

Photolysis ($\lambda = 254$ nm) of tetrachloroethene in aqueous solutions

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Abstract

In the 254 nm photolysis of air-saturated aqueous solutions of tetrachloroethene, the major products (quantum yields in parentheses) are as follows: chloride ion (2.05), carbon dioxide (0.62), trichloroacetic acid (0.41), dichloroacetic acid (0.08) and hypochlorite (0.08). Trichloroacetic acid is not formed in the absence of O_2 ; it is suppressed by the addition of hydrogen donors, such as tert-butanol and also by carbonate/bicarbonate ions. The quantum yield of dichloroacetic acid remains unaffected by O_2 and hydrogen donors.

It is concluded that there are two (or three) major primary processes



From scavenging experiments with alcohols, with and without O_2 , $\Phi(1) = 0.23 \pm 0.03$ has been determined. Reactions (2) and (3) will finally both yield dichloroacetic acid and no distinction can be made between the two routes: $\Phi(2+3) = 0.08$.

In the absence of scavengers, the Cl atoms add to tetrachloroethene yielding the pentachloroethyl radical which, in the presence of O_2 , is converted to the corresponding peroxy radical, the precursor of trichloroacetic acid. In the presence of O_2 , a short chain reaction sets in. The chain carrier is the Cl atom which is liberated in the bimolecular termination reactions of the various peroxy radicals formed in the present system. The rate constants $k(Cl^\cdot + C_2Cl_4) = 2.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k(Cl^\cdot + CO_3^{2-}) = 5.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k(Cl^\cdot + HCO_3^-) = 2.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ have been arrived at in this study. Thus bicarbonate prevents the formation of trichloroacetic acid from potentially present tetrachloroethene in the UV disinfection of drinking water.

Keywords: Photolysis; Tetrachloroethene

1. Introduction

Tetrachloroethene is non-flammable and for many processes the ideal solvent. Being chemically largely inert it is barely consumed, and despite increasing attempts to recycle it and to destroy non-recyclable material in a controlled fashion, most of the annual production eventually reaches the environment. From the atmosphere it is washed down by rain, and in industrialized countries it is now practically omnipresent in trace amounts in the groundwater.

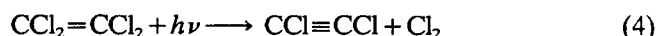
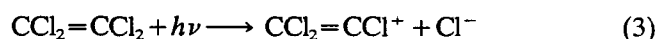
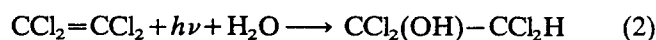
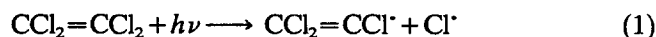
Tetrachloroethene absorbs in the UV ($\lambda_{\text{max}} = 205$ nm) and, at about 254 nm (the line emitted by the low-pressure mercury arc used in the present study), its

molar absorption coefficient is about $200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ [1]. On photolysis in the gas phase it is decomposed in a chain reaction [2]. It has been shown that contaminated drinking water can be freed from tetrachloroethene by stripping and UV treatment [3], but no attempt has been made as yet to determine the by-products. A knowledge of the byproducts, their rate of formation and subsequent degradation is of considerable importance for the acceptance and further use of this technology. As drinking water may be contaminated by tetrachloroethene, it must be ensured that it is not converted by UV disinfection into products more dangerous to the consumer than tetrachloroethene itself.

On photoexcitation, the relatively weak C–Cl bond (of the order of 80 kcal mol^{-1}) will be broken (reaction

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(1). In a protic solvent, such as water, olefins undergo solvent addition [4,5]. Thus we must consider reaction (2) as a further route in the photolytic degradation of tetrachloroethene. In many aromatic halogenides [6–8], the (chlorine-containing) triazine herbicide atrazine [9] and chlorinated dioxins [10], heterolytic C–Cl cleavage is a major decomposition process in polar solvents such as water. Hence for the present system we may also write reaction (3). Often molecular elimination processes also occur. For example, in the photolysis of 1,2-dichloroethene at 185 nm, the formation of chloroacetylene and acetylene has been observed [11]. Hence in the present system, we must also consider the formation of dichloroacetylene and chlorine as an additional pathway.



Thus products will arise from the subsequent reactions of the intermediates formed in these four primary processes.

In the present paper, the photolysis of tetrachloroethene in aqueous solution has been investigated, and it is shown that, in the presence of oxygen, a short chain reaction is induced. Radiation-chemical techniques (using ionizing radiation) were employed to obtain some of the necessary information for the assessment of the mechanistic details.

2. Experimental details

Tetrachloroethene (Merck; minimum purity, 99.8%) was used without further purification. Aqueous solutions were made up in Milli-Q-filtered (Millipore) water. For photolysis at 254 nm, a low-pressure Hg arc (Sterisol N 30/89, Heraeus Noblelight, Hanau; the 185 nm line is not emitted) was used. Irradiations were carried out in 1 cm Suprasil quartz cells (Hellma). The fluence rate was determined by ferrioxalate and peroxodisulphate actinometry [12]. For deoxygenation (for the apparatus, see Ref. [13]), an Ar stream was passed through a bubbler filled with neat tetrachloroethene to avoid tetrachloroethene depletion of the aqueous solution. The final tetrachloroethene concentration was determined spectrophotometrically. UV spectra were run on a Perkin-Elmer Lambda 16 instrument.

For the determination of the consumption of tetrachloroethene and the formation of trichloroethene, these compounds were separated by high performance liquid chromatography [14] on a 250 mm RP-18 column with water-acetonitrile (6 : 4) as eluent. Detection was

at 208 nm, where these compounds have absorption coefficients of the order of $10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ [1]. The anions were determined by high performance ion chromatography on a Dionex 2010i Instrument (Ion Pac AS9 column with an Ion Pac AG9 pre-column; eluent, $1.8\times 10^{-3}\text{ mol dm}^{-3}\text{ CO}_3^{2-}$ plus $1.7\times 10^{-3}\text{ mol dm}^{-3}\text{ HCO}_3^-$; flow rate, 1 ml min^{-1} ; retention times, Cl^- (3.4 min), $\text{HCCl}_2\text{COO}^-$ (4.6 min), CCl_3COO^- (12.6 min), oxalate (15 min; flow rate, 2 ml min^{-1}).

Carbon dioxide and carbon monoxide were determined as methane by gas chromatography [13,15]. Quantitation of the products was possible with an error bar of 5% or less. Considering that there are other systematic errors, the quantum yields compiled in Table 1 (see Section 3.1) are estimated to have slightly larger error bars.

Active chlorine was determined spectrophotometrically at pH 1 with *N,N,N',N'*-tetramethylphenylenediamine. At this low pH, active chlorine still reacts rapidly ($t_{1/2} < 1\text{ min}$) with this compound giving rise to the strong blue colour of the *N,N,N',N'*-tetramethylphenylenediamine radical cation ($\epsilon(565\text{ nm}) = 12\,500\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ [16]), whereas H_2O_2 is unreactive under these conditions on this time scale. Trichloroacetaldehyde was determined spectrophotometrically with 2-thiobarbituric acid [17].

The pulse radiolysis technique and apparatus used in the present study have been described recently [18].

The structure of bis-pentachloroethyltetroxide was simulated using the MOPAC package (version 5.0, QCPE program 455, AM1, full geometry optimization, precise option) on a Silicon Graphics workstation.

3. Results and discussion

3.1. Overall degradation of tetrachloroethene and determination of product quantum yields

The molar absorption coefficient of tetrachloroethene at 254 nm in aqueous solution has been determined to be $225\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. At a concentration of $3\times 10^{-5}\text{ mol dm}^{-3}$, the absorbance in a 1 cm cell is only 0.06, i.e. conditions of “negligible absorption” prevail [19], and a plot of $\ln([\text{tetrachloroethene}]/[\text{tetrachloroethene}]_0)$ vs. the fluence yields a straight line (Fig. 1; $[\text{tetrachloroethene}]_0$ denotes the tetrachloroethene concentration prior to irradiation). From its slope, the quantum yield of tetrachloroethene consumption has been calculated to be 0.84 when the solutions are saturated with oxygen (Table 1).

In the absence of oxygen this value is considerably lower ($\Phi(\text{tetrachloroethene consumption}) = 0.34$). It is shown below that the higher value in the presence of oxygen is due to the contribution of a short chain reaction.

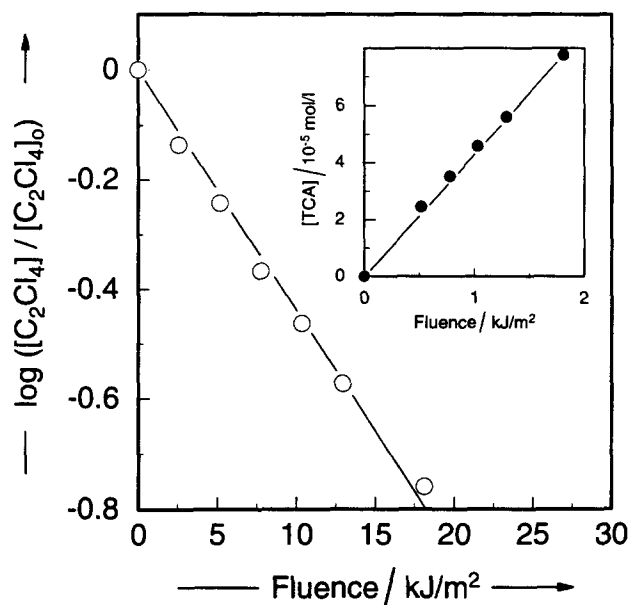


Fig. 1. UV degradation at 254 nm of tetrachloroethene in air-saturated aqueous solutions. $\log([tetrachloroethene]/[tetrachloroethene]_0)$ is plotted against the fluence; $[tetrachloroethene]_0 = 3 \times 10^{-5} \text{ mol dm}^{-3}$. Inset: build-up of trichloroacetic acid (TCA); $[tetrachloroethene]_0 = 1.1 \times 10^{-3} \text{ mol dm}^{-3}$.

Table 1

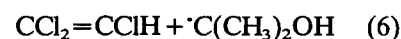
Products and their quantum yields in the 254 nm photolysis of tetrachloroethene in oxygenated aqueous solution

Product	Quantum yield
Chloride ion	2.05
Carbon dioxide	0.62
Trichloroacetic acid	0.41
Dichloroacetic acid	0.08
Hypochlorite	0.08
Carbon monoxide	0.03
Trichloroacetaldehyde	<0.01
Chloroform	0.002
Carbon tetrachloride	0.001
Oxalic acid	<0.001
Hexachloroethane	<0.001
Tetrachloroethene consumption	0.84

The product yields must increase linearly with increasing irradiation time as long as the tetrachloroethene concentration is not significantly depleted and the product in question is not photolysed at the excitation wavelength. Under our conditions, this prerequisite is practically fulfilled for all products at the low UV fluences used, and linear dose–yield plots are obtained (cf. inset in Fig. 1) when near-saturated tetrachloroethene solutions ($1.1 \times 10^{-3} \text{ mol dm}^{-3}$) are photolysed. From the slopes of such dose–yield plots, the quantum yields were calculated. They are compiled in Table 1.

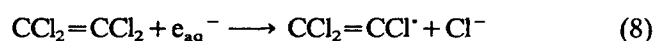
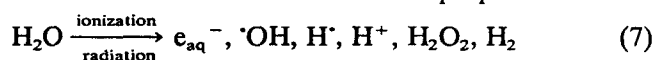
3.2. The quantum yield of reaction (1)

In order to assess the quantum yield of reaction (1), experiments were performed in deoxygenated solutions containing propan-2-ol. Under these conditions, both the Cl atoms and the trichlorovinyl radicals are scavenged by propan-2-ol (reactions (5) and (6)).



The rate constant for reaction (5) is close to diffusion controlled ($k_5 = 6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [20] and that of reaction (6) has recently been determined as $k_6 = 4.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [21] (for a compilation of the rate constants pertinent to this study, see Table 2). Hence, at a propan-2-ol concentration of 0.6 mol dm^{-3} used in these experiments, the lifetime of the trichlorovinyl radicals can be estimated from the pseudo-first-order reaction (6) ($t_{1/2} = 2.8 \times 10^{-8} \text{ s}$), and bimolecular, free radical reactions of the trichlorovinyl radical can be neglected. Under such conditions, the quantum yield of trichloroethene formation, $\Phi(CCl_2 = CClH) = 0.2$, reflects the quantum yield of reaction (1) (for other ways of determining $\Phi(1)$, see Section 3.9).

It is well known that α -hydroxyalkyl radicals and, especially, their corresponding radical anions are capable of reductively dehalogenating halides thus inducing a chain reaction [22,23]. If this happens in the present system, $\Phi(CCl_2 = CClH)$ will not be a measure of $\Phi(1)$. In order to check this, trichlorovinyl radicals were generated radiolytically [24] by reacting the solvated electron from the radiolysis of water (reaction (7)) with tetrachloroethene (reaction (8)) in the presence of the same concentration of propan-2-ol.



The radiolytic yield of the solvated electron is $G(e_{aq}^-) = 2.8 \times 10^{-7} \text{ mol J}^{-1}$ and that of trichloroethene is $G(CCl_2 = CClH) = 2.75 \times 10^{-7} \text{ mol J}^{-1}$ under these conditions (cf. also Ref. [25]), i.e. these values are identical within experimental error, and we conclude that no chain reaction is induced at this pH ($\text{pH} \leq 7$); whether or not a chain reaction occurs at high pH, where the propan-2-ol-derived radical anion, a more powerful reductant [26], predominates [27] has not been investigated.

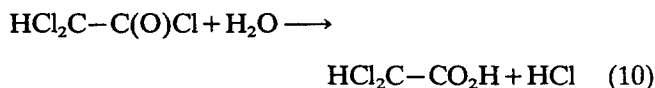
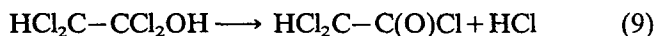
3.3. The quantum yield of reactions (2) and (3)

By analogy with the photolytic behaviour of other olefins, it has been considered that tetrachloroethene

Table 2
Compilation of rate constants pertinent to this study

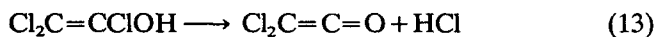
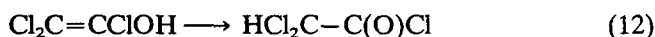
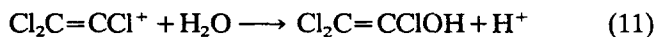
Reaction	Rate constant	Reference
$k_{16}[\text{Cl}^{\cdot} + \text{Cl}_2\text{C}=\text{CCl}_2 \rightarrow \text{CCl}_3-\text{CCl}_2^{\cdot}]$	$2.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	This work
$k_5[\text{Cl}^{\cdot} + \text{HC}(\text{CH}_3)_2\text{OH} \rightarrow \text{HCl} + \cdot\text{C}(\text{CH}_3)_2\text{OH}]$	$6.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[20]
$k_{19}[\text{Cl}^{\cdot} + (\text{CH}_3)_3\text{COH} \rightarrow \text{HCl} + \cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}]$	$3.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[20]
$k_{51}[\text{Cl}^{\cdot} + \text{HCO}_3^- \rightarrow \text{HCl} + \text{CO}_3^{\cdot-}]$	$2.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	This work
$k_{52}[\text{Cl}^{\cdot} + \text{CO}_3^{2-} \rightarrow \text{Cl}^- + \text{CO}_3^{\cdot-}]$	$5.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	This work
$k_{15}[\text{Cl}_2\text{C}=\text{CCl}^{\cdot} + \text{O}_2 \rightarrow \text{Cl}_2\text{C}=\text{CClO}_2^{\cdot}]$	$3.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[21]
$k_6[\text{Cl}_2\text{C}=\text{CCl}^{\cdot} + \text{HC}(\text{CH}_3)_2\text{OH} \rightarrow \text{Cl}_2\text{C}=\text{CHCl} + \cdot\text{C}(\text{CH}_3)_2\text{OH}]$	$4.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[21]
$k_{18}[\text{Cl}_2\text{C}=\text{CCl}^{\cdot} + (\text{CH}_3)_3\text{COH} \rightarrow \text{Cl}_2\text{C}=\text{CHCl} + \cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}]$	$1.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[21]
$k_{30}[\text{Cl}_2\text{C}=\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{CO}_2]$	9 s^{-1}	[28]

may also display a polar structure in the excited state that leads to the addition of a water molecule (reaction (2)). The resulting product $\text{HCl}_2\text{C}-\text{CCl}_2\text{OH}$ will rapidly yield dichloroacetic acid (reactions (9) and (10)).



From what is known about the hydrolysis of trichloromethanol, phosgene [28] and tetrachlorosuccinoyldichloride [29], we estimate that reaction (9) will take place in the submicrosecond to microsecond time range, whereas reaction (10) will be of the order of milliseconds.

An alternative route to dichloroacetic acid may start with reaction (3) as the primary process. The carbocation formed in this reaction will react with water and (after HCl elimination and hydrolysis) yield dichloroacetic acid. Possible pathways are given by reactions (11) and (12), followed by (10) or (13), followed by (14).



Support for a non-radical mechanism comes from the observation that the scavenging with tert-butanol of the two intermediates formed in reaction (1), the trichlorovinyl radical and the Cl atom, has no effect on the quantum yield of dichloroacetic acid formation. Thus the yield of dichloroacetic acid is the same in the absence and presence of O_2 , even at high concentrations of hydrogen-donating scavengers which fully scavenge the Cl atoms (see below). This is shown in Fig. 2.

The present data do not allow us to distinguish between reactions (2) and (3) as the primary process leading to dichloroacetic acid, and hence we do not

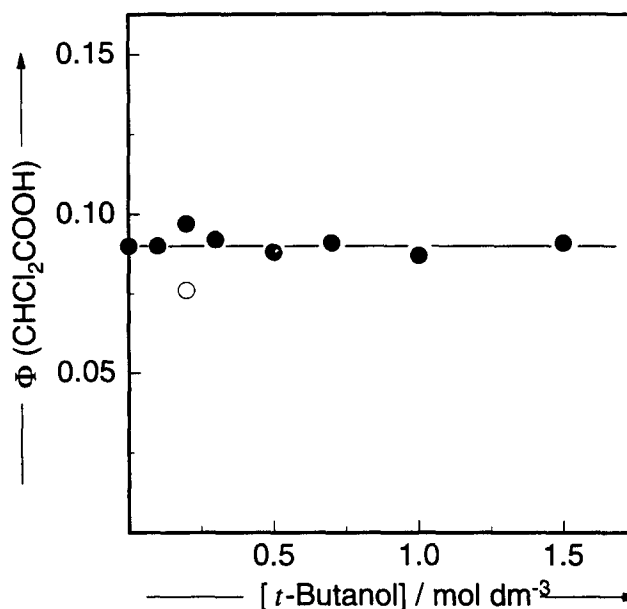


Fig. 2. Quantum yields of dichloroacetic acid formation in the presence of tert-butanol with (○) and without (●) oxygen.

know which reaction predominates. However, the sum of these two processes must have $\Phi(2+3) = 0.08$.

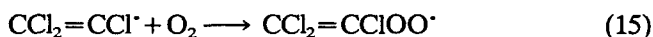
3.4. The quantum yield of reaction (4)

In the primary reaction (4), dichloroacetylene and chlorine are formed. Chlorine (hypochlorite) is observed as a product (Table 1); it may also originate from other sources (see below). Hence in order to assess $\Phi(4)$, we must look for the formation of dichloroacetylene. This product was not detected by gas chromatography/mass spectrometry (GC/MS). If it had hydrolysed, the expected products would be either chloroacetic acid or glyoxal. Neither of these products was detected, even when the photolysis was carried out in the absence of oxygen. This precaution was taken because it has been reported that dichloroacetylene is readily autoxidized [30]. A second attempt to determine dichloroacetylene involved derivatization with bromine water [31] by injection of bromine through a serum cap into the

deoxygenated, photolysed solution. This approach to detect dichloroacetylene also failed. Thus we conclude that reaction (4) must be of minor importance if it occurs at all.

3.5. Formation of the trichlorovinylperoxyl radical

In the presence of O₂ (absence of an excess of propan-2-ol), the trichlorovinyl radical (from reaction (1)) is readily converted into the corresponding peroxy radical (reaction (15)). These trichlorovinylperoxy radicals have a characteristic absorption at 580 nm [21]. This allowed the rate constant of reaction (15) to be determined by pulse radiolysis. A value of $k_{15} = 3.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has been measured [21].



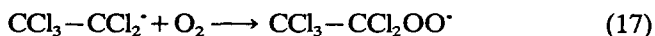
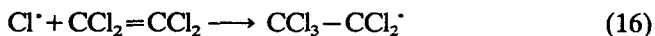
According to pulse radiolytic data, these radicals decay by second-order kinetics without a noticeable contribution from a first-order decay process [21]. However, any unimolecular decay slower than 10^4 s^{-1} would not be recognized at the high radical concentrations prevailing in these experiments.

In order to obtain further information on this system, oxygenated neat tetrachloroethene was pulse irradiated. In this solvent, the trichlorovinylperoxy radicals have an absorption maximum at 540 nm (in water, 580 nm [21]). Even at a prevailing tetrachloroethene concentration of 9.8 mol dm^{-3} , the decay of these intermediates was second order, with a maximum contribution from a first-order decay (when extrapolated to zero peroxy radical concentration) of 500 s^{-1} , i.e. these radicals do not react with tetrachloroethene ($k < 50 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

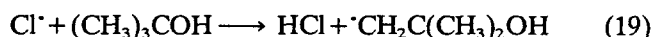
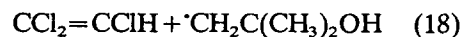
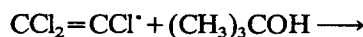
The competition between reactions (6) and (15) in O₂-saturated solutions containing 0.1 mol dm^{-3} propan-2-ol leads to a reduced formation of trichloroethene compared with deoxygenated solutions. From the measured value of $\Phi(\text{Cl}_2\text{C}=\text{CHCl}) = 0.1$ and k_{15} given above, we calculate $k_6 = 4.8 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in good agreement with the value of $4.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [21] which is based on more data points.

3.6. Reaction of the Cl atom

The Cl atom reacts very rapidly with tetrachloroethene by adding to the C=C double bond (reaction (16)). A rate constant of $k_{16} = 2.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has been arrived at below. In the presence of O₂, the pentachloroethyl radical is converted into the corresponding peroxy radical (reaction (17)); $k_{17} = 2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [32,33]).



It has been shown that tert-butanol reacts only slowly with the trichlorovinyl radical ($k_{18} \approx 1.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [21], but rapidly with the Cl atom ($k_{19} = 3.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [20]. Thus, at moderate tert-butanol concentrations, the Cl atoms are effectively scavenged by this alcohol while the trichlorovinyl radicals are not.



Thus scavenging of the Cl atom by tert-butanol will prevent the formation of the pentachloroethylperoxy radical and hence must have a major effect on the yields of those products which have the pentachloroethylperoxy radical as a precursor. A case in point is trichloroacetic acid. In Fig. 3, the quantum yield of formation of trichloroacetic acid is plotted as a function of the logarithm of the tert-butanol concentration. It declines in a sigmoidal fashion as expected from the competition between reactions (16) and (19).

In the inset of Fig. 3 these data are plotted in a Stern–Volmer-type plot. From its slope, $k_{19}/k_{16} = 1.07$ is calculated. Since $k_{19} = 3.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is known, $k_{16} = 2.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ results from the data.

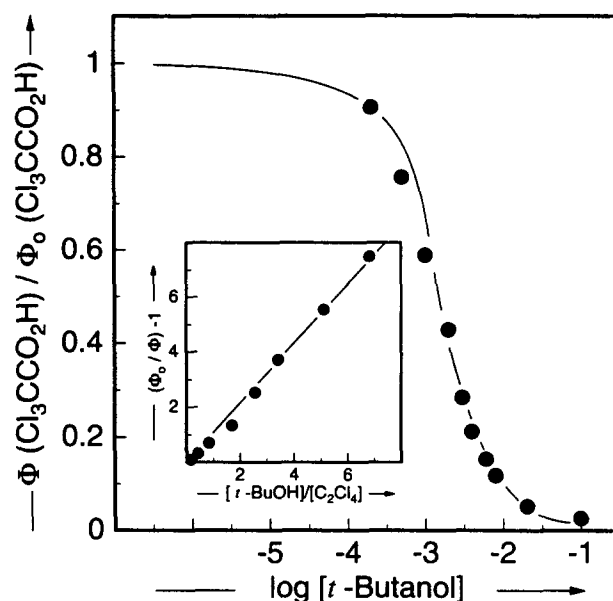
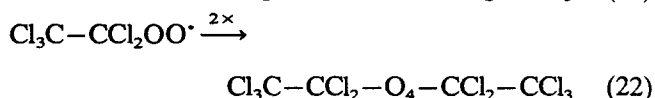
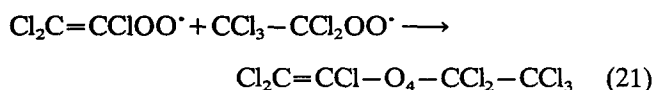
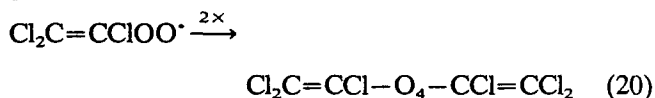


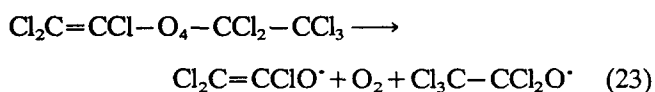
Fig. 3. Effect of tert-butanol on the formation of trichloroacetic acid in the 254 nm photolysis of air-saturated aqueous solutions ($[\text{O}_2] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$) of tetrachloroethene ($[\text{C}_2\text{Cl}_4] = 1.1 \times 10^{-3} \text{ mol dm}^{-3}$). The quantum yield of trichloroacetic acid formation normalized to the value in the absence of tert-butanol is plotted against the logarithm of the tert-butanol concentration. Inset: a Stern–Volmer-type plot using these data.

3.7. Bimolecular decay of the peroxy radicals $\text{Cl}_2\text{C}=\text{CClO}_2^{\cdot}$ and $\text{CCl}_3-\text{CCl}_2\text{O}_2^{\cdot}$

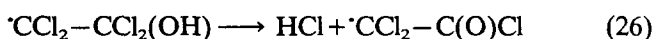
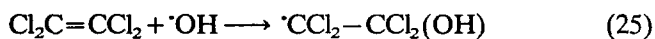
As previously discussed, there are two major primary peroxy radicals, $\text{Cl}_2\text{C}=\text{CClO}_2^{\cdot}$ and $\text{CCl}_3-\text{CCl}_2\text{O}_2^{\cdot}$. These peroxy radicals will decay bimolecularly by reacting with one another and by self-termination reactions. They do not have H atoms in an α -position to the peroxy radical function. Hence the intermediate tetroxides (reactions (20)–(22)) have fewer decay routes compared with primary and secondary peroxy radicals [34].



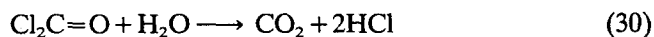
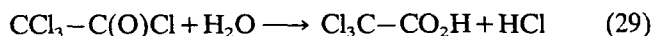
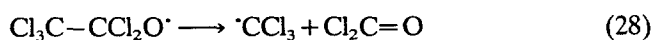
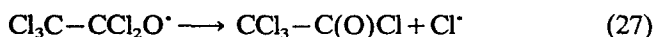
The likely products are O_2 and the corresponding oxyl radicals (e.g. reaction (23)).



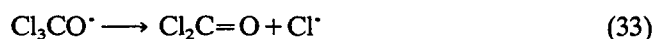
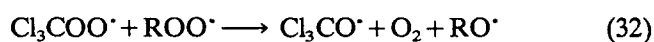
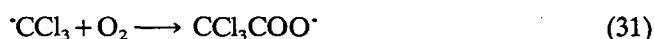
For the radical $\text{Cl}_2\text{C}=\text{CClO}^{\cdot}$, the mesomeric form $^{\cdot}\text{CCl}_2-\text{C}(\text{O})\text{Cl}$ can be written. In its carbon-centred mesomeric form it is capable of reacting with O_2 to yield the secondary peroxy radical $\text{Cl}(\text{O})\text{C}-\text{CCl}_2\text{O}_2^{\cdot}$ (reaction (24)). It is also formed by the addition of OH radicals to tetrachloroethene in the presence of oxygen (reactions (25), (26) and (24)) [35].



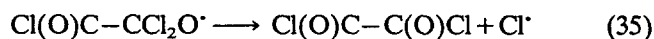
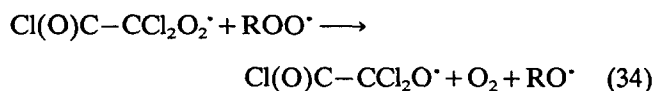
The $\text{Cl}_3\text{C}-\text{CCl}_2\text{O}^{\cdot}$ radicals are expected to decay unimolecularly by splitting either the neighbouring C–Cl or C–C bond (reactions (27) and (28)). Trichloroacetylchloride formed in reaction (27) will rapidly hydrolyse in the aqueous environment, yielding the final products trichloroacetic acid and HCl (reaction (29)). Similarly, phosgene will also rapidly hydrolyse (reaction (28)). The rate constant of the spontaneous hydrolysis of phosgene in water (reaction (30)) has been reported to be around $k_{30} \approx 6 \text{ s}^{-1}$ (at 25 °C) [36]. This rate constant has recently been redetermined by pulse radiolysis as $k_{30} = 9 \text{ s}^{-1}$ [28]. The products of this reaction are carbon dioxide and HCl. They are major final products (Table 1).



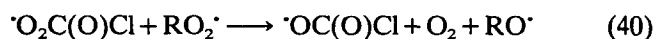
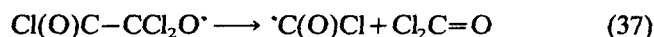
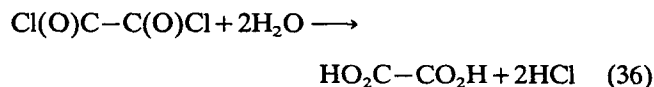
In reaction (28), the trichloromethyl radical is formed which will react with O_2 to yield the corresponding peroxy radical (reaction (31), $k_{31} = 3.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [37]). In bimolecular radical–radical processes it is likely to yield the trichloromethoxyl radical (reaction (32)) which will decay into phosgene and a Cl atom (reaction (33)). In the gas phase the decomposition energy of the trichloromethoxyl radical has an activation energy of only $E_a < 40 \text{ kJ mol}^{-1}$. Thus this radical will not undergo bimolecular termination reactions [38].



A further secondary peroxy radical, $\text{Cl}(\text{O})\text{C}-\text{CCl}_2\text{OO}^{\cdot}$, is formed in reaction (24). In a reaction similar to process (32)/(33), this radical could in principle be a further source of Cl atoms (reactions (34) and (35)).



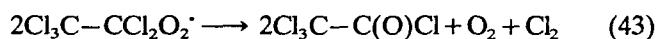
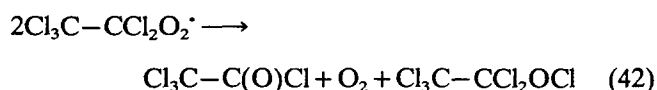
The resulting product $\text{Cl}(\text{O})\text{C}-\text{C}(\text{O})\text{Cl}$ will hydrolyse yielding oxalic acid and HCl (reaction (36)). However, oxalic acid is only a very minor product, if formed at all, and hence reaction (35) can be disregarded as being of any major importance. Instead, we may formulate reaction (37) as the alternative pathway. We were unable to detect major amounts of CO and hence reaction (38) must also be of minor importance. For the energy of the C–Cl bond $^{\cdot}\text{C}(\text{O})\text{Cl}$, we calculate from the data available in the literature [39,40] a value of 30 kJ mol^{-1} . Thus the $^{\cdot}\text{C}(\text{O})\text{Cl}$ intermediate may be sufficiently long lived to be scavenged by O_2 (reaction (39)). Termination with other peroxy radicals would lead to carbon dioxide and a Cl atom (reactions (40) and (41)).



Thus Cl atoms are not only formed in the primary photolysis process (reaction (1)), but all the ensuing peroxy radicals discussed so far have the potential to yield further Cl atoms (reactions (27), (33), (35), (38) and (41)). They will initiate a chain reaction by adding to tetrachloroethene (reaction (16)). This addition reaction is very fast, and a rate constant of $k_{16} = 2.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has been given above. The bimolecular decay rate constant of the $\text{Cl}(\text{O})\text{C}-\text{CCl}_2\text{O}_2^\cdot$ radicals has been determined by pulse radiolysis to be $1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [35], and it is likely that the other chlorinated peroxy radicals decay with similarly high rate constants. Thus, at the low fluence rate of our photolytic experiments, the steady state concentration of the peroxy radicals will not exceed $10^{-8} \text{ mol dm}^{-3}$. Due to the fast addition of O_2 to the vinyl and chlorinated alkyl radicals (cf. reactions (15) and (17)), their steady state concentration is lower by several orders of magnitude. Hence it follows that, in the bulk solution, the Cl atoms will not react with the radicals but will be fully scavenged by tetrachloroethene.

3.8. Possible termination reactions

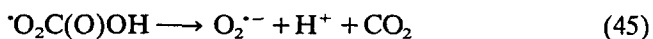
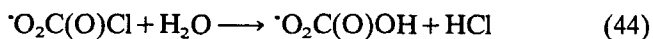
A chain reaction is observed, but the chain length is very short, about two. This raises the question as to the nature of the chain termination reactions. It appears that all bimolecular reactions of the peroxy radicals lead to the formation of Cl atoms, i.e. these reactions are not true termination reactions, since they would continue the chain. Hence we are forced to postulate efficient chain-breaking processes. We may tentatively assume that, besides leading to the formation of Cl atoms, the bimolecular termination of the $\text{Cl}_3\text{C}-\text{CCl}_2\text{O}_2^\cdot$ radicals may also lead to precursors of hypochlorite (e.g. $\text{Cl}_3\text{C}-\text{CCl}_2\text{OCl}$; reaction (42)) or directly to chlorine (reaction (43)).



The overall reaction (43) may involve two Cl atoms (cf. reactions (22) followed by (23) and (27)) which combine in the cage. We observed cage products such as CCl_4 and C_2Cl_6 , but these products have very low quantum yields (Table 1). Hence we wonder whether reaction (43) could also proceed in a true molecular process (as expected for reaction (42)). The difficulty is that this process would have to occur from an eight-membered transition state (cf. intermediate formed in reaction (22)). However, computer modelling of the structure of the bis-pentachloroethyltetroxide shows that, even at energy minimized conditions, the Cl atoms relevant for reaction (43) to proceed approach one

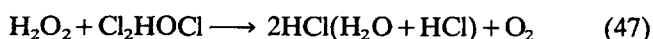
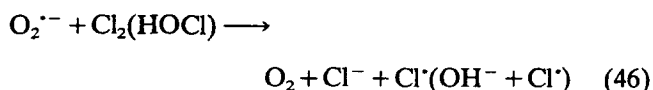
another at a distance close to the van der Waals' distance.

Molecular chlorine (hypochloric acid) is indeed found with a low quantum yield (Table 1). Since the chlorine yield is low, there must be other chain-breaking processes and/or material must be formed which consumes active chlorine in a reasonably rapid reaction during or after photolysis. There are two conceivable reductants, $\text{HO}_2^\cdot/\text{O}_2^{\cdot-}$ and H_2O_2 . The former could be formed when the $^\cdot\text{O}_2\text{C}(\text{O})\text{Cl}$ radical hydrolyses (reactions (44) and (45)).

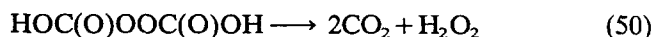
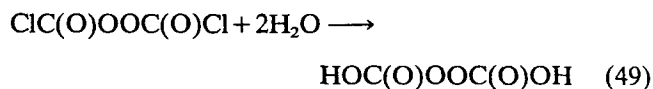


The $^\cdot\text{O}_2\text{C}(\text{O})\text{OH}$ radical is also formed when the OH radical reacts with formic acid in oxygenated solutions and is a well-known source of $\text{O}_2^{\cdot-}$ radicals [24,34].

The superoxide radical $\text{O}_2^{\cdot-}$ is rather long lived with respect to its self-termination reaction [41]. However, it can more rapidly interact with strongly oxidizing peroxy radicals [42,43]. Hence it was of interest to determine whether $\text{O}_2^{\cdot-}$ is an intermediate in the present system. The self-termination of superoxide radicals can be enhanced by the enzyme superoxide dismutase (SOD). In the present system, SOD addition had no effect on the product quantum yield. Although this excludes its interaction with other peroxy radicals, this observation does not indicate the total absence of $\text{O}_2^{\cdot-}$ in this system. The active chlorine reaches much higher levels than the added SOD, and hence may have mopped up the $\text{O}_2^{\cdot-}$ radical anyway (reaction (46)). In this reaction, a Cl atom is formed and hence $\text{O}_2^{\cdot-}$ cannot act as a chain breaker. Hence we are left with H_2O_2 (overall reaction (47), $k_{47} = 2.8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [44].



There are not many obvious routes to H_2O_2 . Free $\text{ClC}(\text{O})\text{O}^\cdot$ radicals formed in reaction (40) will not have a reasonable lifetime [45] and hence will not be able to undergo bimolecular reactions. However, for the bimolecular decay of the $\text{ClC}(\text{O})\text{O}_2^\cdot$ radicals (from reaction (39)), a six-membered transition state leading to O_2 and $\text{ClC}(\text{O})\text{OOC}(\text{O})\text{Cl}$ can be written (reaction (48)). It is recalled that such concerted processes are favoured in the decay of tetroxides (cf. the Russell mechanism [34]). The resulting intermediate will rapidly hydrolyse via the percarbonate into CO_2 and H_2O_2 (reactions (49) and (50)).



As it stands, the chain-breaking process must remain speculative. It is hoped that further studies on similar systems will provide more detailed information.

3.9. The primary photochemical processes: further considerations

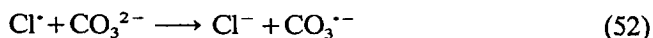
The quantum yield of tetrachloroethene consumption in the absence of oxygen ($\Phi(-\text{C}_2\text{Cl}_4) = 0.34$) mentioned above cannot be used to assess the quantum yields of the sum of all primary processes, because the radicals formed in this reaction can also disproportionate and re-form tetrachloroethene as well as undergo dimerization reactions. However, when the Cl atoms are scavenged by tert-butanol and the trichlorovinyl radicals are scavenged by oxygen, the resulting trichlorovinylperoxyl radicals decay in bimolecular processes by releasing practically all the chlorine content as chloride ions. Under such conditions, $\Phi(\text{Cl}^-) = 1.05$ has been measured. Considering a contribution of reactions (2) and (3) to the chloride yield with $\Phi(\text{Cl}^-) = 0.16$ (twice $\Phi(\text{dichloroacetic acid})$), the remaining chloride must have resulted from reaction (1). Hence, from this experiment, $\phi(1) = \frac{1}{2} \times (1.05 - 0.16) = 0.22$ is calculated. The consumption of tetrachloroethene has been measured under these conditions as $\Phi(-\text{C}_2\text{Cl}_4) = 0.34$. Subtracting $\Phi(2+3) = 0.08$ from this value will result in $\Phi(1) = 0.26$. In Section 3.2, a value of $\Phi(1) = 0.2$ has been determined. The average of these three values is $\Phi(1) = 0.23 \pm 0.03$.

We thus conclude that, at 254 nm, tetrachloroethene undergoes two (or three) primary photolytic processes that lead to products: the homolytic scission of a C-Cl bond which occurs with a quantum yield of $\Phi(1) = 0.23 \pm 0.03$ and water addition and/or heterolytic scission and hence dichloroacetic acid formation. The quantum yield of this acid is 0.08 (Table 1) and thus $\Phi(2+3) = 0.08$. The total quantum yield of product-forming processes is therefore only $\Phi(\text{product-forming processes}) = 0.31 \pm 0.03$. Thus the majority of the excited tetrachloroethene molecules are deactivated and return to their ground state. In 1,2-dichloroethene in the liquid phase, a major reaction of the excited state is the $\text{cis} \rightleftharpoons \text{trans}$ isomerization [11]. A rotation around the C=C double bond in the excited state would not be noticeable in the present system and may well be the major route of deactivation. Also, cage recombination reactions of the species formed in reactions (1) and

(3) are potential processes that lead to a decrease in product quantum yields.

3.10. Relevance for the UV disinfection of drinking water

The product trichloroacetic acid is a registered herbicide (although not in general use) and hence it falls under the German drinking water act (TVO) which sets a lower limit of $0.1 \mu\text{g dm}^{-3}$ for total or $0.05 \mu\text{g dm}^{-3}$ for individual herbicides. The ubiquitous halogenated hydrocarbons must not exceed a concentration of $10 \mu\text{g dm}^{-3}$. Hence at a fluence of 400 J m^{-2} , which is now believed to be adequate for the UV disinfection of drinking water [46], the formation of trichloroacetic acid may reach or even exceed the limiting value of $0.05 \mu\text{g dm}^{-3}$, if we take the values of our study (made in distilled water) and calculate the expected trichloroacetic acid yield in drinking water with the condition that it contains the maximum allowed tetrachloroethene concentration of $10 \mu\text{g dm}^{-3}$. However, drinking water always contains some bicarbonate/carbonate. These ions readily react with the precursor of trichloroacetic acid, the Cl atom (reactions (51) and (52)). Hence they reduce the yield of trichloroacetic acid drastically (Fig. 4).



In the inset of Fig. 4, Stern-Volmer-type plots are shown and from their slopes (using $k_{16} = 2.8 \times 10^8 \text{ dm}^3$

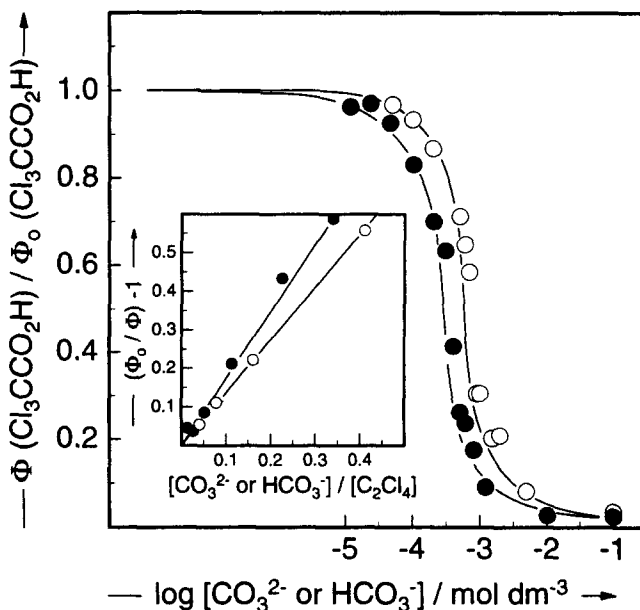


Fig. 4. Effects of carbonate (●) and bicarbonate (○) ions on the formation of trichloroacetic acid in the 254 nm photolysis of air-saturated ($[\text{O}_2] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$) aqueous solutions of tetrachloroethene ($[\text{C}_2\text{Cl}_4] = 1.1 \times 10^{-3} \text{ mol dm}^{-3}$). The observed quantum yield normalized to that in the absence of any additive is plotted as a function of the logarithm of the additive concentration. Inset: Stern-Volmer-type plots using these data.

$\text{mol}^{-1} \text{s}^{-1}$, see above) we calculate $k_{s1} = 2.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{s2} = 5.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It is seen from these data that the carbonate ion reacts more readily with the chlorine atom than does the bicarbonate ion. This observation is in line with the known relative reactivity of these two ions with another reactive electrophilic radical, the OH radical [47].

From these data, it is concluded that trichloroacetic acid formation from the photolysis of potentially present tetrachloroethene will be no problem in the UV disinfection of drinking water using 254 nm irradiation.

Acknowledgements

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