the experiments of Møgelberg et al.[11] They used pulsed radiolysis to generate F atoms in the presence of CCl_3CCl_2H, O_2, and NO and followed the formation of NO_2 by absorption at 400 nm in experiments performed with different concentrations of NO present. It was assumed that NO_2 was formed in reaction 3, following the creation of CCl_3CCl_2 radicals in the reaction of F atoms with CCl_3CCl_2H and their conversion to $CCl_3CCl_2O_2$ radicals.

In the analysis of Møgelberg et al.,[11] the rate constants for reactions 2 and 16 were assumed by analogy with similar systems. In the case of k_2 this meant that a value of 3 × 10^{-12} cm^3 molecule^{-1} s^{-1} was assumed, rather than the value of 1.66 × 10^{-13} cm^3 molecule^{-1} s^{-1} determined in the admittedly rather old experiments of Huybrechts and co-workers.[21] In addition, under the conditions of the experiments of Møgelberg et al.,[11] it would appear that the three reactions leading to NO_2 formation, i.e., F + CCl_3CCl_2H, CCl_3CCl_2 + O_2, and CCl_3CCl_2O + NO, would have had similar pseudo-first-order rates, making it difficult to have confidence in the derived rate coefficient for reaction 3.

Having said that, the rate constants k_3 and k_{16} that we have had to assume to match the experimental data displayed in Figures 1 and 4 are surprisingly large. Thus, most reactions of

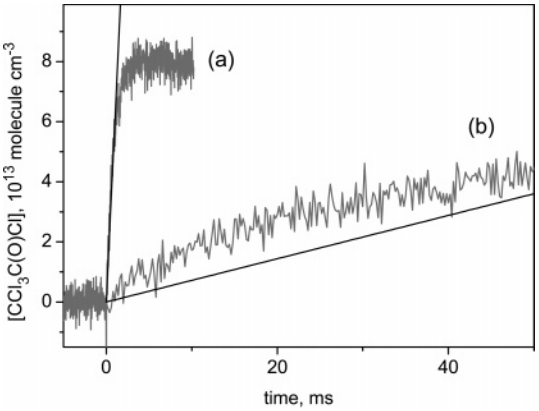

Figure 5. Comparison between the formation of $CCl_3C(O)Cl$ in the presence and absence of NO. The gas mixtures contained 15×10^{14} molecule cm^{-3} of Cl_2, 11.4×10^{14} molecule cm^{-3} of C_2Cl_4, and 9.8×10^{17} molecule cm^{-3} of O_2. Curve a, which was obtained with 9.4×10^{14} molecule cm^{-3} of NO included in the gas mixture, is the same as that in Figure 1 but plotted on the present time scale; curve b was obtained in the absence of NO. The lines represent estimates of the initial rates of formation of $CCl_3C(O)Cl$; i.e., in the absence of NO, $2k_4[CCl_3CCl_2O_2]^2$, with k_4 given the value listed in Table 1, and in the presence of NO, $k_3[CCl_3CCl_2O_2][NO]$, with $k_3 = 3.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

fully and partly halogenated radicals of general formula $CX_3CY_2O_2$, where X and Y are hydrogen or (the same or different) halogen atoms, fall in the range $(1.2-1.8) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1};[16-19] that is, 2−3 times greater than the value of k_3 inferred by Møgelberg et al.,[11] but a third to half the value used to get the agreement shown in Figures 1 and 4 between our experimental data and our model calculations.

There appear to be no experimental data on the kinetics of reaction 16 between $CCl_3CCl_2O_2 + NO_2$ or indeed on any other halogenated C_2 peroxy radical reacting with NO_2. For the reactions of halogenated C_1 peroxy radicals with NO_2, the IUPAC panel recommends a limiting high-pressure rate constant of 7.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, whereas the JPL panel recommends 6.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The rate constant k_{16} (and k_{15}) that we need in our model to reproduce our experimental data is approximately 2−3 times greater than these values.

Figure 5 compares the formation of $CCl_3C(O)Cl$ in two experiments using the same concentrations of Cl_2, C_2Cl_4, and O_2 but with 9.4×10^{14} molecule cm^{-3} of NO present in one experiment but no NO present in the other experiment. It is obvious that the rate of formation of $CCl_3C(O)Cl$ in the experiment without NO, and therefore where CCl_3CCl_2O radicals must be formed by reaction 4, is very much slower than when NO is present and reaction 3 creates CCl_3CCl_2O radicals. Of course, when NO is absent, nearly all of the chain termination steps listed in Table 1 cannot play any role. The long time scale of these experiments, which may, for example, allow for significant diffusive loss, and other uncertainties have dissuaded us from attempting to model this system. However, we do compare the rise of $[CCl_3C(O)Cl]$ with time to that calculated on the basis of its formation in reaction 4 with the rate constant measured many years ago by Huybrechts and co-workers.[21] The agreement is fair and provides some support to the value they determined for k_4 and which is listed in Table 1.

4. Summary and Conclusions

We have used time-resolved infrared absorption to observe the formation of $CCl_3C(O)Cl$ and $C(O)Cl_2$ after pulsed laser photolysis created Cl atoms and initiated the oxidation of C_2Cl_4, in the presence and absence of NO. Our results confirm that the relative yields of $CCl_3C(O)Cl$ and $C(O)Cl_2$ do not depend on $[C_2Cl_4]_0$, the concentration of C_2Cl_4 initially included in the reaction mixture. In this respect, the present results firmly support the conclusions of Thüner et al.[9] but not those of Hasson and Smith.[8] However, as found by both Hasson and Smith[8] and Thüner et al.,[9] the yields do depend on whether the products are formed in the decomposition of CCl_3CCl_2O radicals formed in the reaction between $CCl_3CCl_2O_2$ and NO, or in the reaction of two $CCl_3CCl_2O_2$ radicals. In the former case, we find that the fraction of CCl_3CCl_2O radicals that decompose (a) to $CCl_3C(O)Cl + Cl$, rather than (b) to $CCl_3 + C(O)Cl_2$, is 0.69 ± 0.13, whereas in the latter case this fraction is 0.91 ± 0.21. These results are in good agreement with those of Thüner et al.[9] who found 0.68 ± 0.06 in the presence of NO, and 0.87 ± 0.11 in the absence of NO.

We have attempted to model (a) our observations of how $[CCl_3C(O)Cl]$ increases with time following the initiation of reaction and (b) how the *absolute* yield of $CCl_3C(O)Cl$ depends on $[C_2Cl_4]_0$ using values of the rate constants for reaction in the mechanism taken from the literature. The observed and calculated results differ markedly. The results of further modeling calculations lead us to believe that the rate constants for the reactions between both $CCl_3CCl_2O_2$ and NO and between $CCl_3CCl_2O_2$ and NO_2 may have been underestimated previously. On the other hand, our measurements on the initial rate of formation of $CCl_3C(O)Cl$ from $CCl_3CCl_2O_2 + CCl_3CCl_2O_2$ are reasonably consistent with the single previous measurement[21] of this rate constant.

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