Reaction of the OH Radical with Tetrachloroethene and Trichloroacetaldehyde (Hydrate) in Oxygen-free Aqueous Solution

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Hydroxyl radicals are generated radiolytically in N_2O-saturated aqueous solutions and are reacted with either tetrachloroethene or trichloroacetaldehyde hydrate. The primary products after irradiation are tetrachlorosuccinic acid ($G = 2.3 \times 10^{-7}$ mol J^{-1} and 2.7×10^{-7} mol J^{-1}, respectively) and chloride ions ($G = 11.6 \times 10^{-7}$ mol J^{-1} and 7.3×10^{-7} mol J^{-1}, respectively). The former decomposes into trichloroacrylic acid and carbon dioxide ($E_a = 115$ kJ mol^{-1}). From tetrachloroethene some dichloroacetic acid is also formed ($G = 0.2 \times 10^{-7}$ mol J^{-1}). Trichloroacetic acid is not among the products.

Kinetic studies were carried out by pulse radiolysis. In the case of trichloroacetaldehyde hydrate there is a jump in conductivity increase of $G(H^+) \approx 2 \times G(^{\bullet}OH)$ within ≤ 5 μs and no further increase in conductivity at later times. It is concluded that the OH-radicals abstract the carbon-bound H-atom and the resulting $CCl_3C(OH)_2^{\bullet}$ radicals rapidly eliminate HCl forming $^{\bullet}CCl_2CO_2H$ radicals which dissociate and dimerize yielding tetrachlorosuccinic acid.

In the case of the reaction of the OH-radical with tetrachloroethene the conductivity build-up is biphasic. In the first step one equivalent H^+ is formed when the primary $^{\bullet}CCl_2CCl_2OH$ radical eliminates HCl yielding the $^{\bullet}CCl_2C(O)Cl$ radical ($k > 7 \times 10^5$ s^{-1}). Upon dimerization ($2k = 6.9 \times 10^8$ dm^3 mol^{-1} s^{-1}) $Cl(O)CCCl_2CCl_2C(O)Cl$ is formed which hydrolyses ($k = 5$ s^{-1}). Only one conductivity equivalent is liberated, and it is concluded that the ensuing monoanion rapidly eliminates a chloride ion (no conductivity change) yielding tetrachlorosuccinic anhydride. It subsequently hydrolyses at a later stage, not resolved by pulse radiolysis, to tetrachlorosuccinic acid.

Worldwide, chlorinated hydrocarbons such as tetrachloroethene and trichloroethene are produced in the order of 10^6 tons per year. Despite careful recycling and controlled disposal of non-recyclable material most of them reach the atmosphere; they are washed down by the rain, eventually, and together with (*Z*)-1,2-dichloroethene and vinyl chloride (formed by their bacterial degradation in the soil), they are now ubiquitous contaminants of the ground water. In addition, they also can reach the ground water by industrial accidents and criminal negligence. In many industrial zones they are now of major concern in drinking-water processing. Besides, adsorption on active carbon transfers the problem only from the liquid to solid phase and hence destructive methods are more adequate for dealing with this problem. It has been shown that it is possible to strip the halogenated hydrocarbons and destroy them in the gas phase photolytically[1,2] or radiolytically by high-energy electrons (E-beam technology).[2] Their destruction by E-beam *in situ*, *i.e.* while still dissolved in the water has also been considered.[3-5]

There is an increasing interest in utilizing OH-radicals for the degradation of chlorinated hydrocarbons for pollution control in drinking-water and waste water treatment. Hydroxyl radicals are generated in radiolysis, as well as in the so-called 'advanced oxidation processes' involving UV–photolysis of H_2O_2, UV–photolysis of O_3 or by reacting H_2O_2 with O_3;[6,7] for reviews see refs. 8 and 9. OH-Radicals are also produced in the conventional ozonation of drinking-water and it is believed that the degradation of pollutants with relatively low reactivity towards O_3 [$k(O_3 + C_2Cl_4) < 0.1$ dm^3 mol^{-1} s^{-1}][10] occurs mainly *via* an OH-radical-induced route.[11]

In these technical processes oxygen is always present which converts the OH-radical-induced radicals into their corresponding peroxyl radicals which undergo a complex chemistry (for a review see ref. 12). Nevertheless, for a more complete characterization of the free-radical chemistry of organohalides, the behaviour of these radicals under anoxic conditions must also be explored. In the present paper we discuss the reaction of OH radicals with tetrachloroethene in the absence of oxygen. Following OH-radical addition to tetrachloroethene [reaction (1); $k_1 = 2.6 \times 10^9$ dm^3 mol^{-1} s^{-1}][13] two alternative reactions

$$Cl_2C{=}CCl_2 + {}^{\bullet}OH \longrightarrow HOCl_2C\text{–}C(Cl_2)^{\bullet} \qquad (1)$$

have been discussed in the literature: a rapid HCl elimination[14] [reaction (2); $k_2 > 10^5$ s^{-1}] and a rapid chlorine shift [reaction

$$HOCl_2C\text{–}C(Cl_2)^{\bullet} \longrightarrow HCl + Cl(O)C\text{–}C(Cl_2)^{\bullet} \qquad (2)$$

(3)] prior to a rapid HCl elimination [reaction (4)].[15,16]

$$HOCl_2C\text{–}C(Cl_2)^{\bullet} \longrightarrow Cl_3C\text{–}C(OH,Cl)^{\bullet} \qquad (3)$$

$$Cl_3C\text{–}C(OH,Cl)^{\bullet} \longrightarrow HCl + Cl_3C\text{–}C(O)^{\bullet} \qquad (4)$$

Reaction (3) had been invoked to explain the observed formation of trichloroacetic acid (in the presence of O_2). We have recently shown that this acid is also formed in the UV-photolysis of tetrachloroethene in the presence of oxygen.[17] There its precursor is the $Cl_3C\text{–}Cl_2^{\bullet}$ radical generated by the addition of a photolytically generated Cl-atom to tetrachloroethene. It is well known that in the course of the peroxyl radical reactions of chlorinated hydrocarbons Cl-atoms can be released,[2,18-20] and hence the observed formation of trichloroacetic acid in the OH-radical induced reaction (in the presence of O_2) is in fact due to a secondary, Cl-atom-induced reaction.[17]

In the absence of oxygen this complication cannot occur and a detailed product and kinetic study should allow one to decide whether the Cl-shift [reaction (3)] is a rapid reaction that is capable of competing with the HCl-elimination [reaction (2)].

Table 1 γ-Radiolysis of N_2O-saturated aqueous solutions of tetrachloroethene and trichloracetaldehyde hydrate (10^{-3} mol dm^{-3}) at a dose rate of 0.19 Gy s^{-1}. Products and their G values (in units of 10^{-7} mol J^{-1})

Product	$CCl_2{=}CCl_2$	$CCl_3CH(OH)_2$
H^+ (total)	14.7	10.9
Cl^- (immediate)	11.6	7.3
Cl^- (after heating)	14.1	10.4
Tetrachlorosuccinic acid	2.3	2.7
Trichloroacrylic acid (intermediate)	Absent	0.2
Trichloroacrylic acid (after heating)	1.8	2.4
Dichloroacetic acid	0.2	<0.1
Trichloroacetic acid	Absent	Absent
Oxalic acid	0.1	<0.1
Carbon dioxide (after heating)	n.d.[a]	2.6

[a] n.d. = not determined.

Here data will be presented which show that reaction (3) does not compete effectively with reaction (2). Additional experiments have been done with trichloroacetaldehyde hydrate (chloral hydrate) in order to confirm our conclusions.

Experimental

Tetrachloroethene (>99%, Merck) was used without further purification. Aqueous solutions were made up in Milli-Q-filtered (Millipore) water. The solutions were saturated for 20 min with O_2-free N_2O (Messer Griesheim) and the required amount of tetrachloroethene injected through a serum cap.

γ-Irradiations were carried out in a ^{137}Cs-γ-source at a dose rate of 0.19 Gy s^{-1}. Some experiments were also carried out with a ^{60}Co-γ-source at a dose rate of 0.25 Gy s^{-1}. The pulse-radiolysis set-up has been described recently.[21] The yields of chloride ions and organic acids were determined by high-performance ion chromatography (HPIC) (Dionex 2010i). Tetrachlorosuccinic acid elutes on the AS9–SC column only very slowly (*ca.* 50 min) and as a broad peak, even with the most powerful eluent (3.6×10^{-3} mol dm^{-3} sodium carbonate–3.4×10^{-3} mol dm^{-3} sodium hydrogen carbonate), but reasonable retention times (12 min) were achieved when only the short guard column was used.

Products were extracted from the irradiated solutions with freshly distilled diethyl ether with the help of a Ludwig-extractor (Normag). The solutions had been acidified with sulfuric acid to protonate the organic acid for more facile extraction. The extract was dried over sodium sulfate, concentrated and analysed by gas chromatography–mass spectrometry (GC–MS) (Hewlett-Packard MSD 5971A) directly and after trimethylsilylation (rms). The most abundant peaks (m/z) in the mass spectra were (% in parentheses): trichloroacrylic acid (M_W = 174) 174 (62), 157 (25), 139 (100), 129 (30), 94 (98), 59 (20) and 45 (30); its TMS–diethyl ether (M_W = 246) 246 (2), 231 (52), 157 (10), 129 (9), 93 (100) and 73 (20); tetrachlorosuccinic acid anhydride (M_W = 236) 164 (72), 157 (60), 129 (22) and 94 (24); tetrachlorosuccinic acid (M_W = 254), 174 (5), 165 (5), 130 (100), 110 (20), 95 (62), 83 (90), 60 (32) and 45 (28); its bis-TMS–diethyl ether (M_W = 398) 383 (9), 319 (11), 231 (25), 147 (15) and 73 (100).

Results and Discussion

Generation of OH-*Radicals.*—The OH-radicals were generated radiolytically. When the energy of the ionizing radiation is absorbed by the solvent water, OH-radicals, solvated electrons and H-atoms are formed as reactive intermediates [reaction (5)].[22,23]

$$H_2O \xrightarrow[\text{radiation}]{\text{ionization}} e^-_{aq}, {}^{\bullet}OH, H^{\bullet}, H^+, OH^-, H_2O_2, H_2 \qquad (5)$$

The solvated electrons can be converted by saturating the solution with nitrous oxide [reaction (6); $k_6 = 9.8 \times 10^9$

$$e^-_{aq} + N_2O \longrightarrow {}^{\bullet}OH + N_2 + OH^- \qquad (6)$$

$dm^3\ mol^{-1}\ s^{-1}$] into further OH-radicals.[13] Since tetrachloroethene also reacts rapidly with the solvated electron [reaction (7), $k_7 = 1.3 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$][13] its concentration must

$$e^-_{aq} + Cl_2C{=}CCl_2 \longrightarrow Cl_2C{=}CCl^{\bullet} + Cl^- \qquad (7)$$

remain at $\leq 10^{-3}$ mol dm^{-3} to ensure predominant (>95%) conversion of the solvated electrons into OH-radicals. Under these conditions OH-radicals are formed with radiation chemical yields of *ca.* $G({}^{\bullet}OH) = 6 \times 10^{-7}$ mol J^{-1}. There is also a minor contribution of H-atoms [$G(H^{\bullet}) = 0.6 \times 10^{-7}$ mol J^{-1}] which add to tetrachloroethene.

Thus the majority of the tetrachloroethene-derived radicals formed in the present system are the OH-adduct radicals [*cf.* reaction (1)] with a 10% contribution of the H-atom adduct radicals from reaction (8) and some <5% trichlorovinyl radicals from reaction (7).

$$H^{\bullet} + Cl_2C{=}CCl_2 \longrightarrow HCl_2C{-}CCl_2^{\bullet} \qquad (8)$$

Determination and Quantification of the Products.—N_2O-Saturated aqueous solutions of tetrachloroethene (10^{-3} mol dm^{-3}) were γ-irradiated at a dose rate of 0.19 Gy s^{-1} up to a total dose of 342 Gy, *i.e.* a tetrachloroethene conversion of ≤20%. Under these conditions total acid formation (titration), as well as chloride and dichloroacetate yields (HPIC) increased linearly with dose. From the slope of such plots G values were calculated. They are compiled in Table 1. It has been shown by HPIC that trichloroacetic acid is not among the products.

From the much higher yields of H^+ compared with the sum of hydrochloric and dichloroacetic acid it follows that further unknown acid(s) must be formed as well. For their identification γ-irradiated solutions were further acidified with sulfuric acid to fully protonate any organic acid present and the organic acids extracted into diethyl ether. The dried and concentrated ether extract was analysed by GC–MS. Three major components were observed and their mass spectra assigned as shown in the experimental part. The organic acids can be trimethylsilylated and the mass spectra of their corresponding TMS-derivatives yield further information upon which an assignment can be based.

The three major products detected under these conditions are tetrachlorosuccinic acid, its anhydride and trichloroacrylic acid. The primary product is most likely tetrachlorosuccinic acid. Its anhydride forms when the etheric solutions are dried; the formation of trichloroacrylic acid is perhaps more interesting and results from the decarboxylation of tetrachlorosuccinic acid [reaction (9)].

$$HO_2C{-}CCl_2{-}CCl_2{-}CO_2H \longrightarrow HCl + CO_2 + CCl_2{=}CCl{-}CO_2H \qquad (9)$$

These two acids can be separated by HPIC and it has been shown that tetrachlorosuccinic acid is indeed the primary product. Its decay (and the concomitant formation of trichloroacrylic acid) has been measured at 80 °C. First-order kinetics are observed as shown in Fig. 1. At this temperature it decays with a half-life of 9 min. (For a compilation of rate constants obtained in this study see Table 2.) Similar

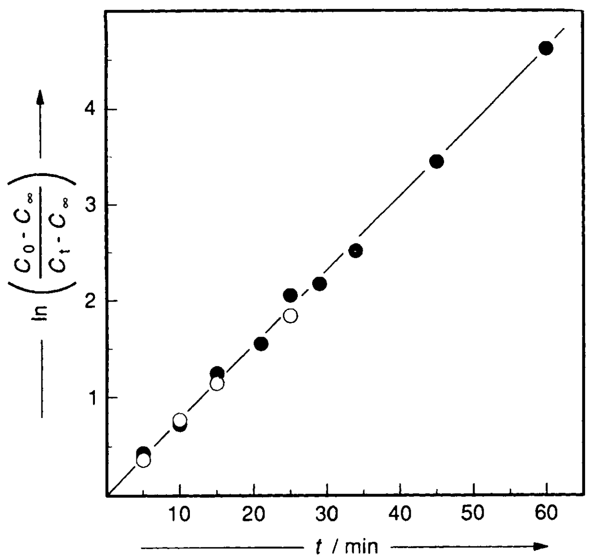


Fig. 1 Decarboxylation of tetrachlorosuccinic acid at 80 °C. Kinetics of the decay of tetrachlorosuccinic acid (○) and the formation of trichloroacrylic acid (●) (c_0, c_∞ and c_t indicate the concentrations at zero time, at infinite time and at the given time, respectively).

Table 2 Compilation of rate constants (at 25 °C if not stated otherwise) measured in the present study

Reaction	Rate constant
$k[^{\bullet}CCl_2CCl_2OH \longrightarrow HCl + {}^{\bullet}CCl_2C(O)Cl]$	$>7 \times 10^5\ s^{-1}$ $(>7 \times 10^5\ s^{-1})$[a]
$2k\{2^{\bullet}CCl_2C(O)Cl \longrightarrow [CCl_2C(O)Cl]_2\}$	$6.9 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$
$k[^{\bullet}CCl_2C(O)Cl + H_2O \longrightarrow {}^{\bullet}CCl_2CO_2^- + 2H^+ + Cl^-]$	$<10^3\ s^{-1}$
$k\{[CCl_2C(O)Cl]_2 + H_2O \longrightarrow {}^-O_2CCCl_2CCl_2C(O)Cl + H^+ + Cl^-\}$	$5\ s^{-1}$
$k\ [(CCl_2CO_2^-)_2 \longrightarrow CCl_2{=}CClCO_2^- + CO_2 + Cl^-]$	$6.2 \times 10^{-5}\ s^{-1}$ (55 °C)

[a] Ref. 14.

experiments have been made at other temperatures. The rate of reaction can be followed either by HPIC or by UV spectroscopy, since the resulting trichloroacrylic acid displays a pronounced absorption at 243 nm (inset in Fig. 2). This absorption maximum agrees well with the calculated one (λ = 240 nm) applying the extended Woodward rules.[24] An Arrhenius plot is shown in Fig. 2.

From these data an activation energy of E_a = 115 kJ mol^{-1} is calculated. Upon decarboxylation of tetrachlorosuccinic acid HCl is also liberated [reaction (9)]. Upon heating, the chloride yield does indeed increase [$\Delta G(Cl^-) = 2.5 \times 10^{-7}$ mol J^{-1}]. For quantitation of tetrachlorosuccinic acid by HPIC reference material was not available (in fact tetrachlorosuccinic acid has not yet been described in the literature so far) hence for the determination of its G value an estimate of the response factor using similar dibasic acids (*e.g.* chlorosuccinic acid) had to be made. From this procedure we arrive at G(tetrachlorosuccinic acid) = 2.3×10^{-7} mol J^{-1}. A more reliable estimate may be based on the measurement of the trichloroacrylic acid (after heating). This is a monobasic acid and dichloroacetic acid might serve as a reference. From this we estimate G(trichloroacrylic acid) = 1.8×10^{-7} mol J^{-1}. These data agree reasonably well with $\Delta G(Cl^-) = 2.5 \times 10^{-7}$ mol J^{-1} mentioned above. From mechanistic considerations (see below) we would arrive at an estimated value of G(tetrachlorosuccinic acid) = 2.4×10^{-7} mol J^{-1} which is in reasonable agreement with these various assessments.

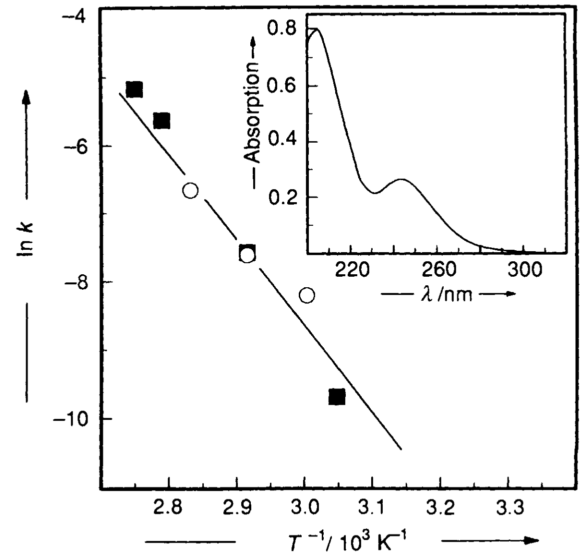


Fig. 2 Arrhenius plot of the decarboxylation of tetrachlorosuccinic acid (■: by UV spectroscopy; ○: by HPIC). Inset: UV spectrum of trichloroacrylic acid.

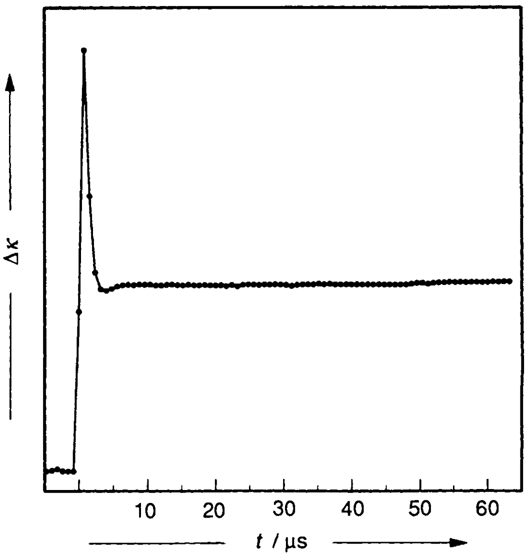


Fig. 3 Pulse radiolysis of tetrachloroethene (10^{-3} mol dm^{-3}) in N_2O-saturated aqueous solutions. Change of conductivity as a function of time (short time range).

The products of the OH radical reaction with trichloroacetaldehyde hydrate are the same as the ones formed from tetrachloroethene. Their radiation chemical yield are compiled in Table 1.

We hence conclude that there are only two major primary products: HCl and tetrachlorosuccinic acid. These are two acids and the kinetics of their formation can be followed by pulse radiolysis using conductometric detection.

Kinetic Studies.—The OH-radicals generated in N_2O-saturated solutions of tetrachloroethene (10^{-3} mol dm^{-3}) react rapidly with the substrate ($k_1 = 2.6 \times 10^9$ dm^3 mol^{-1} s^{-1}).[13] As has been reported before[14] concomitant with this reaction there is a rapid increase in the formation of $H^+ + Cl^-$ leading to an increase in conductivity and a quantification of the signal shows that $G(H^+)$ equals $G(^{\bullet}OH)$ (Fig. 3). It is attributed to reaction (2), and it is concluded that $k_2 > 7 \times 10^5$ s^{-1} in agreement with the value reported earlier.[14] Subsequent to this rapid increase in conductivity there is a lower further increase (Fig. 4). Again, $G(H^+)$ equals $G(^{\bullet}OH)$. The kinetics of the reaction is of first

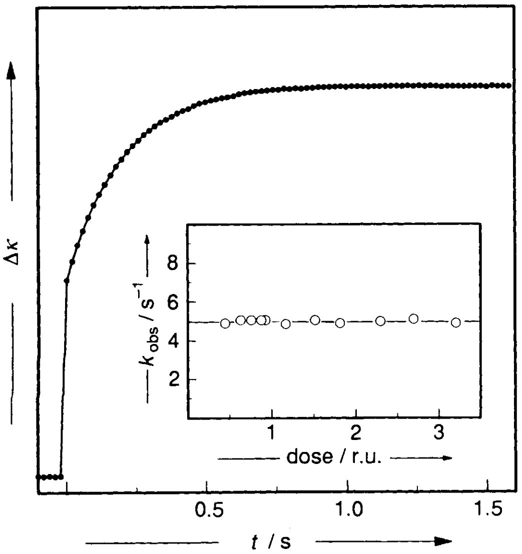


Fig. 4 Pulse radiolysis of tetrachloroethene (10^{-3} mol dm^{-3}) in N_2O-saturated aqueous solutions. Change of conductivity as a function of time (long time range). Inset: rate of conductivity change as a function of the dose per pulse; one relative unit (r. u.) is approximately 4 Gy.

order ($k_{obs} = 5$ s^{-1}) and independent of the dose per pulse (inset in Fig. 4).

The bimolecular decay of the $^{\bullet}CCl_2C(O)Cl$ radicals [reaction (10)] can be followed at 265 nm where they show an absorption

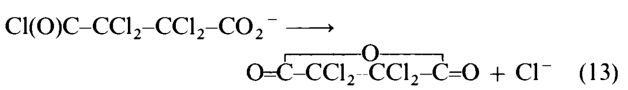
$$2^{\bullet}CCl_2\text{–}C(O)Cl \longrightarrow Cl(O)C\text{–}CCl_2\text{–}CCl_2\text{–}C(O)Cl \quad (10)$$

maximum ($\varepsilon = 4100$ dm^3 mol^{-1} cm^{-1}, somewhat higher than the value published previously[14]).[25] Their bimolecular combination rate constant has been measured at $2k_{10} = 6.9 \times 10^8$ dm^3 mol^{-1} s^{-1}. It can be calculated readily that these radicals must have decayed [reaction (10)] before the slow conductivity increase sets in. We hence conclude that the $^{\bullet}CCl_2C(O)Cl$ radicals do not hydrolyse in this time scale. Otherwise a conductivity increase should have been observed prior or during the bimolecular decay process. The yield of the slow conductivity increase in the bimolecular decay shows that a product is formed which yields only one mol of acid per mol $^{\bullet}CCl_2C(O)Cl$. In assigning this acid formation to a certain process one has to keep in mind that on the way from tetrachlorosuccinyl dichloride to tetrachlorosuccinic acid four mol H^+ are released while in this step only two mol H^+ are formed, *i.e.* only one of the acyl chloride functions seems to be hydrolysed. We suggest that the first hydrolytic step [reaction (11); $k_{11} = 5$ s^{-1}) is followed by a fast intramolecular S_N2

$$Cl(O)C\text{–}CCl_2\text{–}CCl_2\text{–}C(O)Cl + H_2O \longrightarrow Cl(O)C\text{–}CCl_2\text{–}CCl_2\text{–}CO_2^- + 2\,H^+ + Cl^- \quad (11)$$

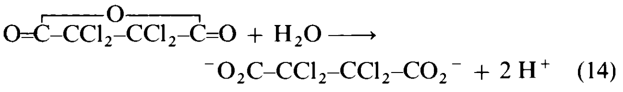
$$Cl(O)C\text{—}CCl_2\text{–}CCl_2\text{–}CO_2^- + H_2O \longrightarrow {}^-O_2C\text{–}CCl_2\text{–}CCl_2\text{–}CO_2^- + 2\,H^+ + Cl^- \quad (12)$$

reaction leading to the anhydride [reaction (13)]. This reaction



$$Cl(O)C\text{–}CCl_2\text{–}CCl_2\text{–}CO_2^- \longrightarrow O{=}C\text{–}CCl_2\text{–}CCl_2\text{–}C{=}O\ (\text{ring via }O) + Cl^- \quad (13)$$

is not connected with a change in conductivity since the anions $[ClC(O)CCl_2CCl_2CO_2^-$ and $Cl^-]$ have about the same equivalent conductance. The rate constant of the hydrolysis of tetrachlorosuccinoyl dichloride is very close to that observed for the hydrolysis of phosgene (9 s^{-1} at 25 °C).[26] Apparently the intramolecular S_N2 reaction (13) is much faster than the hydrolysis of the second acylchloride group [reaction (12)] which should have about the same rate constant as the hydrolysis of the first acyl chloride function [reaction (11)]. The hydrolysis of the tetrachlorosuccinic anhydride [(reaction 14)]



$$O{=}C\text{–}CCl_2\text{–}CCl_2\text{–}C{=}O\ (\text{ring via }O) + H_2O \longrightarrow {}^-O_2C\text{–}CCl_2\text{–}CCl_2\text{–}CO_2^- + 2\,H^+ \quad (14)$$

could not be followed under our conditions because of base line instabilities at longer times. However, the expected conductivity change (release of a further two mol H^+) was found after γ-radiolysis. Succinic anhydride hydrolyses with a rate constant of 1.8×10^{-3} s^{-1}.[27] The tetrachlorosuccinic anhydride seems to hydrolyse faster than the unsubstituted one, since measuring the conductivity immediately after a sample had been γ-irradiated for one minute the full conductivity had already developed. However, a cautionary remark is in order. Under the dose rate used in the γ-radiolytic experiment (0.19 Gy s^{-1}) the radicals live for about 0.1 s. Although it has been excluded that they hydrolyse [reaction (15)] over much shorter times (lifetime

$$^{\bullet}CCl_2C(O)Cl + H_2O \longrightarrow {}^{\bullet}CCl_2CO_2^- + H^+ + Cl^- \quad (15)$$

in the pulse radiolysis experiments ≤ 0.1 ms) they might do so in the time scale of the γ-radiolysis experiment so that here, tetrachlorosuccinic acid might be formed directly from $^{\bullet}CCl_2CO_2^-$ rather than *via* reaction (14).

It has been shown that no trichloroacetic acid but some dichloroacetic acid is formed. So far we have not accounted for the minor primary radical in this system, the $^{\bullet}CCl_2CHCl_2$ radical [$G(^{\bullet}CCl_2CHCl_2) \approx 0.6 \times 10^{-7}$ mol J^{-1}]. For statistical reasons it must decay largely in a reaction with the major primary radical $^{\bullet}CCl_2C(O)Cl$. In a disproportionation reaction it may yield dichloroacetic acid [reactions (16) and (17)]. Its

$$^{\bullet}CCl_2CHCl_2 + {}^{\bullet}CCl_2C(O)Cl \longrightarrow Cl_2C{=}CCl_2 + HCCl_2C(O)Cl \quad (16)$$

$$^{\bullet}CCl_2CHCl_2 + {}^{\bullet}CCl_2C(O)Cl \longrightarrow CCl_3CHCl_2 + CCl_2{=}C{=}O \quad (17)$$

addition to the major radical will yield 2,2,3,3,4,4-hexachlorobutanoic acid [reaction (18)] which also readily decarboxylates

$$^{\bullet}CCl_2CHCl_2 + {}^{\bullet}CCl_2C(O)Cl + H_2O \longrightarrow CHCl_2CCl_2CCl_2CO_2H + HCl \quad (18)$$

yielding 1,1,2,3,3-pentachloropropene [reaction (19)]. This

$$CHCl_2CCl_2CCl_2CO_2H \longrightarrow CO_2 + HCl + CHCl_2CCl{=}CCl_2 \quad (19)$$

product has been recognized in yields higher than dichloroacetic acid in the ether extract (comparison of its mass spectrum with a reference spectrum).

Trichloroacetaldehyde (*Hydrate*).—Hydroxyl radicals react with trichloroacetaldehyde hydrate by abstracting predominantly the carbon-bound hydrogen [reaction (20); k_{20} =

$$Cl_3C\text{–}CH(OH)_2 + {}^{\bullet}OH \longrightarrow Cl_3C\text{–}C(OH)_2^{\bullet} + H_2O \quad (20)$$

3.1×10^9 dm^3 mol^{-1} s^{-1}].[13] Abstraction of an oxygen-bound hydrogen must be a minor process (*cf.* ref. 28). The resulting radical is structurally related to the α-hydroxyalkyl radicals

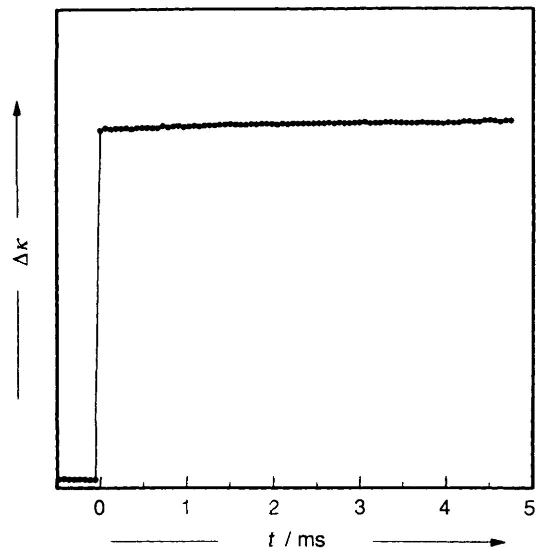


Fig. 5 Pulse radiolysis of trichloroacetaldehyde hydrate (10^{-3} mol dm^{-3}) in N_2O-saturated aqueous solutions. Change of conductivity as a function of time.

derived from chloroethanol, 2-acetylethanol or glycerol phosphates all of which readily eliminate the substituent in the β-position to the radical site and a proton.[22] This reaction is related to the (slower) water elimination reaction which governs the free-radical chemistry of carbohydrates.[22,29] In the case of trichloroacetaldehyde hydrate the HCl-elimination leads to a $CCl_2CO_2^-$ radical and a proton [reaction (21)]. When these

$$Cl_3C\text{–}C(OH)_2^{\bullet} \longrightarrow {}^{\bullet}CCl_2\text{–}CO_2^- + 2H^+ + Cl^- \quad (21)$$

radicals combine tetrachlorosuccinic acid is formed [reaction (22)], *i.e.* the same as the major product from the reaction of

$$2{}^{\bullet}CCl_2\text{–}CO_2^- \longrightarrow {}^-O_2C\text{–}CCl_2\text{–}CCl_2\text{–}CO_2^- \quad (22)$$

OH-radicals with tetrachloroethene (*cf.* Table 1).

However, in the present case this acid is formed directly in reaction (22), without any further intermediates such as the tetrachlorosuccinyl dichloride and the tetrachlorosuccinic anhydride, the precursors of this acid in the tetrachloroethene case [*cf.* reactions (10), (11) and (13)]. This can be shown readily by pulse radiolysis. Right after the pulse the conductivity rises to its full value, *i.e.* to an equivalent of two protons and two anions per OH-radical (Fig. 5).

Conclusions

The present study has shown that in aqueous solutions the $^{\bullet}CCl_2C(OH)Cl_2$ radical rapidly loses HCl to give $^{\bullet}CCl_2C(O)Cl$ radicals [reaction (2)] and that a Cl-shift yielding $CCl_3CCl(OH)^{\bullet}$ [reaction (3)] must be a minor process if it occurs at all. The pulse radiolysis technique has allowed us to follow the kinetics of the tetrachlorosuccinoyl dichloride, the dimerization product of the $^{\bullet}CCl_2C(O)Cl$ radicals which by themselves undergo no or comparatively slow hydrolysis.

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