Kinetics of the Self-Reactions of Peroxy Radicals Arising from Chlorine-Initiated Oxidation of Chloroethenes

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The kinetics of the self-reactions of $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ have been investigated using a conventional flash photolysis/UV absorption setup at room temperature and at atmospheric pressure. The UV absorption spectra of $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ were determined between 230 and 290 nm. All spectra present a broad band centered around 250 nm, with a decrease of cross sections going from the less chlorinated to the more chlorinated radicals. Spectra of $CCl_3C(O)Cl$ and $CHCl_2C(O)Cl$, formed in the self-reactions of $CCl_3CCl_2O_2$ and $CHCl_2CHClO_2$, respectively, were also measured between 220 and 290 nm. Values of $(3.6 \pm 0.9) \times 10^{-12}$, $(7.0 \pm 1.5) \times 10^{-12}$, and $(5.0 \pm 1.5) \times 10^{-12}$ (units of cm^3 $molecule^{-1}$ s^{-1}, statistical errors 2σ) have been obtained at 298 K for the rate constants of the self-reactions of $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ radicals, respectively. Kinetic analyses of self-reactions were very sensitive to the reaction mechanism used and, in particular, to the way chloroethoxy radicals reacted. Our experimental observations are totally consistent with end-product studies reported in the literature and provide a valuable confirmation of the mechanisms. As the determination of rate constants depends on complex reaction systems, a total uncertainty factor of nearly 2 has been estimated for all rate constants measured, and no clear reactivity trend can be extracted from these data. Nevertheless, we propose for the rate constants of chloroethylperoxy radical self-reactions an average value of $(5 \pm 2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Introduction

The atmospheric oxidation processes of chlorine-containing organic compounds have been extensively studied during the past few years, since such compounds can contribute to the transport of chlorine species to remote areas. The knowledge of kinetic and mechanistic properties regarding degradation of chlorinated compounds is primordial as such data are required to assess the impact of their degradation products on the environment. A great deal of work has been done recently on photooxidation mechanisms of chloroethenes.[1−3] Chloroethenes, like tetrachloroethene or trichloroethene, are chlorinated compounds of major interest as they are widely used for dry cleaning, metal degreasing, or as industrial solvents. Peroxy radical reactions, as the first steps in their oxidation processes, may provide key information about the way chloroethoxy radicals react under tropospheric conditions. Under low NO_x concentrations, it is widely accepted that the principal loss process for peroxy radicals in the troposphere is by reaction with HO_2, and, to a lesser extent, by reaction with the other most abundant organic peroxy radicals (like CH_3O_2 and $CH_3C(O)O_2$). If the interest of peroxy radical self-reactions is limited from an atmospheric point of view, their kinetics must be known, not only to extend the database but also to improve the accuracy of studies of peroxy radical cross-reactions involving these self-reactions in their mechanisms.

In this work, we have been interested in the kinetic study of the self-reactions of the $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ radicals arising from the chlorine-initiated oxidation of 1,2-dichloroethene, trichloroethene, and tetrachloroethene, respectively.

$$CHCl_2CHClO_2 + CHCl_2CHClO_2 \rightarrow 2CHCl_2CHClO + O_2 \quad (1a)$$

$$CHCl_2CHClO_2 + CHCl_2CHClO_2 \rightarrow CHCl_2CHClOH + CHCl_2C(O)Cl + O_2 \quad (1b)$$

$$CHCl_2CCl_2O_2 + CHCl_2CCl_2O_2 \rightarrow 2CHCl_2CCl_2O + O_2 \quad (2)$$

$$CCl_3CCl_2O_2 + CCl_3CCl_2O_2 \rightarrow 2CCl_3CCl_2O + O_2 \quad (3)$$

According to a recent review on peroxy radical reactions,[4] the alkylperoxy self-reactions are known to present rate constants varying over several orders of magnitude, depending principally on the class of the radical and on the nature of functional groups. It has been shown that substitution in alkylperoxy radicals, either in the α or in the β position relative to the peroxy group, always results in significant increase of the self-reactions rate constants, whatever the nature of the substituent. For example, the presence of a Cl atom in the α position results in an increase of about 10 times in the self-reaction rate constant of CH_3O_2: $k(CH_3O_2 + CH_3O_2) = 3.7 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} [5] and $k(CH_2ClO_2 + CH_2ClO_2) = 3.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[5] A larger effect has been observed when the Cl atom is in the β position, with an increase of about 100 times of the self-reaction rate constant: $k(CH_3CH_2O_2 + CH_3CH_2O_2) = 6.8 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} [6] and $k(CH_2ClCH_2O_2 + CH_2ClCH_2O_2) = 6.0$

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$\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[7] Another interesting feature is that no particular effect of subsequent substitution of H atoms by Cl atoms compared to the first one has been observed for chloromethylperoxy radicals. For example, the CCl_3O_2 radical presents a similar rate constant for its self-reaction as those measured for CH_2ClO_2 and $CHCl_2O_2$.[8] Another objective of this work was to expand the kinetic database for self-reactions, with the principal aim of improving the characterization of the effect of the Cl functionality on the reactivity of peroxy radicals.

Experimental Section

Kinetic studies were performed at atmospheric pressure and room temperature, using the conventional flash photolysis technique coupled with UV absorption spectrometry for real-time monitoring of radical concentrations. This technique has been already described in detail elsewhere[9] and is only dealt with briefly here.

The setup consisted of a 68 cm long Pyrex reaction cell, fitted with a thermostated jacket. Flashes were generated by discharging two capacitors through external argon flash lamps. The UV analysis beam from a deuterium lamp was directed along the length of the cell and was focused onto the slit of a monochromator−photomultiplier unit. Radical concentrations were typically monitored from 230 to 290 nm. The signal was recorded using a digital oscilloscope and transferred to a PC for signal averaging and further data analysis.

Chlorinated peroxy radicals were generated by photolyzing molecular chlorine, producing chlorine atoms which added to the double bond of chloroethenes, according to the following sequence:

$$Cl_2 + h\nu\ (\lambda > 280\ \text{nm}) \rightarrow 2Cl \qquad (4)$$

$$Cl + CX_2{=}CX_2 + M \rightarrow ClCX_2CX_2 + M \qquad (X = Cl \text{ or } H) \quad (5)$$

with k_5(298 K) = 9.6 × 10^{-11} (for CHCl=CHCl),[10] 7.2 × 10^{-11} (for CCl_2=CHCl),[3] and 4.0 × 10^{-11} cm^3 molecule^{-1} s^{-1} (for CCl_2=CCl_2).[6]

$$ClCX_2CX_2 + O_2 + M \rightarrow ClCX_2CX_2O_2 + M \qquad (6)$$

where k_6 was estimated to be similar to $k(CH_2ClCHCl + O_2)$ = 2.4 × 10^{-12} cm^3 molecule^{-1} s^{-1} at 760 Torr and 298 K.[11]

The concentration of molecular chlorine was measured by its absorption at 330 nm ($\sigma = 2.56 \times 10^{-19}$ cm^2 molecule^{-1}) [6] and maintained in the range (1.4−2.4) × 10^{16} molecule cm^{-3}. Concentrations of precursors (1,2-dichloroethene, trichloroethene, or tetrachloroethene) and oxygen were chosen such that the conversion of initial chlorine atoms into radicals was very rapid (<2.5 μs) compared to the time scale of the reactions of interest (between 8 and 800 ms) and dominated all other loss processes of Cl atoms. Concentrations were controlled using calibrated mass flow controllers and verified by UV absorption in the case of trichloroethene and tetrachloroethene (σ_{250nm}(CCl_2=CHCl) = 1.22 × 10^{-19} cm^2 molecule^{-1} and σ_{260nm}(CCl_2=CCl_2) = 5.0 × 10^{-19} cm^2 molecule^{-1}),[12] the 1,2-dichloroethene used for experiments being a mixture of *Z* and *E* isomers, which absorb slightly differently between 190 and 230 nm. Concentrations of chloroethenes were in the range (0.6−6.0) × 10^{16} molecule cm^{-3}. The oxygen partial pressure was adjusted between 150 and 760 Torr.

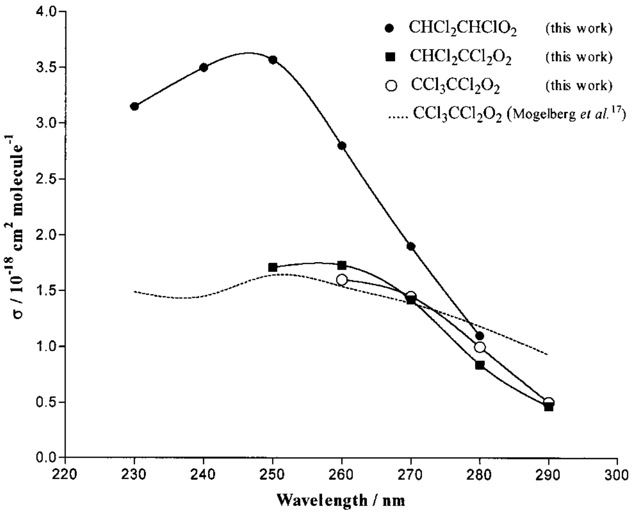

Figure 1. UV absorption spectra of $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ radicals determined in this work. The spectrum of $CCl_3CCl_2O_2$ determined by Mogelberg et al.[17] is shown for comparison.

The total initial concentration of radicals was determined by replacing the precursor by CH_4 under the same experimental conditions, producing the CH_3O_2 radical, which has a well-established cross section (σ_{240nm} = 4.24 × 10^{-18} cm^2 molecule^{-1}).[13] Initial radical concentrations were in the range (3−6) × 10^{13} molecule cm^{-3}.

Oxygen (AGA Gaz Spéciaux, >99.995%), methane (AGA Gaz Spéciaux, >99.995%), chlorine (AGA Gaz Spéciaux, 5% in nitrogen, >99.9%), 1,2-dichloroethene (Acros Organics, 99%), trichloroethene (Aldrich, 99.5+%), and tetrachloroethene (Acros Organics, 99+%) were all used without purification. As chloroethenes are liquid at room temperature, they were introduced into the gas mixture by passing a slow flow of oxygen through a bubbler containing the appropriate precursor cooled in a water−ice bath.

The residence time of the flowing gas mixture was such that the gas mixture was replaced between two consecutive flashes, thus preventing secondary reactions involving reaction products. A typical experiment required between 10 and 50 flashes to obtain a satisfactory signal-to-noise ratio. Decay traces were analyzed by numerical simulation of the complete reaction systems, taking into account the absorption of all species and using a nonlinear least-squares fitting procedure.

Results

UV Absorption Spectra. The present kinetic study required an accurate determination of the ultraviolet absorption cross sections of $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ radicals. The UV spectra were obtained by extrapolating the transient signal back to the time origin to measure the initial absorbance precisely at each wavelength. This was necessary as the scattered light from the flash rendered the first 100 μs of the trace unusable. Thus, initial radical concentrations were kept low enough (around 3 × 10^{13} molecule cm^{-3}) to prevent too fast a recombination of radicals during this dead time, so extrapolation errors were minimized. Absorption cross sections were calibrated against those of CH_3O_2 as described in the Experimental Section.

The spectra of $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ were measured in the spectral range 230−290 nm, with a rather low signal-to-noise ratio, below 250 nm, due to the overlap with chloroethene absorptions. They are shown in Figure 1

TABLE 1: Absolute UV Absorption Cross Sections for $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ Radicals at 298 K[a]

λ/nm	$\sigma(CHCl_2CHClO_2)$[b]	$\sigma(CHCl_2CCl_2O_2)$[b]	$\sigma(CCl_3CCl_2O_2)$[b]
230	3.15 ± 0.20		
240	3.50 ± 0.13		
250	3.57 ± 0.15	1.71 ± 0.07	
260	2.80 ± 0.07	1.73 ± 0.02	1.60 ± 0.01
270	2.00 ± 0.13	1.42 ± 0.10	1.45 ± 0.05
280	1.10 ± 0.21	0.84 ± 0.16	1.00 ± 0.10
290		0.46 ± 0.07	0.50 ± 0.20

[a] Errors are the 95% confidence level components due to random effects only. [b] σ in 10^{-18} cm^2 $molecule^{-1}$.

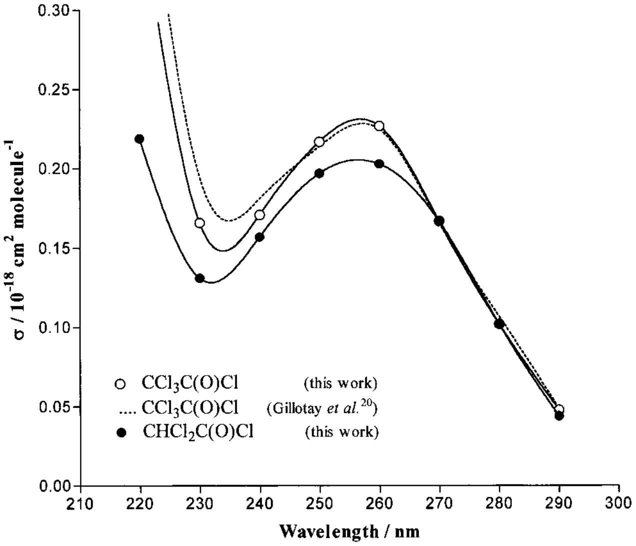

Figure 2. UV absorption spectra of $CHCl_2C(O)Cl$ and $CCl_3C(O)Cl$ measured in this work. A previous determination of $CCl_3C(O)Cl$ spectrum by Gillotay et al.[20] is shown for comparison.

with the corresponding absorption cross sections given in Table 1. The three spectra present a broad band of absorption peaking at around 250 nm. Similar spectra are observed for most alkylperoxy and halogen-substituted alkylperoxy radicals.[14]

As the products formed by chloroethylperoxy radical self-reactions significantly influenced the shape of experimental traces (see next section), it was necessary to determine their contribution to the total absorption by measuring their absolute cross sections. Spectra of dichloroacetyl chloride $CHCl_2C(O)Cl$ and trichloroacetyl chloride $CCl_3C(O)Cl$, formed in the self-reactions of $CHCl_2CCl_2O_2$ and $CCl_3CCl_2O_2$, respectively, are presented in Figure 2, with the corresponding absorption cross sections listed in Table 2. These spectra have been measured using a Hewlett-Packard 8452 A spectrophotometer (2 nm resolution). Both samples of $CHCl_2C(O)Cl$ and $CCl_3C(O)Cl$ were from Aldrich (99% purity). The spectra have been measured between 220 and 300 nm at five different partial pressures between 2 and 25 Torr. Both spectra present very similar shapes, with a strong absorption below 220 nm and a weaker broad absorption band between 230 and 280 nm.

TABLE 2: UV Absorption Cross Sections for Dichloroacetyl Chloride and Trichloroacetyl Chloride Measured at Room Temperature

λ/nm	$\sigma(CHCl_2C(O)Cl)$[a]	$\sigma(CCl_3C(O)Cl)$[a]
220	2.17	3.72
230	1.32	1.66
234		1.58
240	1.57	1.71
250	2.0	2.17
256	2.09	2.3
260	2.08	2.27
270	1.71	1.67
280	1.05	1.02
290	0.47	0.48
300	0.14	

[a] σ in 10^{-19} cm^2 $molecule^{-1}$.

Kinetics of the $CHCl_2CHClO_2$ Self-Reaction. The kinetics of the self- reaction

$$CHCl_2CHClO_2 + CHCl_2CHClO_2 \rightarrow 2CHCl_2CHClO + O_2 \quad (1a)$$

$$CHCl_2CHClO_2 + CHCl_2CHClO_2 \rightarrow CHCl_2CHClOH + CHCl_2C(O)Cl + O_2 \quad (1b)$$

has been investigated using the photolysis of Cl_2 in the presence of a mixture of *cis*- and *trans*-1,2-dichloroethene in excess oxygen. Experiments were carried out at room temperature, at atmospheric pressure, and at monitoring wavelengths systematically varied from 230 to 280 nm. The only end-product study available for this reaction was performed by Hasson and Smith.[2] As no evidence for the molecular channel 1b has been clearly characterized, we have considered that reaction 1a is the dominant channel in reaction 1 and thus, that no $CHCl_2C(O)Cl$ was produced from channel 1b. This assumption seems reasonable as similar branching ratios $k_{1a}/k_1 \approx 1$ have been found in the case of most halogenated alkylperoxy radical self-reactions.[4]

Hasson and Smith[2] have shown that the alkoxy radical $CHCl_2CHClO$ undergoes either C−C bond scission (channel 7a), reaction with O_2 (channel 7b) yielding HO_2 and $CHCl_2C(O)Cl$, or HCl elimination (channel 7c) with formation of the dichloroacetyl $CHCl_2C(O)$ radical:

$$CHCl_2CHClO + M \rightarrow CHCl_2 + CHClO + M \quad (7a)$$

$$CHCl_2CHClO + O_2 \rightarrow HO_2 + CHCl_2C(O)Cl \quad (7b)$$

$$CHCl_2CHClO + M \rightarrow HCl + CHCl_2C(O) + M \quad (7c)$$

The values of the branching ratios are $k_{7a}/k_7 = 0.77$, $k_{7b}/k_7 = 0.08$, and $k_{7c}/k_7 = 0.15$.[2]

Absorption traces exhibited a decay at all wavelengths, from 230 to 280 nm, followed by an apparent residual absorption, as shown in Figure 3. This absorption was accounted for by the regeneration of RO_2 due to the chain reaction initiated by the decomposition of the $CHCl_2O$ radical (reaction 10) into Cl atoms and CHClO.

$$CHCl_2 + O_2 + M \rightarrow CHCl_2O_2 + M \quad (8)$$

$$CHCl_2O_2 + CHCl_2O_2 \rightarrow 2CHCl_2O + O_2 \quad (9)$$

$$CHCl_2O + M \rightarrow Cl + CHClO \quad (10)$$

No significant formation of HO_2 could be observed at 230 nm, meaning that the value of the branching ratio k_{7b}/k_7 proposed by Hasson and Smith[2] is an upper limit.

The carbonyl radical $CHCl_2C(O)$ formed by channel 7c was assumed to react mainly with O_2 with a pseudo-first-order rate constant $k_{11} = 7.8 \times 10^7$ s^{-1} in 750 Torr of O_2 at 298 K,[15] considering preliminary theoretical calculations (DFT BHandHLYP/cc-pVdz level) of $CHCl_2C(O)$ decomposition rate by

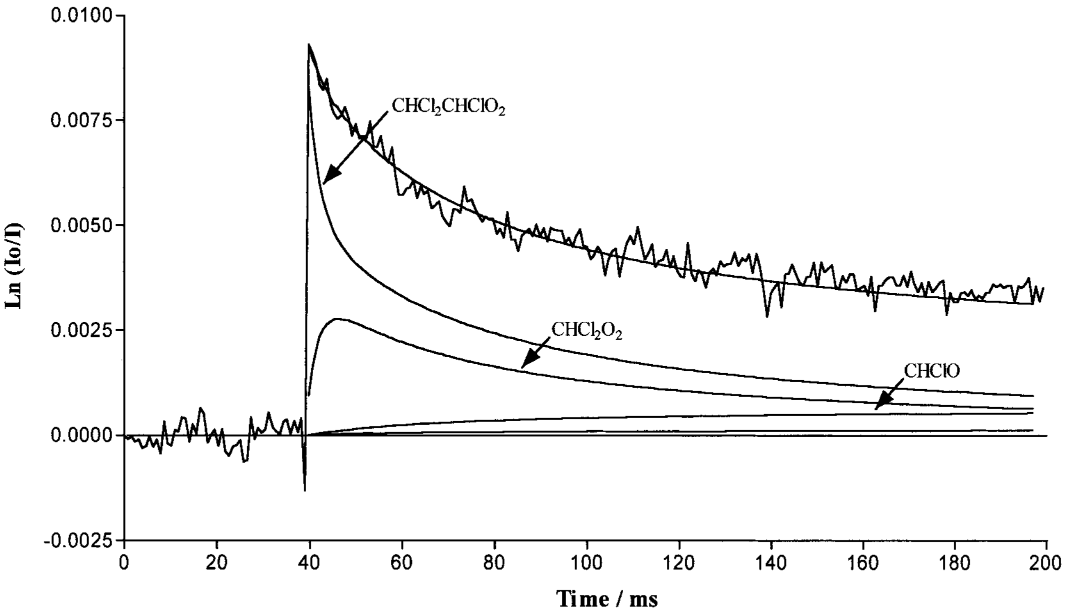

Figure 3. Experimental decay trace observed for the self-reaction $CHCl_2CHClO_2 + CHCl_2CHClO_2$ and its best fit, recorded at 240 nm; the initial peroxy radical concentration was 4.16×10^{13} molecule cm^{-3}, averaged from 17 flashes.

TABLE 3: Reaction Mechanism Used in Simulations of the $CHCl_2CHClO_2$ Self-Reaction[a]

reaction	$k_{298\ K}$[b]	reference
$Cl_2 + h\nu \rightarrow 2Cl$		
$Cl + CHCl{=}CHCl + M \rightarrow CHCl_2CHCl + M$	9.6×10^{-11}	Atkinson et al.[10]
$CHCl_2CHCl + O_2 + M \rightarrow CHCl_2CHClO_2 + M$	2.4×10^{-12}	*c*
$2CHCl_2CHClO_2 \rightarrow 2CHCl_2CHClO + O_2$	3.6×10^{-12}	this work
$CHCl_2CHClO + M \rightarrow CHCl_2 + CHClO + M$	fast (77%)	*d*
$CHCl_2CHClO + O_2 \rightarrow HO_2 + CHCl_2C(O)Cl$	fast (8%)	*d*
$CHCl_2CHClO + M \rightarrow HCl + CHCl_2C(O) + M$	fast (15%)	*d*
$CHCl_2 + O_2 + M \rightarrow CHCl_2O_2 + M$	2.8×10^{-12}	DeMore et al.[6]
$2CHCl_2O_2 \rightarrow 2CHCl_2O + O_2$	3.8×10^{-12}	Catoire et al.[8]
$CHCl_2O + M \rightarrow Cl + CHClO$	fast	*d*
$CHCl_2C(O) + O_2 + M \rightarrow CHCl_2C(O)O_2 + M$	3.2×10^{-12}	*e*
$2CHCl_2C(O)O_2 \rightarrow 2CHCl_2C(O)O + O_2$	1.4×10^{-11}	*e*
$CHCl_2C(O)O + M \rightarrow CHCl_2 + CO_2$	fast	*d*
$CHCl_2CHClO_2 + CHCl_2O_2 \rightarrow CHCl_2CHClO + CHCl_2O + O_2$	3.7×10^{-12}	*f*
$CHCl_2CHClO_2 + CHCl_2C(O)O_2 \rightarrow CHCl_2CHClO + CHCl_2C(O)O + O_2$	1.0×10^{-11}	*g*
$CHCl_2O_2 + CHCl_2C(O)O_2 \rightarrow CHCl_2O + CHCl_2C(O)O + O_2$	1.0×10^{-11}	*g*
$CHCl_2CHClO_2 + HO_2 \rightarrow$ products	1.0×10^{-11}	Bridier et al.[22]
$CHCl_2O_2 + HO_2 \rightarrow CCl_2O + H_2O + O_2$	1.8×10^{-12}	Catoire et al.[8]
$CHCl_2O_2 + HO_2 \rightarrow \_CHClO + HOCl + O_2$	4.1×10^{-12}	Catoire et al.[8]
$CHCl_2C(O)O_2 + HO_2 \rightarrow O_3 + CHCl_2C(O)OH$	4.0×10^{-12}	*e*
$CHCl_2C(O)O_2 + HO_2 \rightarrow O_2 + CHCl_2C(O)OOH$	1.0×10^{-11}	*e*
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	3.0×10^{-12}	DeMore et al.[6]

[a] In the case of the $CHCl_2CCl_2O_2$ and $CCl_3CCl_2O_2$ self-reactions, changes in mechanism are detailed in the text. [b] In cm^3 molecule^{-1} s^{-1}. [c] Estimated from $k(CH_2ClCHCl + O_2)$.[11] [d] Instantaneous under the time scale of observation. [e] Assumed to be equal to the acetyl analogue.[15] [f] Assumed to be identical to the rate constants of the $CHCl_2CHClO_2$ and $CHCl_2O_2$ self-reactions. [g] Assumed to be equal to the $(RC(O)O_2 + RO_2)$ rate constant.[23]

Méreau et al.,[16] who proposed $k_\infty(298\ K) = 6.5 \times 10^6\ s^{-1}$ for the $CHCl_2C(O) + M \rightarrow CHCl_2 + CO + M$ reaction.

$$CHCl_2C(O) + O_2 + M \rightarrow CHCl_2C(O)O_2 + M \quad (11)$$

$$CHCl_2C(O)O_2 + CHCl_2C(O)O_2 \rightarrow 2CHCl_2C(O)O + O_2 \quad (12)$$

$$CHCl_2C(O)O + M \rightarrow CHCl_2 + CO_2 + M \quad (13)$$

As $CHCl_2O$ was also formed by channel 7c, considering the reaction sequence (7c)−(11)−(12)−(13)−(8)−(9), we had no possibilities in our simulations to distinguish between the two channels 7a and 7c. Nevertheless, experimental traces could never be satisfactorily simulated using the branching ratios proposed by Hasson and Smith.[2] In particular, the branching ratio k_{7a}/k_7 had to be set at a smaller value, with an upper limit of 0.65. Taking into account the complete mechanism, detailed in Table 3, the following rate constant was derived from seven measurements of k_1, all listed in Table 4, along with the experimental conditions $k_1 = (3.6 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K, where the quoted uncertainties represent 95% confidence limits. To quantify the sensitivity of the rate constant k_1 toward the parameters used for analysis, a systematic analysis of error propagation was carried out as described previously.[9] It appears that the self-reaction rate constant k_1 is mainly sensitive to the variations of $\sigma(CHCl_2CHClO_2)$ and $\sigma(CHCl_2O_2)$, to the rate constants of the $CHCl_2O_2$ self-reaction, and to the $CHCl_2CHClO_2 + CHCl_2O_2$ cross-reaction, and to the branching ratios k_{7a}/k_7, k_{7b}/k_7, and k_{7c}/k_7. Variations of 20% in the values of the cross sections $\sigma(CHCl_2CHClO_2)$ and $\sigma(CHCl_2O_2)$ result in variations of 28% and 36%,

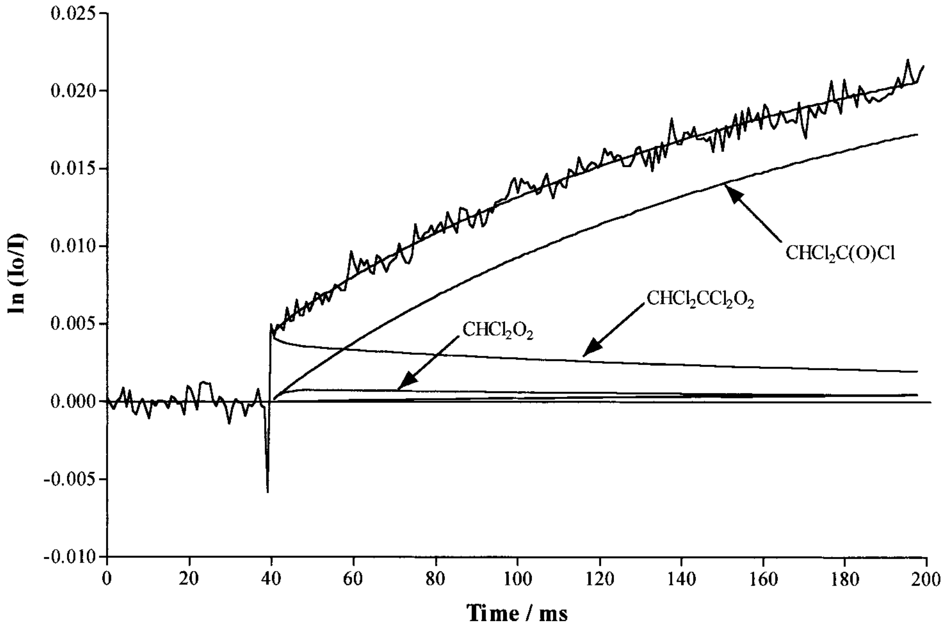

Figure 4. Experimental trace recorded at 260 nm, and its best simulation, in the case of the $CHCl_2CCl_2O_2$ self-reaction; the initial peroxy radical concentration was 3.59×10^{13} molecule cm^{-3}, averaged from 10 flashes.

TABLE 4: Experimental Values of the Rate Constants of the $CHCl_2CHClO_2$ Self-Reaction at 298 K

λ/nm	$[Cl_2]/10^{16}$ [a]	$[CHCl_2CHClO_2]/10^{13}$ [a]	k_{7a}/k_7 [b]	$k_1/10^{-12}$ [c]
240	2.06	4.16	0.61	3.2
240	1.54	3.11	0.61	2.9
250	1.54	3.10	0.68	4.3
250	1.54	3.12	0.67	3.8
260	1.54	3.10	0.62	3.6
260	1.90	3.84	0.70	3.2
270	1.79	3.60	0.65	4.1

[a] In molecule cm^{-3}. [b] Optimized in the simulations (see text). [c] In cm^3 molecule^{-1} s^{-1}.

respectively, in k_1. Varying reasonably the values of the rate constants $k(CHCl_2O_2 + CHCl_2O_2)$ and $k(CHCl_2CHClO_2 + CHCl_2O_2)$ by a factor of 2 results in changes of 24% and 47% in the value of k_1, respectively. Small changes in the values of the branching ratios k_{7a}/k_7, k_{7b}/k_7, and k_{7c}/k_7 resulted in increasingly unsatisfactory simulations of experimental decays. This provides a valuable confirmation of the fact that the branching ratio k_{7a}/k_7 has to be set at a smaller value than that reported by Hasson and Smith.[2] All systematic uncertainties listed above, combined with statistical errors, yield an overall uncertainty of 74% for k_1.

Kinetics of the $CHCl_2CCl_2O_2$ Self-Reaction. The self-reaction 2

$$CHCl_2CCl_2O_2 + CHCl_2CCl_2O_2 \rightarrow 2CHCl_2CCl_2O + O_2 \quad (2)$$

has been investigated at room temperature. $CHCl_2CCl_2O_2$ was produced using the photolysis of Cl_2 in $Cl_2/CCl_2{=}CHCl/O_2$ mixtures. Previous end-product analyses[2,3] have shown that Cl atoms essentially add to the CHCl moiety of trichloroethene, and thus, only the subsequent reactions of the $CHCl_2CCl_2O_2$ radical were considered. The same end-product studies[2,3] have shown that $CHCl_2C(O)Cl$, CHClO, and CCl_2O are the major products. These products result from the following reactions:

$$CHCl_2CCl_2O + M \rightarrow Cl + CHCl_2C(O)Cl + M \quad (14a)$$

$$CHCl_2CCl_2O + M \rightarrow CHCl_2 + CCl_2O + M \quad (14b)$$

with the Cl atoms produced in channel 14a initiating a chain reaction. The branching ratios reported by Catoire et al.[3] and Hasson and Smith[2] are $k_{14a}/k_{14} = 0.91$ and $k_{14b}/k_{14} = 0.09$. Both determinations are in excellent agreement.

The analyses of our experimental data are totally consistent with such a mechanism, as absorption signals recorded at wavelengths between 250 and 290 nm show unusual shapes with a strong increase of absorption with time for time scales of up to 800 ms. Figure 4 shows a typical experimental trace along with the results of numerical simulations. The signals were easily fitted by considering the chain reaction propagated by the regeneration of Cl atoms via channel 14a and also via the reaction sequence (14b)−(8)−(9)−(10). Since reaction 14 was instantaneous under our experimental conditions, the rate-determining step of the chain was the self-reaction, and the rate constant k_2 could be extracted from the initial slope of the experimental curve. The chain reaction was equivalent to converting trichloroethene into $CHCl_2C(O)Cl$, which is the principal stable absorbing product, as shown in Figure 4. CCl_2O and CHClO are formed with lower yields, corresponding to the small value of the branching ratio of channel 14b. The UV absorption spectrum of $CHCl_2C(O)Cl$ had to be determined in this study, as the resulting value of k_2 is directly proportional to the absorption cross sections of $CHCl_2C(O)Cl$. It is presented in Figure 2, and the corresponding absorption cross sections are given in Table 2. Note that the traces showed curvature at long time scales (=200 ms), indicating chain termination. This curvature was easily accounted for by introducing a pseudo-first-order loss for $CHCl_2CCl_2O_2$ radicals (or for Cl atoms) in the kinetic scheme.

$$CHCl_2CCl_2O_2 \text{ (or Cl)} \rightarrow \text{products} \quad (15)$$

Values of k_2 and k_{15} were optimized to provide the best fit to the experimental traces, while all other parameters were fixed. The loss of $CHCl_2CCl_2O_2$ at each cycle was estimated to be about 1%, which was too small to definitely identify the nature of termination. This observation is consistent with end-product studies[2,3] which show no significant terminating channel for reaction 2.

TABLE 5: Experimental Values of the Rate Constants of the $CHCl_2CCl_2O_2$ Self-Reaction at 298 K

λ/nm	$[Cl_2]/10^{16\,a}$	$[CHCl_2CCl_2O_2]/10^{13\,a}$	$k_2/10^{-12\,b}$
250	1.50	3.05	6.1
250	1.90	3.88	5.2
250	1.77	3.59	7.5
250	1.75	3.60	8.0
250	1.83	3.75	6.1
250	1.64	3.36	6.0
250	1.49	3.08	6.5
260	1.53	3.11	6.7
260	1.89	3.86	6.5
260	1.75	3.59	7.5
260	1.57	3.23	8.5
260	1.44	3.02	5.3
270	1.88	3.83	8.5
270	1.73	3.54	7.5
270	1.53	3.11	6.8
280	1.84	3.76	6.9
280	1.73	3.51	8.6
280	1.53	3.14	6.0
290	1.82	3.71	7.3
290	1.72	3.50	6.5
290	1.52	3.12	8.1

[a] In molecule cm^{-3}. [b] In cm^3 $molecule^{-1}$ s^{-1}.

TABLE 6: Experimental Values of the Rate Constants of the $CCl_3CCl_2O_2$ Self-Reaction at 298 K

λ/nm	$[CCl_2{=}CCl_2]$ $/10^{16\,a}$	$[O_2]/10^{18\,a}$	$[Cl_2]/10^{16\,a}$	$[CCl_3CCl_2O_2]$ $/10^{13\,a}$	$k_3/10^{-12\,b}$
250	0.56	4.9	1.89	4.80	4.4
250	5.83	4.9	2.35	6.13	5.4
260	0.56	4.9	1.89	4.83	3.5
260	5.83	4.9	2.34	6.10	6.2
260	5.83	4.9	2.36	6.16	6.0
260	2.18	24	1.50	3.83	4.2
270	0.56	4.9	1.92	4.82	6.5
270	5.83	4.9	2.35	6.13	5.1
270	5.83	4.9	2.35	6.12	5.2
270	2.18	24	1.47	3.75	3.7
280	0.56	4.9	1.90	4.88	5.6
280	2.18	24	1.43	3.65	5.1
290	0.56	4.9	1.89	4.83	4.0

[a] In molecule cm^{-3}. [b] In cm^3 $molecule^{-1}$ s^{-1}.

Analyses of 21 signals have resulted in rate constant values for the $CHCl_2CCl_2O_2$ self-reaction, which varied between 5×10^{-12} and 8.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. They are all listed in Table 5 along with the experimental conditions and yield the following average value: $k_2 = (7.0 \pm 1.5) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, where the quoted uncertainties again represent the 95% confidence limits. A study of error propagation similar to that performed for the case of the $CHCl_2CHClO_2$ self-reaction has been carried out. The self-reaction rate constant k_2 is mainly sensitive to the variations of $\sigma(CHCl_2CCl_2O_2)$ and $\sigma(CHCl_2C(O)Cl)$, where variations of 20% in both cross sections result in variations of 26% and 36% in k_2, respectively. The resulting global uncertainty in k_2, including both systematic and statistical errors, was estimated to be about 50%.

Kinetics of the $CCl_3CCl_2O_2$ Self-Reaction. The end-products of reaction 3

$$CCl_3CCl_2O_2 + CCl_3CCl_2O_2 \rightarrow 2CCl_3CCl_2O + O_2 \quad (3)$$

have been studied by several groups.[1,2,17,18] The alkoxy radical CCl_3CCl_2O presents two different decomposition pathways, channel 16a leading to the formation of CCl_2O and channel 16b resulting in the formation of $CCl_3C(O)Cl$ and Cl atoms, leading to $CCl_3CCl_2O_2$ regeneration.

$$CCl_3CCl_2O + M \rightarrow CCl_3 + CCl_2O + M \quad (16a)$$

$$CCl_3CCl_2O + M \rightarrow Cl + CCl_3C(O)Cl + M \quad (16b)$$

The branching ratios reported in the literature are all in excellent agreement: $k_{16a}/k_{16} = 0.15$ and $k_{16b}/k_{16} = 0.85$.

As one can see in Figure 5, experimental traces present very different shapes depending on the wavelength of analysis. The decay observed at 250 nm corresponds mainly to the consumption of tetrachloroethene by the chain reaction, while that recorded at 280 nm corresponds principally to the formation of the stable product $CCl_3C(O)Cl$. Therefore, both experiments were complementary and allowed us to confirm the chemical mechanism proposed in the literature. Note that channel 16a, forming CCl_3 radicals, leads also to a chain reaction by regenerating Cl atoms by the following sequence:

$$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M \quad (17)$$

$$CCl_3O_2 + CCl_3O_2 \rightarrow 2CCl_3O + O_2 \quad (18)$$

$$CCl_3O + M \rightarrow Cl + CCl_2O + M \quad (19)$$

As in the case of the $CHCl_2CCl_2O_2$ self-reaction, it was necessary to accurately determine the UV spectrum of the principal absorbing product, here $CCl_3C(O)Cl$. Values of cross sections are presented in Table 2. No discernible effect of O_2 and $CCl_2{=}CCl_2$ concentrations ($CCl_2{=}CCl_2$ concentrations being changed by a factor of 10) have been observed, neither on kinetics nor on product yields. This confirms the observations of Thüner et al.[1] and contrasts with those of Hasson and Smith,[2] where possible heterogeneous processes may have occurred.

The curvature of traces was accounted for by introducing a loss for $CCl_3CCl_2O_2$ smaller than 2% at each cycle.

The rate constant value for the $CCl_3CCl_2O_2$ self-reaction was extracted from the average of 13 experiments, described in Table 6, yielding the following value: $k_3 = (5.0 \pm 1.5) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, where the quoted uncertainties represent the 95% confidence limits. The study of error propagation showed that the self-reaction rate constant k_3 is mainly sensitive to the variations of $\sigma(CHCl_2CCl_2O_2)$ and $\sigma(CCl_3C(O)Cl)$ above 260 nm and to variations the of $\sigma(CCl_2{=}CCl_2)$ below 260 nm. The resulting global uncertainty in k_3, including both systematical and statistical errors, was estimated to be about 80%.

Discussion and Conclusion

UV Absorption Spectra. The absorption spectra of chloroethylperoxy radicals, measured in this work, are typical of the spectra of alkylperoxy radicals, with broad bands in the wavelength range 200−300 nm. It appears that they all present lower cross sections than those of the unsubstituted ethylperoxy radical ($\sigma_{240nm} = 4.52 \times 10^{-18}$ cm^2 $molecule^{-1}$) [13] and that the effect of each substitution of a hydrogen atom by a chlorine atom is to decrease the cross sections. A similar trend has already been observed for chloromethylperoxy radicals on going from CH_2ClO_2 to $CHCl_2O_2$ and CCl_3O_2.[8] On the other hand, no evidence for a shift of spectra to shorter wavelengths has been characterized as was observed for α-halogenated peroxy radicals.[19] This is mainly due to the strong absorption of chloroethenes below 250 nm (below 230 nm for 1,2-dichloro-

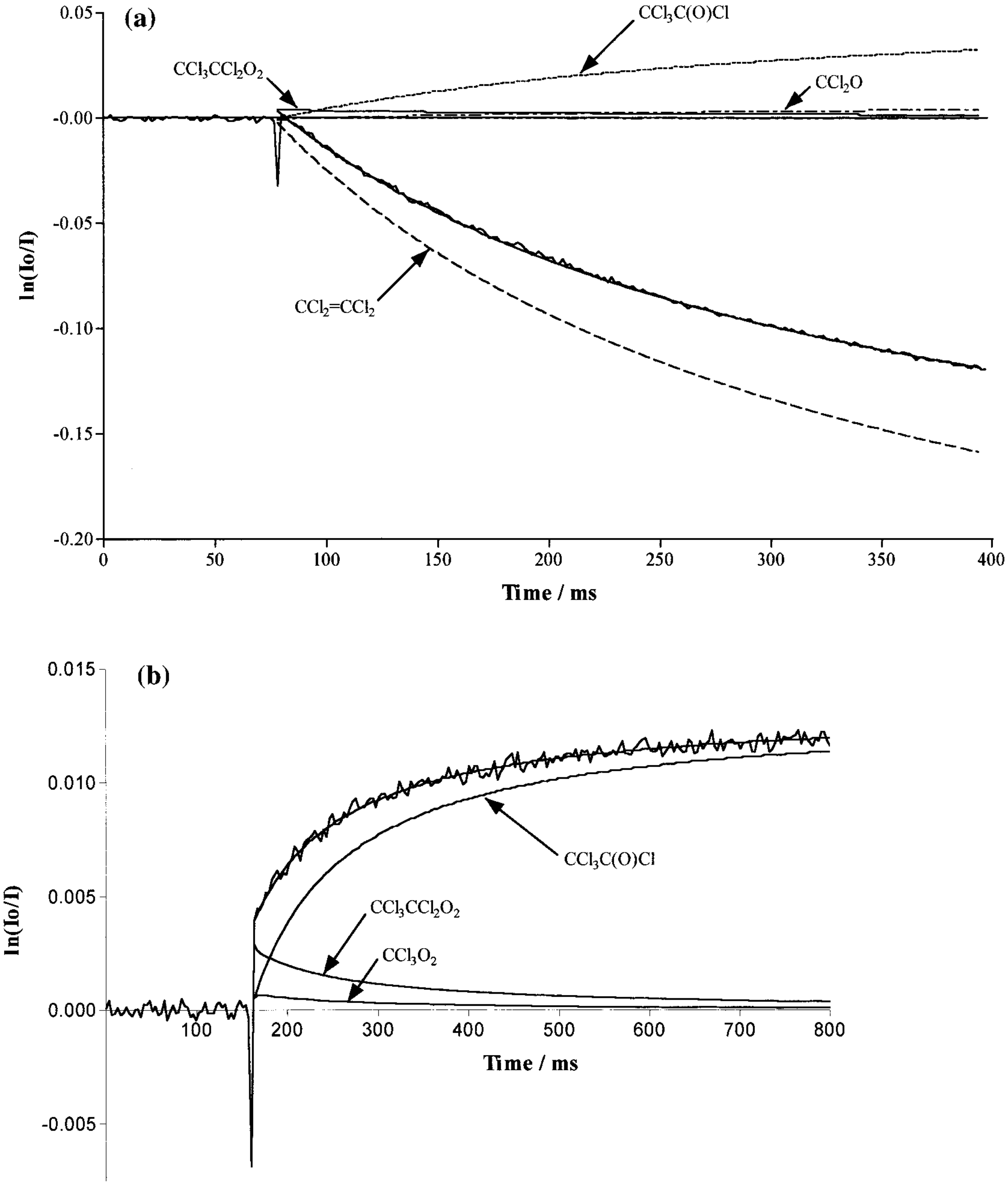

Figure 5. Typical decay traces and their best fits, observed for the $CCl_3CCl_2O_2$ self-reaction: (a) recorded at 250 nm, where tetrachoroethene absorbs; (b) recorded at 280 nm, where tetrachoroethene does not absorb. The initial peroxy radical concentration was 4.84×10^{13} molecule cm^{-3}, averaged from 12 flashes.

ethene), which did not allow us to characterize the maximum of spectra accurately.

The UV spectrum of $CCl_3CCl_2O_2$ was previously determined by Mogelberg et al.,[17] using the pulse radiolysis of SF_6 in the presence of a CCl_3CCl_2H/O_2 mixture. It is presented in Figure 1 for comparison. The spectrum, calibrated against the F atom yield, presents one maximum in the range 230−290 nm: $\sigma_{255nm} = 1.76 \times 10^{-18}$ cm^2 molecule^{-1}. In the wavelength range 260−270 nm, there is a good agreement between both spectra, with differences smaller than 5% on the cross-section values. At 280 nm, a discrepancy appears between both determinations, reaching up to 50% at 290 nm. Such discrepancies are of course difficult to account for and cannot arise from simple systematic errors. The discrepancy may result from problems in the deconvolution of $CCl_3CCl_2O_2$ and FO_2 spectra in radiolysis experiments. Nevertheless, we can note that most of our measurements were performed at wavelengths lower than 280 nm, where the signal-to-noise ratio was maximum and where discrepancies with the spectrum of Mogelberg et al.[17] are negligible.

The spectrum of $CHCl_2C(O)Cl$ has been determined for the first time in this work, and there was only one previous determination of that of $CCl_3C(O)Cl$—by Gillotay et al.[20] Both spectra present a strong absorption below 220 nm and a band with a maximum around 255 nm. Spectra of $CCl_3C(O)Cl$ determined in this work and by Gillotay et al.[20] are in very good agreement between 250 and 290 nm (which corresponds to the range where experiments were performed), with differences of less than 2% in absolute cross-section values.

Reaction Mechanisms and Kinetics. Kinetic analyses of self-reactions were very sensitive to the reaction mechanism used and, in particular, to the way chloroethoxy radicals reacted. It is very satisfying to note that our results are totally consistent with end-product studies reported in the literature.[1,2] This provides a valuable confirmation of those previous data, since

TABLE 7: Rate Constants at 298 K for Self-Reactions of Chlorinated Alkylperoxy Radicals

radical	$k(RO_2 + RO_2)$ 10^{-12} cm^3 molecule^{-1} s^{-1}	reference
CH_2ClO_2	3.7 ± 0.4	Catoire et al.[24]
$CHCl_2O_2$	3.8 ± 0.7	Catoire et al.[8]
CCl_3O_2	4.0 ± 1.0	Catoire et al.[8]
$CHCl_2CHClO_2$	3.6 ± 0.9	this work
$CHCl_2CCl_2O_2$	7.0 ± 1.5	this work
$CCl_3CCl_2O_2$	5.0 ± 1.5	this work
CCl_3CHClO_2	5.0 ± 1.2	Mogelberg et al.[25]
$CCl_3CH_2O_2$	4.7 ± 1.6	Platz et al.[26]
$CH_2ClCH_2O_2$	6.0 ± 0.8	Maricq et al.[7]
CH_3CHClO_2	5.2 ± 1.3	Maricq et al.[7]

branching ratios of alkoxy radical reaction pathways are always difficult to measure accurately. It seems now well established that Cl-atom elimination from chloroalkoxy radicals bearing two α-chlorine atoms ($R-CCl_2O$) is the main reaction pathway. Radicals such as CH_3CCl_2O have also been shown to decompose in this way.[21] The situation is not as clear for radicals bearing one H atom and one Cl atom in the α position ($R-CHClO$). C−C bond splitting or HCl elimination can be the dominant reaction pathway, according to the nature of R.

The present work represents the first determination of the rate constants for self-reactions of the $CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$ radicals at room temperature. The values are reported in Table 7, along with previous data reported for self-reactions of other chlorinated alkylperoxy radicals.

It must be kept in mind when comparing rate constants that the uncertainty ranges for our measurements are fairly large as the determination of rate constants depends on complex reacting systems, including chain reactions, on absorption of end-products, and on branching ratios of alkoxy radical reaction channels. A global uncertainty factor of nearly two has been estimated for most rate constants measured in this work. It results that, despite the differences observed between the measured rate constants, no clear reactivity trend can be extracted from the data. There is a slight discernible increase in the rate constants for the chloroethylperoxy radical self-reactions compared to those reported for chloromethylperoxy radicals, but the increase is within the experimental uncertainties. It can be observed that chlorinated ethylperoxy radicals have all similar rate constants, whatever the position of the substituent. The striking feature is the large increase of the rate constant on going from the $C_2H_5O_2$ radical ($k(C_2H_5O_2 + C_2H_5O_2) = 6.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K)[6] to $CH_2ClCH_2O_2$ ($k(CH_2ClCH_2O_2 + CH_2ClCH_2O_2) = 6.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K),[7] whereas the following substitutions by Cl atoms do not further increase the rate constants. This contrasts with fluorine-substituted peroxy radicals, where a slight decrease of the rate constant was observed for multiple fluorine atom substitution.[4]

Considering all these remarks, an average value of $(5 \pm 2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K can be proposed for chloroethylperoxy self-reaction rate constants.

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