

Reactions of hydroxyl radicals with trichloroethene and tetrachloroethene in argon matrices at 12 K

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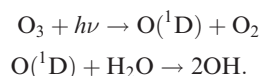
Received 29th August 2003, Accepted 12th November 2003

First published as an Advance Article on the web 2nd December 2003

Irradiation of argon matrices at 12 K containing hydrogen peroxide and tetrachloroethene using the output from a medium-pressure mercury lamp gives rise to the carbonyl compound trichloroacetyl chloride (CCl_3CClO). Similarly trichloroethene gives dichloroacetyl chloride (CCl_2HCClO) – predominantly in the *gauche* form – under the same conditions. It appears that the reaction is initiated by homolysis of the O–O bond of H_2O_2 to give OH radicals, one of which adds to the double bond of an alkene molecule. The reaction then proceeds by abstraction of the H atom of the hydroxyl group and Cl-atom migration. This mechanism has been explored by the use of DFT calculations to back up the experimental findings. The mechanism is analogous to that shown by the simple hydrocarbon alkenes.

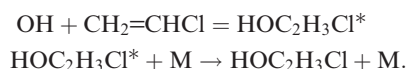
Introduction

The chemistry of the troposphere is dominated by the oxidation of hydrocarbons and during daytime the hydroxyl radical is the most important oxidant. It is formed by photolysis of ozone to yield $\text{O}(^1\text{D})$ atoms which then react with water to give hydroxyl radicals:^{1–4}



For most hydrocarbons in the troposphere oxidation is initiated by the hydroxyl radical and indeed this radical acts as a cleaning agent since many of the products of oxidation are water-soluble and can be rained out of the atmosphere.⁴ The reactions of hydroxyl radicals with alkenes have been studied in some detail both in the gas phase and in low-temperature matrices.^{5–8} It is clear that the first stage of reaction is addition of the OH radical to the double bond to form hydroxy-alkyl radicals. These may be further oxidised to carbonyl products.^{5–8}

Compared to the information available for simple alkenes much less is known about the chloroalkenes. However, these man-made pollutants have been identified in urban areas and have several industrial and non-industrial sources. They have been found in samples taken from points adjacent to a municipal incinerator, a waste collection centre and a sewage treatment plant.⁹ Gas-phase measurements show that the initial step of the reaction is analogous to that of the hydrocarbon alkenes *i.e.* addition of the OH radical to give an energy-rich OH-haloalkene complex,³ which may either decompose back to reactants, or be collisionally stabilised to give the hydroxy-alkyl radical:-



It is possible also that a halogen atom may be eliminated from the activated complex to give a vinyl alcohol – for the activated complex of chloroethene and OH the elimination of a Cl atom is exothermic by about 45 kJ mol^{-1} :-



However, it appears that Cl-atom elimination is, in fact, a relatively minor pathway under these conditions.^{3,10}

Decomposition of the hydroxychloroalkyl radicals certainly occurs in the troposphere but the mechanisms are uncertain. The reactions probably proceed by further oxidation.³ Product analysis has shown that $\text{HC}(\text{O})\text{Cl}$ is formed in the reaction of vinyl chloride or trichloroethene and OH radicals, and that phosgene (COCl_2) is formed in the reaction of trichloroethene or tetrachloroethene and OH radicals.¹⁰ These C_1 products are unlikely to be primary products, however. Accordingly, we have carried out a study of the reactions of trichloroethene and tetrachloroethene with hydroxyl radicals in argon matrices at 12 K. In this way we hoped to identify products of these reactions and hence to learn something of the reaction mechanisms. In particular we wished to search for and identify chlorine-containing carbonyl products and to obtain evidence that, like the hydrocarbon alkenes, the reaction within the matrix is initiated by addition of the OH radical to the double bond of the alkene.

Experimental section

The matrix-isolation apparatus used at Reading has been described in detail elsewhere.^{11,12} The experiments were carried out in a very similar manner to previous experiments on hydrocarbon alkenes.⁶ Samples of trichloroethene (Aldrich, 99.5% pure), tetrachloroethene (Aldrich, > 99% pure), dichloroacetyl chloride (Aldrich, 99% pure) and trichloroacetyl chloride (Aldrich, 99% pure) were used as supplied after freeze-pump-thaw purification. Gas phase mixtures of the alkene under investigation with argon were made up on a vacuum line using standard manometric techniques. Hydrogen peroxide vapour was obtained from the H_2O_2 -urea adduct¹³ and was co-condensed with the alkene/argon mixture. Matrices were photolysed using the broad-band ultraviolet output from a medium-pressure mercury lamp. It has been shown elsewhere that this method is an efficient route to generate OH radicals.^{5–8,13,14} Spectra were recorded on a Perkin-Elmer 983 dispersive spectrophotometer with a typical resolution of 2 cm^{-1} or better. Data were saved onto a Perkin-Elmer data station, transferred to a computer and manipulated using GRAMS software.

Calculations

DFT calculations were carried out using the Gaussian 98 computational package¹⁵ with the 6-31G(d) basis sets and the B3-LYP functional. There were no imaginary frequencies generated by any of the calculations.

Results and discussion

When a hydrogen peroxide-doped argon matrix (at 12 K) initially containing *ca.* 1% of tetrachloroethene was subjected to broad-band UV-visible photolysis for a period of 2 h the infrared bands of tetrachloroethene^{16,17} (916 (vs) 781 (vs) cm^{-1} with weaker features at 898 (m), 811 (m) and 760 (m) cm^{-1}) and of hydrogen peroxide¹³ (3582 (s) and 1291 (s) cm^{-1}) were seen to decay. At the same time new features appeared which may be assigned to H_2O ^{18–21} (3590 and 1624 cm^{-1}), CO_2 ^{22–24} (2342 and 665 cm^{-1}) and $\text{CO}^{25,26}$ (2143 cm^{-1}). Bands were also observed at 1809, 870 and 852 cm^{-1} . These are assigned to the product trichloroacetyl chloride CCl_3CClO .^{8,15,16,27}

In order to confirm that the product of this reaction is indeed trichloroacetyl chloride an authentic sample of this compound was isolated at 1% concentration in an argon matrix at 12 K and the infrared spectrum was recorded. In Table 1 are compared the infrared spectra of the matrix-isolated and liquid²⁷ compound. Unfortunately only three absorptions were observed for the product of the matrix reaction of C_2Cl_4 with OH radicals. However, these correspond well to the two strongest bands of matrix-isolated CCl_3CClO (see Table 1). The band at 1809 is assigned to the $\nu(\text{C}=\text{O})$ vibration and those at 870 and 852 to a matrix-split band (see Fig. 1) arising from the antisymmetric stretch of the CCl_3 moiety.²⁷ The match between these spectra, although not entirely unambiguous, does suggest that CCl_3CClO is produced by the reaction of C_2Cl_4 with OH radicals in an argon matrix. When photolysis was continued for further periods of 2 h and 17 h, the spectral changes reported above continue in that bands of the reactants decayed while those of the product trichloroacetyl chloride and of H_2O , CO_2 and CO increased. Following photolysis the matrix was annealed to 40 K and re-cooled to 12 K for 5 cycles. This had the effect of sharpening the bands but did not have any noticeable effect on their intensities. The behaviour of the spectral features upon photolysis and annealing is detailed in Table 2 and the spectra are illustrated in Fig. 1.

We have previously carried out similar experiments where hydrogen peroxide is photolysed in matrices containing ethene or other simple alkenes.^{6–8} It was shown that under the conditions of these experiments photolysis of H_2O_2 proceeds *via*

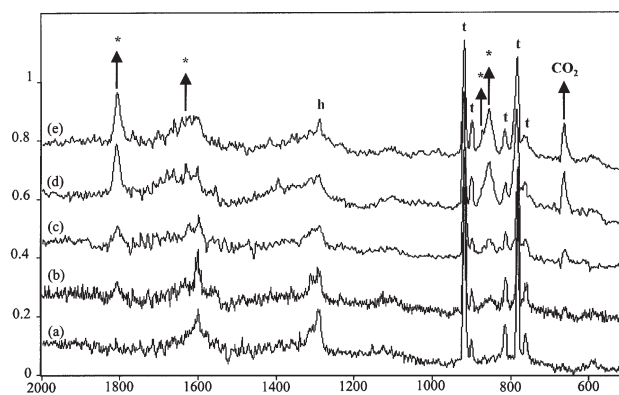


Fig. 1 The region 2000–500 cm^{-1} of the absorbance infrared spectra of an argon matrix (12 K) initially containing tetrachloroethene and hydrogen peroxide ($\text{C}_2\text{Cl}_4/\text{H}_2\text{O}_2/\text{Ar} = 1:1:100$), after (a) deposition, (b) 2 h, (c) 4 h, (d) 21 h broad-band UV-visible photolysis using a medium-pressure mercury lamp, and (e) 5 \times annealing to 40 K, then re-cooling to 12 K. Symbols: t = tetrachloroethene, h = H_2O_2 , and * = new band.

O–O bond rupture to yield OH radicals.^{5–8} Reaction of the OH radical with the alkene substrate yields a hydroxyalkyl radical which may suffer one of two fates. Upon annealing, reaction with a second OH radical in the matrix cage gives the diol, whereas prolonged photolysis causes decomposition of the radical to form a carbonyl product. It seems reasonable to suppose that a similar mechanism (Scheme 1) operates in the case of tetrachloroethene. In this case, however, there is no sign of any bands belonging to a radical intermediate, nor were any major changes detected upon annealing the matrix. It is pertinent, therefore, to discuss briefly why the two systems may behave rather differently.

First is the possibility that it is the absorption properties of the radicals that determines their lifetime within the matrix. Addition of chlorine atoms to a saturated organic compound typically red-shifts the absorbance maximum by some 5–10 nm,¹⁶ making photolysis, under the conditions of our experiments, more efficient. We found it impossible to verify this point by specifically excluding certain irradiation wavelengths by using filters. This was because of the long photolysis

Table 2 Bands seen in an argon matrix (12 K) initially containing tetrachloroethene (1%) and H_2O_2 upon photolysis using a medium-pressure mercury lamp and on annealing^a

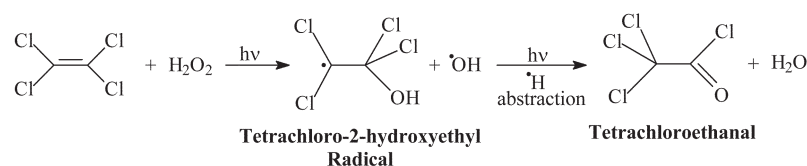
ν/cm^{-1}	$h\nu$ 2 h	$h\nu$ 4 h	$h\nu$ 21 h	Anneal	Origin	Assignment
3590	*	↑	↑	–	H_2O	$\nu(\text{OH})$
3582	↓	↓	↓	–	H_2O_2	$\nu(\text{OH})$
2342	*	↑	↑	–	CO_2	$\nu_{\text{as}}(\text{OCO})$
2143	*	↑	↑	–	CO	$\nu(\text{CO})$
1809	*	↑	↑	–	CCl_3CClO	$\nu(\text{CO})$
1624	*	↑	↑	–	H_2O	$\delta(\text{OH})$
1291	↓	↓	↓	–	H_2O_2	$\nu(\text{O}=\text{O})$
916	↓	↓	↓	–	C_2Cl_4	$\nu(\text{C}=\text{Cl})$
898	↑	–	↑	–	CCl_3CClO	$\nu(\text{C}=\text{Cl})$
870	*	↑	↑	–	CCl_3CClO	$\nu(\text{C}=\text{Cl})$
852	*	↑	↑	–	CCl_3CClO	$\nu(\text{C}=\text{Cl})$
811	↓	↓	↓	–	C_2Cl_4	$\nu(\text{C}=\text{Cl})$
781	↓	↓	↓	–	C_2Cl_4	$\nu(\text{C}=\text{Cl})$
760	↓	↓	↓	–	C_2Cl_4	$\nu(\text{C}=\text{Cl})$
665	*	↑	↑	–	CO_2	$\delta(\text{OCO})$

^a Definition of symbols: * = appears, ↑ = increases in intensity, ↓ = decreases in intensity, – = unchanged intensity.

Table 1 Bands seen for liquid and matrix-isolated samples of trichloroacetyl chloride

CCl_3CClO (liquid) (ref. 27) ^a	CCl_3CClO (Ar matrix) (this work) ^b	Assignment
1800	1800 (vs)	$\nu(\text{C}=\text{O})$
1020	1023 (ms)	$\nu(\text{C}=\text{C})$
850	857 (vs)	$\nu_{\text{as}}(\text{CCl}_3)$
800	792 (s)	$\nu_{\text{as}}(\text{CCl}_3)$
735	745 (ms)	$\nu(\text{C}=\text{Cl})$
620	623 (ms)	$\rho(\text{C}=\text{O})$
512	513 (ms)	$\delta(\text{O}=\text{C}=\text{Cl})$
428	427 (m)	$\nu_{\text{sym}}(\text{CCl}_3)$
362	360 (m)	$\delta(\text{C}=\text{C}=\text{O})$
284	278 (w)	$\delta(\text{CCl}_3)$

^a No band intensities are given in ref. 27. ^b s = strong, m = medium, w = weak, v = very.

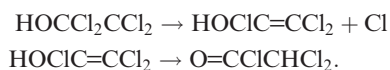


Scheme 1 Proposed pathway for the reaction of tetrachloroethene with hydrogen peroxide in an argon matrix at 12 K upon irradiation using a medium-pressure mercury lamp.

times required, which become impossibly long when filters are employed and the light intensity is substantially reduced. A second important point concerns the *stability* of the radical intermediates. Chloroalkenes with one or more vinylic chlorine atoms are stabilised by a mesomeric interaction between the chlorine atom and the C=C double bond. When hydroxyl radicals react with the chloroalkene this mesomeric interaction is lost. This destabilisation is reflected in the lower rate constants for the reaction of OH radicals with steadily more chlorinated alkenes as shown in Table 3.^{3,28,29} Once a carbonyl product is formed, provided an acyl chlorine atom is present, a mesomeric effect with the carbonyl double bond is possible. Thus the radical intermediate is *destabilised* with respect to both reactant alkene and product carbonyl. Finally it is known that chlorine atom migration in a system like this is more efficient than hydrogen atom migration because a chlorine atom readily forms a cyclical transition state between the two carbon atoms.¹⁰ These factors probably all contribute to the destabilisation of the hydroxychloroalkyl radical with respect to the carbonyl product and suggest why the radical was not seen in the matrix in this case.

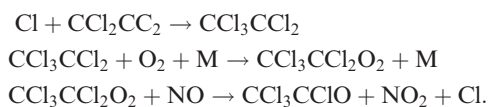
One important feature to emerge from our experiments with tetrachloroethene is that no product containing a C–H bond was formed. This counts against an alternative mechanism in which the carbonyl product is formed by Cl-atom elimination

or abstraction from the hydroxychloroalkyl radical intermediate. This would yield an enol which could rearrange, upon photolysis, to give a keto product, but in this case the keto product would contain a C–H group:-



The observation that no C–H-containing product was seen provides strong support for the mechanism shown in Scheme 1, where H-atom abstraction is followed by Cl-atom migration to give the carbonyl product. This observation is in keeping with the findings from gas-phase studies where Cl-atom elimination from similar hydroxy radicals was found to be only a minor pathway.¹⁰

It is of interest to note that CCl_3CClO has previously been detected on oxidation of C_2Cl_4 in gaseous mixtures containing O_2 and NO .³⁰ Under these conditions it was suggested that this reaction proceeds by addition of a Cl atom to C_2Cl_4 to yield the C_2Cl_5 radical which adds to O_2 . Subsequent loss of an O (by oxidation of NO to NO_2) and a Cl atom yields CCl_3CClO :-



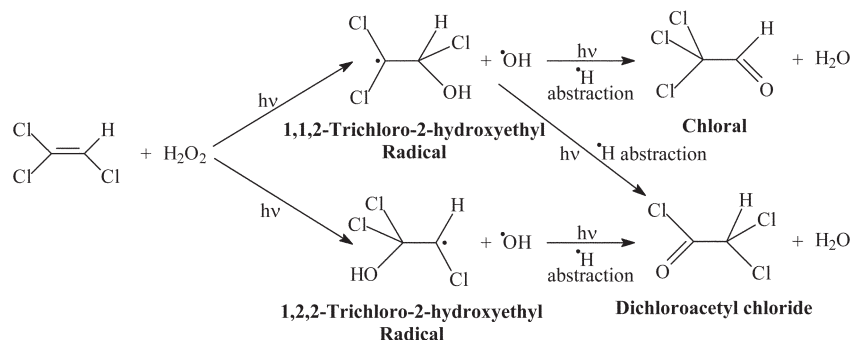
Although a similar mechanism cannot operate in our system where neither O_2 nor NO is present it is nonetheless pertinent to note the production of CCl_3CClO as a product of oxidation of C_2Cl_4 .

We next turned our attention to the reaction of trichloroethene with hydroxyl radicals. Here the reaction is potentially more complicated because there are two possible radical intermediates and two possible carbonyl products. The possible reaction pathways are shown in Scheme 2.

Two hours' irradiation of a hydrogen peroxide-doped argon matrix at 12 K containing *ca.* 1% of trichloroethene led to a reduction in the intensity of the bands of hydrogen peroxide¹³ (3583 and 1291 cm^{-1}) and of trichloroethene^{16,17} (3094, 1593, 936, 846, 784 and 632 cm^{-1}). At the same time new bands appeared (alongside those of H_2O , CO_2 and CO) at 2792,

Table 3 Rate constants for the reactions of a series of progressively more chlorinated alkenes with OH radicals in the gas phase (from ref. 3)

Alkene	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Ethene	8.52×10^{-12}
Chloroethene	6.60×10^{-12}
1,1-Dichloroethene	1.12×10^{-12}
<i>cis</i> -1,2-Dichloroethene	2.71×10^{-12}
<i>trans</i> -1,2-Dichloroethene	2.50×10^{-12}
Trichloroethene	2.35×10^{-12}
Tetrachloroethene	1.55×10^{-12}



Scheme 2 Proposed pathways for the reaction of trichloroethene with hydrogen peroxide in an argon matrix at 12 K upon irradiation using a medium-pressure mercury lamp.

1804, 993, 766 and 587 cm^{-1} . Prolonged photolysis for a total period of 4 or 21 h caused product bands to increase further in intensity. Annealing to 40 K and recooling to 12 K had little effect other than to sharpen the bands slightly. The spectral changes are illustrated in Figs. 2 and 3 and the behaviour of the bands upon photolysis is listed in Table 4.

The new bands seen upon photolysis clearly belong to a carbonyl product. Assuming that the reaction mechanism is analogous to that of the hydrocarbon alkenes or of trichloroethene, the question is, is this product chloral or dichloroacetyl chloride? In order to attempt to answer this question an authentic sample of dichloroacetyl chloride was isolated at 1% concentration in an argon matrix. Bands were observed for this matrix-isolated compound at 2801 (s), 1815 (vs), 1784 (vs), 1083 (s), 993 (s), 800 (s), 786 (s), 756 (vs) and 583 (s) cm^{-1} . Comparison with literature data for the gaseous and liquid compound show that both *syn* and *gauche* forms of this molecule have been isolated. The bands at 2801, 1815, 993, 800, 756 and 583 cm^{-1} may be assigned to the *gauche* form, while those at 2801, 1784, 1083 and 786 cm^{-1} arise from the *syn* conformer.³¹ When these spectra are compared with the spectrum obtained by photolysing $\text{C}_2\text{Cl}_3\text{H}$ and H_2O_2 in an argon matrix it is suggested that the *gauche* form of dichloroacetyl chloride is formed predominantly under these conditions. All of the product bands match well with observed bands of *gauche*- CCl_2HCClO (see Table 5).

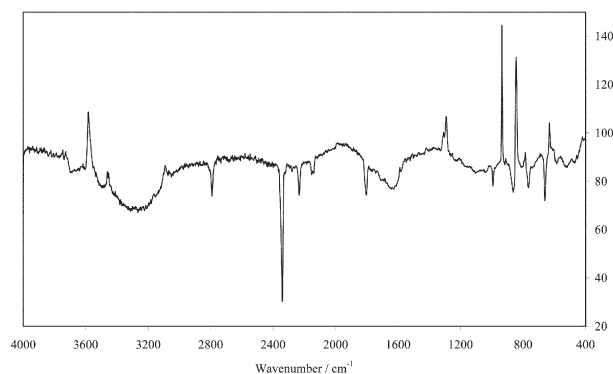


Fig. 2 Difference of the infrared spectrum of an argon matrix (12 K) initially containing trichloroethene and hydrogen peroxide ($\text{C}_2\text{Cl}_3\text{H}/\text{H}_2\text{O}_2/\text{Ar} = 1:1:100$) after 21 h of photolysis minus the spectrum of the same matrix after deposition but before photolysis.

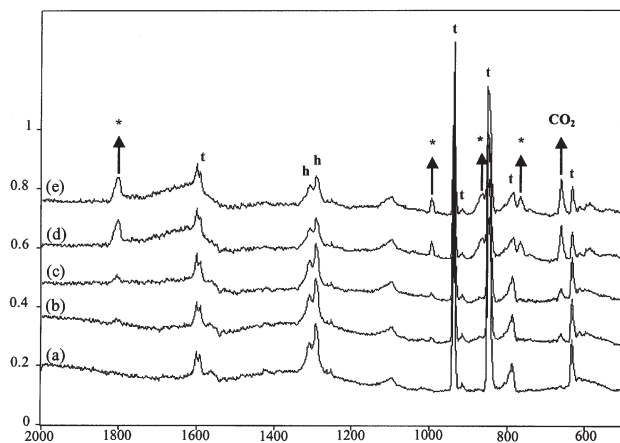


Fig. 3 The region 2000–500 cm^{-1} of the absorbance infrared spectra of an argon matrix (12 K) initially containing trichloroethene and hydrogen peroxide ($\text{C}_2\text{Cl}_3\text{H}/\text{H}_2\text{O}_2/\text{Ar} = 1:1:100$), after (a) deposition, (b) 2 h, (c) 4 h, (d) 21 h broad-band UV-visible photolysis using a medium-pressure mercury lamp, and (e) annealing to 40 K, then re-cooling to 12 K. Symbols: t = trichloroethene, h = H_2O_2 , and * = new band.

Table 4 Bands seen in an argon matrix (12 K) initially containing trichloroethene (1%) and H_2O_2 upon photolysis using a medium-pressure mercury lamp and on annealing^a

ν/cm^{-1}	$h\nu$ 2 h	$h\nu$ 4 h	$h\nu$ 21 h	Anneal	Origin	Assignment
3583	↓	↓	↓	–	H_2O_2	$\nu(\text{OH})$
3398	*	↑	↑	–	H_2O	$\nu(\text{OH})$
3094	↓	↓	↓	–	$\text{C}_2\text{Cl}_3\text{H}$	$\nu(\text{CH})$
2792	*	↑	↑	–	$\text{C}_2\text{Cl}_3\text{HO}$	$\nu(\text{CH})$
2342	*	↑	↑	–	CO_2	$\nu_{\text{as}}(\text{OCO})$
2142	*	↑	↑	–	CO	$\nu(\text{CO})$
1804	*	↑	↑	–	$\text{C}_2\text{Cl}_3\text{HO}$	$\nu(\text{CO})$
1602	*	↑	↑	–	H_2O	$\delta(\text{OH})$
1593	↓	↓	↓	–	$\text{C}_2\text{Cl}_3\text{H}$	$\delta(\text{CH})$
1291	↓	↓	↓	–	H_2O_2	$\nu(\text{OO})$
993	*	↑	↑	–	$\text{C}_2\text{Cl}_3\text{HO}$	$\nu(\text{CCl})$
936	↓	↓	↓	–	$\text{C}_2\text{Cl}_3\text{H}$	$\nu(\text{CCl})$
846	↓	↓	↓	–	$\text{C}_2\text{Cl}_3\text{H}$	$\nu(\text{CCl})$
784	↓	↓	↓	–	$\text{C}_2\text{Cl}_3\text{H}$	$\nu(\text{CCl})$
766	*	↑	↑	–	$\text{C}_2\text{Cl}_3\text{HO}$	$\nu(\text{CCl})$
661	*	↑	↑	–	CO_2	$\delta(\text{OCO})$
632	↓	↓	↓	–	$\text{C}_2\text{Cl}_3\text{H}$	$\delta(\text{CCl})$
587	*	↑	↑	–	$\text{C}_2\text{Cl}_3\text{HO}$	$\delta(\text{CCl})$

^a Definition of symbols: * = appears, ↑ = increases in intensity, ↓ = decreases in intensity, – = unchanged intensity.

Table 5 A comparison of the positions and intensities of infrared bands observed for the product of reaction of trichloroethene with hydroxyl radicals in an argon matrix at 12 K with those seen for an authentic sample of dichloroacetyl chloride (CHCl_2CClO , 1%) in an argon matrix at 12 K

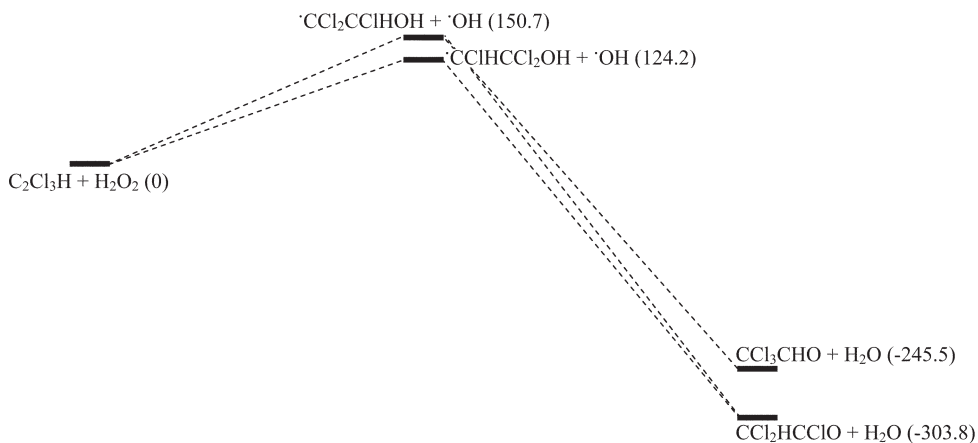
CHCl_2CClO (ν/cm^{-1}) <i>gauche</i> ^a	$\text{OH} + \text{C}_2\text{HCl}_3$ product (ν/cm^{-1})	Δ^b
2801 (s)	2792 (s)	0.321
1815 (vs)	1804 (s)	0.606
993 (s)	993 (ms)	0.000
800 (s)	– ^c	–
756 (vs)	766 (ms)	1.32
583 (s)	587 (wm)	0.686

^a s = strong, m = medium, w = weak, v = very ^b Δ is the percentage difference in wavenumber between the position of a band of the $\text{OH} + \text{C}_2\text{HCl}_3$ photoproduct and of the corresponding band of the authentic sample of CHCl_2CClO . ^c Band not observed: probably obscured by absorption of $\text{C}_2\text{Cl}_3\text{H}$.

Table 6 Energies (enthalpies) for products and reactants in the reaction between trichloroethene and hydrogen peroxide calculated using the B3-LYP DFT approximation with the 6-31G(d) basis set (zero point energies have been added to all values)

Species	E/E_h	$E/\text{kJ mol}^{-1}$	$\Delta E/\text{kJ mol}^{-1}$ ^a
$\text{C}_2\text{Cl}_3\text{H}$	–1457.3380	–3 826 240	0 ^b
H_2O_2	–151.5034	–397 772	0 ^b
$\text{CCl}_2\text{CClHOH}$	–1533.0693	–4 025 073	–150.7 ^c
$\text{CClHCCl}_2\text{OH}$	–1533.0794	–4 025 100	–124.2 ^c
OH	–75.7147	–198 789	–
CCl_3CHO	–1532.5480	–4 023 704	–245.5 ^d
CCl_2HCClO	–1532.5702	–4 023 763	–303.8 ^d
H_2O	–76.3869	–200 554	–
CO_2	–188.5429	–495 019	–

^a Energy changes for reaction steps – see Scheme 3. ^b Energy of $\text{C}_2\text{Cl}_3\text{H} + \text{H}_2\text{O}_2$ set at zero. ^c Includes energy of OH. ^d Includes energy of H_2O .



Scheme 3 Energy (kJ mol⁻¹) diagram for the reaction of trichloroethene with hydrogen peroxide calculated using the B3-LYP functional with the 6-31G(d) basis set. Numbers in parentheses are the energy changes for the reactions indicated.

There is no obvious match between our product spectrum and the reported spectrum of chloral (CCl_3CHO).^{32,33} In particular the reported position of $\nu(\text{C}=\text{O})$ for chloral vapour (1778 cm⁻¹) or CCl_4 solution (1768 cm⁻¹) does not match well with our observed product band at 1804 cm⁻¹. Other strong bands of chloral vapour are seen at 1030, 987, 857 and 739 cm⁻¹. The band at 987 cm⁻¹ matches one of our product bands quite well but the others do not have any obvious counterparts. It therefore appears that the product of reaction of trichloroethene with OH radicals in an argon matrix is dichloroacetyl chloride, predominantly in the *gauche* form. We have no detailed mechanistic explanation as to why the *gauche* form should be favoured but we note that this is the lower-energy form by some 3.5 kJ mol⁻¹.³¹

DFT calculations were carried out in order to identify the most energetically favourable species with the lowest value of ΔE . Table 6 gives the energy (enthalpy) values obtained for reactants and possible products. Zero point energies were added to all values. The energy values for the various possible reaction steps are illustrated by the diagram in Scheme 3.

These calculations serve to back up the experimental findings in that dichloroacetyl chloride and water are calculated to be the most stable reaction products. The overall energy value of this pathway is -303.8 kJ mol⁻¹. The first step of the reaction, the formation of a hydroxyalkyl radical, is strongly exothermic. The energy to overcome this step is provided by photolysis of the reaction mixture. It is calculated that the 1,2,2-trichloro-2-hydroxyethyl radical is favoured over the isomeric 1,1,2-trichloro-2-hydroxyethyl radical. This is perhaps somewhat surprising in that it might be expected that the radical with the unpaired electron on the CCl_2 moiety would be the more stable. The 1,2,2-trichloro-2-hydroxyethyl radical proceeds to the product dichloroacetyl chloride by H-atom abstraction and migration of a Cl atom. The alternative 1,1,2-trichloro-2-hydroxyethyl radical would need to undergo H-atom migration to form dichloroacetyl chloride. As mentioned previously Cl-atom migration is expected to be favoured over H-atom migration. The conversion of radical intermediate to carbonyl product is calculated to be strongly exothermic (-428.0 kJ mol⁻¹) in line with the failure to observe the radical intermediates in our experiments.

Conclusions

Our experiments have identified the products of reaction of tetrachloroethene and of trichloroethene with hydroxyl radicals as being the carbonyl compounds trichloroacetyl chloride and dichloroacetyl chloride respectively. It is likely that the reactions proceed *via* addition of an OH radical to the double bond of the alkene in a reaction entirely analogous to that of

the simple hydrocarbon alkenes. This addition reaction forms a hydroxychloroalkyl radical which reacts further by abstraction of the hydroxyl hydrogen atom. In keeping with the findings from gas phase studies¹⁰ chlorine-atom loss from this radical is, at best, a very minor pathway. For trichloroethene, where two carbonyl products are possible, the observed product – dichloroacetyl chloride – has an acyl chlorine atom which gives a mesomeric stabilisation. This product is probably formed by Cl-atom rather than H-atom migration. It is found that this product is formed predominantly in the low-energy *gauche* form. Our experiments suggest that carbonyl products of the type observed may be important in the atmospheric oxidation of chloroalkenes, just as acetaldehyde is important in ethene oxidation.^{1,2,34} The use of DFT calculations in support of the experimental results from matrix isolation is shown to be important in exploring these reaction mechanisms.

Acknowledgements

We thank EPSRC for a studentship for KSW and the Leverhulme Trust for the award of an Emeritus Fellowship to PCHM.

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