Acid Formation in the Radical-mediated Degradation of Chlorinated Ethanes in Aqueous Environment. A Radiation Chemical Study

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High yields of HCl and organic acids RCOOH are found to result from a one-electron- and ˙OH-radical-induced degradation of polychlorinated ethanes in oxygen-containing aqueous solutions. The following organic acids (depending on the initiating radical e_{aq}^- or ˙OH) have been identified and quantitatively been measured: CH_3COOH from 1,1,1-trichloroethane and 1,1-dichloroethane; $CH_2ClCOOH$ from 1,2-dichloroethane and 1,1,2-trichloroethane; $CHCl_2COOH$ from 1,1,2-trichloroethane; HCOOH from 1,2-dichloroethane and 1,1,2-trichloroethane; and CO_2 from all substrates. The mechanism of the organic acid formation proceeds *via* peroxyl radicals as key intermediates. The nature of the latter must be either $RCCl_2OO^•$ or $RCHClOO^•$, *i.e.* the carbon atom carrying the peroxyl group must also carry at least one chlorine atom. The present radiation chemical findings corroborate other observations made in the one-electron- and free-radical-induced degradation of various individual halogenated alkanes and may therefore be generalized. The studies help to provide a chemical understanding of the biological and environmental action of halogenated compounds in general.

Halogenated hydrocarbons are utilized as solvents, drugs, herbicides, pesticides, propellants, flame retardants, dielectric fluids, *etc.* Many of these compounds are quite hazardous if not toxic. Their widespread and continuous use bears, therefore, considerable toxicological and environmental implications.

The mode of the toxic action of halogenated hydrocarbons has not yet been completely understood. It has been demonstrated, however, that the deleterious action is related to free radicals generated in the metabolism of these compounds, which most often occurs in the liver.[1–6] The radicals are generally thought to be formed *via* a one-electron transfer from cytochrome P-450,[7] an enzyme system which is located mainly in the smooth part of the endoplasmic reticulum. Radiation chemical model studies on, for example, carbon tetrachloride (CCl_4),[8,9] halothane ($CF_3CHBrCl$),[9–11] and 1,2-dibromoethane (CH_2BrCH_2Br)[12] have revealed that the metabolic and free radical-mediated degradation of these substrates results in similar product patterns, suggesting that the underlying chemical reactions are alike.

In oxygen-containing solutions the key intermediates have been shown to be peroxyl radicals which are readily formed *via* the general reaction sequence (RX = aliphatic halide) of essentially diffusion-controlled processes (1) and (2). Particularly interesting have been those compounds where the radical R˙ still contained further halide substituents at the tervalent carbon.[9] Their peroxyl radicals were partly converted into organic acids in aqueous environment, *e.g.* CO_2, HCOOH, and CF_3COOH derived from $CCl_3OO^•$, $CCl_2HOO^•$, and $CF_3CH(Cl)OO^•$, respectively. These processes were accompanied by the formation of inorganic acid (HCl). Generation of high yields of acids from halogenated compounds could be relevant for biological and environmental consideration. The latter is particularly evident since primary radicals R˙ are generated *via* dissociative electron capture [*i.e.* analogous to reaction (1)] at light-induced semiconductor surfaces.[9,13,14] In order to elucidate the mechanism of acid formation as a general phenomenon we have therefore extended our previous radiation chemical model studies to further simple polychlorinated ethanes.

$$RX + e_{aq}^- \longrightarrow R^• + X^- \qquad (1)$$

$$R^• + O_2 \longrightarrow ROO^• \qquad (2)$$

Experimental

Reagent grade 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2-trichloroethane were used as provided by Fluka Chemicals. The solvent was deionized, Millipore-filtered water, the quality of which corresponded to triply distilled water. Volatile compounds were always introduced into the solutions which were already gas saturated. The sample size was generally 20 ml contained in a rubber-sealed glass vessel.

Exposure of water or dilute aqueous solutions to high energy radiation leads to primary species e_{aq}^-, ˙OH, H˙, and H_{aq}^+ with the yields of *G* 2.8, 2.8, 0.6, and 2.8 species per 100 eV absorbed energy, respectively. To convert hydrated electrons into ˙OH radicals the solutions were saturated with either N_2O–O_2 (4:1) mixtures or just N_2O ($e_{aq}^- + N_2O \longrightarrow {}^•OH + OH^- + N_2$). For studies of e_{aq}^- reactions in the absence of ˙OH, t-butyl alcohol was added [t-butyl alcohol + ˙OH $\longrightarrow$ $^•CH_2C(CH_3)_2OH + H_2O$].

Irradiations were carried out in the field of a ^{60}Co γ-source. Total absorbed doses were in the range of 50—300 Gy (1 Gy = 1 J kg^{-1} = 100 rad). Dosimetry was made by using the Fricke dosimeter.

Radiation chemical conversions were kept to $\leqslant 5\%$ to avoid reaction of the primary radicals with any of the radiation chemical products.

Ionic products (Cl^-, $HCOO^-$, CH_3OO^-, CH_2ClCOO^-, $CHCl_2COO^-$) were identified and quantified by high performance ion chromatography employing a DIONEX 2010 machine. Except for the determination of $HCOO^-$ and CH_3COO^- the latter was equipped with a HPIC-AS 4 separator column and a fibre suppressor. The eluant was a mixture of $NaHCO_3$ and Na_2CO_3 (2.8×10^{-3} mol dm^{-3} and 2.24×10^{-3} mol dm^{-3}, respectively) for Cl^- measurements, or 5×10^{-4} mol dm^{-3} Na_2CO_3 for analysis of Cl^-, $CHCl_2COO^-$, CH_2ClCOO^- mixtures. For $HCOO^-$ and CH_3COO^- determination a separator column HPICE-AS 1 and a silver salt

Table 1. Anionic end products and their radiation chemical yields (given in terms of G in parentheses) from γ-irradiated, pH 5.5—6.0 (phosphate buffered), N_2- or air-saturated solutions of 3×10^{-3} mol dm^{-3} halogenated ethanes and 10^{-1} mol dm^{-3} t-butyl alcohol; yields were independent of dose rate within a 300—6 000 Gy h^{-1} range)

		Anionic products	
Compound	Primary radicals formed	N_2-t-butyl alcohol	air-saturated-t-butyl alcohol
1,1,1-TCE	$CH_3\text{-}\dot{C}Cl_2$	Cl^- (2.9)	Cl^- (6.6); CH_3COO^- (2.3)
1,1,2-TCE	$CHCl_2\text{-}\dot{C}H_2$ $CH_2Cl\text{-}\dot{C}HCl$	Cl^- (3.1)	Cl^- (4.2); $CClH_2COO^-$ (1.0); $HCOO^-$ (0.25)
1,1-DCE	$CH_3\text{-}\dot{C}HCl$	Cl^- (2.9)	Cl^- (4.6); CH_3COO^- (1.5)
1,2-DCE	$CH_2Cl\text{-}\dot{C}H_2$	Cl^- (3.2)	Cl^- (1.7)

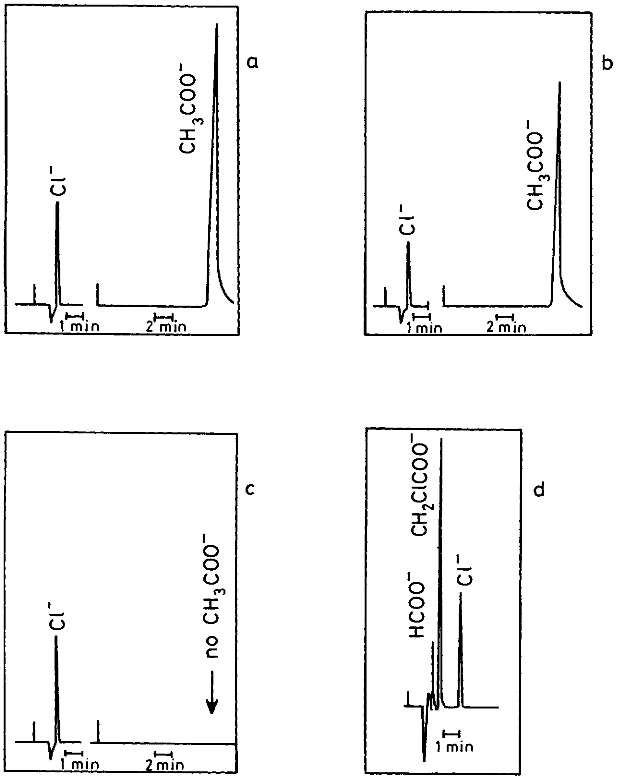


Figure 1. Ion chromatograms obtained from γ-irradiated, air-saturated, aqueous solutions of 10^{-1} mol dm^{-3} t-butyl alcohol and 3×10^{-3} mol dm^{-3} chlorinated ethanes. a, 1,1-DCE; b, 1,1,1-TCE; c, 1,2-DCE; and d, 1,1,2-TCE (separate analysis for Cl^- and CH_3COO^- on two different columns in a—c)

suppressor were used. The eluant in this case was 1×10^{-3} mol dm^{-3} HCl. CO_2 was also determined by ion chromatography, namely by conversion into HCO_3^- ions. Experimental details on this have already been published.[15] Calibrations were made daily. All experiments were carried out at room temperature.

Results

The free radical chemistry of the following polychlorinated ethanes was investigated: 1,1,1-trichloroethane (1,1,1-TCE, $CH_3\text{-}CCl_3$), 1,1,2-trichloroethane (1,1,2-TCE, $CHCl_2\text{-}CH_2Cl$), 1,1-dichloroethane (1,1-DCE, $CH_3\text{-}CHCl_2$), and 1,2-dichloroethane (1,2-DCE, $CH_2Cl\text{-}CH_2Cl$). These compounds were subjected to γ-irradiation under various conditions in aqueous solution, *i.e.* they were reduced by hydrated electrons and they reacted with $^{\bullet}OH$ radicals, both in the presence and absence of molecular oxygen. The radiation chemical yields were generally calculated from the slopes of standard concentration *versus* dose plots with 4—5 points. The dose rate was 300 Gy h^{-1} if not stated otherwise.

(1) e_{aq}^-*-induced Degradation*.—One-electron reduction by hydrated electrons has been studied with N_2-saturated solutions of the chlorinated ethanes and 0.1 mol dm^{-3} t-butyl alcohol. The only ionic species which could be analysed from such solutions were Cl^- ions resulting from reaction (**1**), but no acetic acids. The Cl^- yields are listed in Table 1 and are seen to correspond essentially to $G(e_{aq}^-)$ 2.8.

If O_2 was present high yields of H_{aq}^+, Cl^-, and organic acid anions were detected. Typical ion chromatograms from irradiated air-saturated solutions of 1,1-DCE, 1,1,1-TCE, 1,2-DCE, and 1,1,2-TCE are shown in Figures 1a—d. The anionic products together with their yields (in terms of G) are listed in Table 1. They were obtained from solutions of 3×10^{-3} mol dm^{-3} of the various halogenated ethanes. For most experiments phosphate buffer was added to adjust the pH to 5.5—6.0. This was advised to prevent competitive scavenging of e_{aq}^- by reaction (3).

$$e_{aq}^- + H_{aq}^+ \longrightarrow H^{\bullet} \qquad (3)$$

The absolute yields of Cl^- and CH_3COO^- (expressed in terms of G) obtained from irradiated solutions of various 1,1,1-TCE concentrations are shown in Figure 2. Both are seen to level off at high 1,1,1-TCE concentrations. The limiting CH_3COO^- yield of G *ca.* 2.8 corresponds to the yield of e_{aq}^- initially available for reduction while the Cl^- ion yield of G 8.5 amounts to three times this value. This result suggests the complete release of all three chlorine atoms from 1,1,1-TCE and a quantitative conversion of the carbon skeleton into acetic acid *via* the overall reaction sequence (4)—(6).

$$e_{aq}^- + CH_3\text{-}CCl_3 \longrightarrow CH_3\text{-}\dot{C}Cl_2 + Cl^- \qquad (4)$$

$$CH_3\text{-}\dot{C}Cl_2 + O_2 \longrightarrow CH_3\text{-}C(Cl)_2OO^{\bullet} \qquad (5)$$

$$CH_3\text{-}C(Cl)_2OO^{\bullet} \rightsquigarrow CH_3COO^- + 2\ Cl^- + \cdots \qquad (6)$$

Lower absolute yields, but with the same concentration ratio $Cl^-:CH_3COO^- = 3$, were measured at lower 1,1,1-TCE concentrations. This can quantitatively be accounted for by an increasing competition of oxygen ($[O_2]$ 2.8×10^{-4} mol dm^{-3}) for the hydrated electron [reaction (7)].

$$O_2 + e_{aq}^- \longrightarrow O_2^{\bullet -} \qquad (7)$$

Applying standard competition kinetics and assuming that every e_{aq}^- reacting with 1,1,1-TCE leads to one CH_3COO^- and three Cl^- relationship (8) is given. Corresponding plots of

Table 2. Anionic end products and their radiation chemical yields (given in terms of G in parentheses) from γ-irradiated, pH 5.5—6.0 (phosphate buffered), N_2O- or N_2O–O_2 (4:1)-saturated solutions of 3×10^{-3} mol dm^{-3} halogenated ethanes. (* High error limit due to analytical technique; HCO_3^- peak is partially hidden in CH_3COO^- peak)

Compound	Primary radicals formed	Anionic products	
		N_2O	N_2O–O_2
1,1,1-TCE	$CCl_3\text{–}\dot{C}H_2$	Cl^- (4.4)	Cl^- (4.3); CO_2 (2.3)
1,1,2-TCE	$CH_2Cl\text{–}\dot{C}Cl_2$ $CHCl_2\text{–}\dot{C}HCl$	Cl^- (3.5)	Cl^- (8.4); $CClH_2COO^-$ (2.0); CCl_2HCOO^- (1.0); HCOOH (0.35); CO_2 (1.6)
1,1-DCE	$CH_3\text{–}\dot{C}Cl_2$ $CHCl_2\text{–}\dot{C}H_2$	Cl^- (1.7)	Cl^- (10.9); CH_3COO^- (3.9) CO_2 (<0.8)*
1,2-DCE	$CH_2Cl\text{–}\dot{C}HCl$	Cl^- (0.8)	Cl^- (7.1); $CClH_2COOH$ (3.0); HCOOH (0.65); CO_2 (1.5)

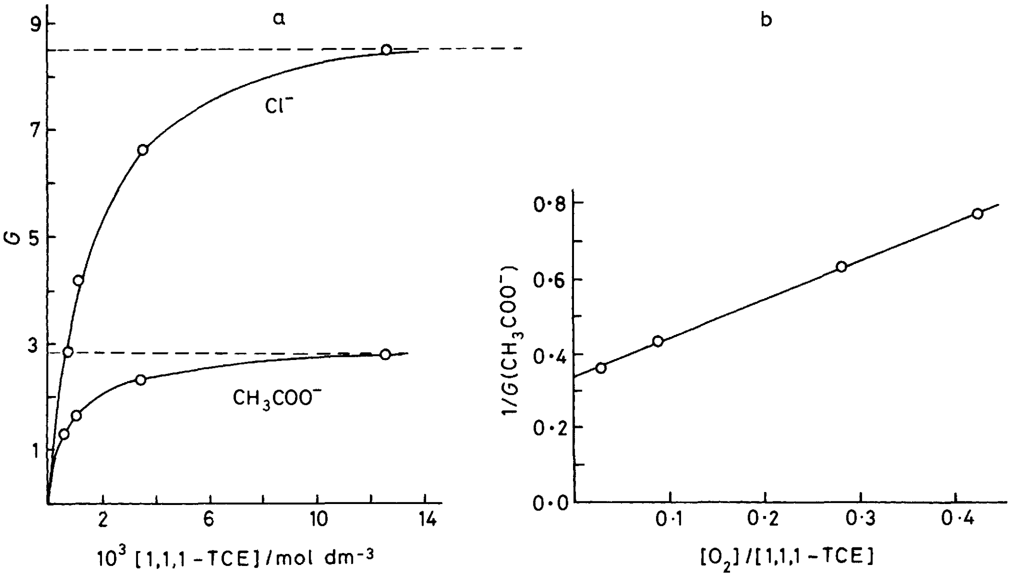


Figure 2. (a) Yields of Cl^- and CH_3COO^- (in terms of G) from γ-irradiated, pH 5.5—6.0 (phosphate-buffered), air-saturated solution as a function of 1,1,1-TCE concentration. Dashed lines: $G(e_{aq}^-)$ and 3 $G(e_{aq}^-)$. (b) Plot of $1/G(CH_3COO^-)$ *versus* $[O_2]/[1,1,1\text{-TCE}]$ according to equation (8)

$$\frac{1}{G(CH_3COO^-)} = \frac{3}{G(Cl^-)} = \frac{1}{G(e_{aq}^-)} + \frac{1}{G(e_{aq}^-)} \times \frac{k_7}{k_4} \times \frac{[O_2]}{[1,1,1\text{-TCE}]} \quad (8)$$

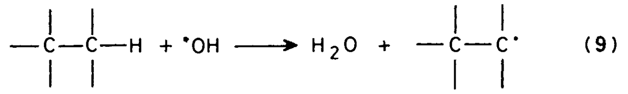
$1/G(CH_3COO^-)$ or $3/G(Cl^-)$ *versus* the $[O_2]/[1,1,1\text{-TCE}]$ ratio show indeed straight lines as is demonstrated for the acetate in Figure 2b. The intercept amounts, as expected, to $1/G(e_{aq}^-) = 0.35 = 1/2.85$, and from the slope a rate constant ratio of $k_7/k_4 = 2.85$ is derived. Taking k_7 *ca.* 2.0×10^{10} mol^{-1} dm^3 s^{-1}[16] the rate constant for the electron reaction with 1,1,1-TCE is evaluated to k_4 *ca.* 0.7×10^{10} mol^{-1} dm^3 s^{-1}. Considering the possible error limits (*e.g.* for the exact O_2 concentration) this value agrees reasonably well with k_4 1.4×10^{10} mol^{-1} dm^3 s^{-1} obtained by direct optical pulse radiolysis measurements.[17] The above results also imply that $O_2^{-\bullet}$ is not able to transfer an electron to 1,1,1-TCE. Similar observations have been made for CCl_4[8] and $CF_3CHBrCl$[8] in aqueous solutions. This is interesting because in aprotic solvents $O_2^{-\bullet}$ does readily react with CCl_4 and other halogenated compounds.[18]

Qualitatively very similar results were obtained upon one-electron reduction of the other halogenated ethanes in air-saturated aqueous solution. Increasing solute concentrations always resulted in higher acid yields since reaction (7) is suppressed. As shown in Figure 1a reduction of 1,1-DCE leads to Cl^- and CH_3COO^-. The chloride ion yields at all solute concentrations correspond to twice the number of e_{aq}^- which had reacted with 1,1-DCE. The latter was calculated using a rate constant of 9×10^9 mol^{-1} dm^3 s^{-1} measured by pulse radiolysis for the 1,1-DCE + e_{aq}^- reaction.[17] The product ratio $[Cl^-]$:[acetic acid] is, however, *ca.* 3. This signifies that although all chlorine atoms are cleaved from 1,1-DCE the remaining carbon skeleton is not quantitatively converted into acetic acid.

No organic acids were detected from the reduction of 1,2-DCE. The actual Cl^- yields reflect again the competition for e_{aq}^- by 1,2-DCE and O_2, respectively, the rate constant for the former being 2.9×10^9 mol^{-1} dm^3 s^{-1}.[17] One-electron reduction of 1,1,2-TCE, finally (k 8.4×10^9 mol^{-1} dm^3 s^{-1}[17]) leads to chloride, monochloroacetic acid, and minute amounts of formic acid. The yield of CH_2ClCOO^- is always about one-fourth of the Cl^- yield. It is noted that two types of primary radicals, $\dot{C}H_2CHCl_2$ and $CH_2Cl\dot{C}HCl$, are formed from 1,1,2-TCE upon dissociative electron uptake.

(2) $^{\bullet}OH$ *Radical-induced Degradation.*—The reaction of $^{\bullet}OH$ radicals with the investigated compounds was studied in phosphate-buffered solutions which were either saturated with N_2O or with N_2O–O_2 (80:20) gas mixtures. In the latter case the oxygen concentration was about the same as in air-saturated solutions. The identified acid anions are listed in Table 2 together with their respective G values which were determined in irradiated solutions of (2—3) × 10^{-3} mol dm^{-3} substrate.

All the chlorinated ethanes react with $^{\bullet}OH$ radicals quite fast with absolute rate constants in the order of (1—2) × 10^8 mol^{-1} dm^3 s^{-1}.[17] The general mode of reaction is considered to be hydrogen-atom abstraction (9) which is a common type of $^{\bullet}OH$ reaction. Abstraction of chlorine by $^{\bullet}OH$ radicals is endothermic by 90 kJ mol^{-1} and should, therefore, not occur.[19] All ethyl radicals which could possibly be derived by hydrogen-atom abstractions from the various chlorinated compounds are shown in Table 2. Organic acids are only obtained in the presence of oxygen, and their generation is associated with Cl^- elimination from the peroxyl radicals. The formation of appreciable yields of formic acid and CO_2 indicates that the ethane skeleton does not necessarily remain intact in this process.



$$\text{—C—C—H} + {}^{\bullet}OH \longrightarrow H_2O + \text{—C—C}^{\bullet} \qquad (9)$$

A surprising result in the light of our above considerations is the formation of considerable amounts of chloride ions even in the absence of oxygen. For further discussion it is also noted that in oxygen-containing solutions the product yields do not depend on the dose rate, while a slight dependence was indicated in oxygen-free systems. For example, $G(Cl^-)$ decreased from 1.7 to 1.3 when the dose rate was increased from 300 to 6 000 h^{-1} Gy for the $^{\bullet}OH$ radical-induced degradation of 1,1-DCE in purely N_2O-saturated solutions.

Reaction Mechanism and Discussion.—Any reaction mechanisms that are inferred for the radical-mediated formation of acids from chlorinated ethanes must account for the following facts which emerge from inspection of Tables 1 and 2.

(a) Organic acids are only formed from chlorinated ethyl radicals when oxygen is present, *i.e.* when peroxyl radicals are formed.

(b) The carboxyl group of the acetic acid derivatives always arises from the carbon atom where the initial reaction occurred, *i.e.* at the primary radical site.

(c) At least one chlorine substituent must be located at the radical carbon for the organic acid formation to occur. Peroxyl radicals of the structure $R\text{–}CH_2OO^{\bullet}$ do not form any acid.

(d) Chloride ions result from $^{\bullet}OH$ radical attack at chlorinated ethanes even in the absence of oxygen.

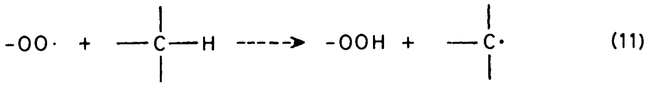
(e) Formic acid and carbon dioxide as a result of C–C cleavage are produced in small amounts from chlorinated ethyl peroxyl radicals. The extent of C–C bond scission is considerably higher in the $^{\bullet}OH$-induced degradation of the substrates than in the corresponding process initiated by e_{aq}^-.

This list of experimental facts should be completed by our assumption that $^{\bullet}OH$ radicals do not abstract chlorine atoms. The latter is concluded from the lack of acetic acid formation in N_2O–O_2-saturated solutions of 1,1,1-TCE. (If $^{\bullet}OH$ radicals were able to abstract Cl-atoms the resulting $CH_3\dot{C}Cl_2$ would quantitatively be converted into acetic acid *via* the $CH_3CCl_2OO^{\bullet}$ radical.)

Three different types of peroxyl radicals can be formed from chlorinated ethanes depending on the chlorine substitution at the carbon atom which carries the peroxyl group. These three types are the tertiary $R\text{–}C(Cl)_2OO^{\bullet}$, the secondary $R\text{–}CH(Cl)OO^{\bullet}$, and the primary $R\text{–}CH_2OO^{\bullet}$ radicals. They behave differently with respect to the acid formation. $R\text{–}C(Cl)_2OO^{\bullet}$ radicals are quantitatively converted into R–COOH, while radicals of the structure $R\text{–}CH_2OO^{\bullet}$ do not yield R–COOH at all. $R\text{–}CH(Cl)OO^{\bullet}$ radicals show an intermediate efficiency.

The first step in the conversion of $R\text{–}C(Cl)_2OO^{\bullet}$ into R–COOH is likely to be a bimolecular process (10) which yields oxy radicals *via* a tetraoxide intermediate. Such a mechanism is well documented in connection with tertiary peroxyl radicals in general.[20] Possible hydrogen abstraction (11), *e.g.* from t-butyl alcohol or any C–H bond in the halogenocarbons, is not likely to occur since such reactions are known to be very inefficient and slow.[21,22]

$$2R\text{-}C(Cl_2)OO^{\bullet} \longrightarrow [R\text{-}C(Cl_2)OOOOC(Cl)_2\text{-}R]$$
$$\downarrow$$
$$O_2 + 2R\text{-}C(Cl)_2O^{\bullet} \qquad (10)$$



$$\text{-OO}^{\bullet} + \text{—C—H} \dashrightarrow \text{-OOH} + \text{—C}^{\bullet} \qquad (11)$$

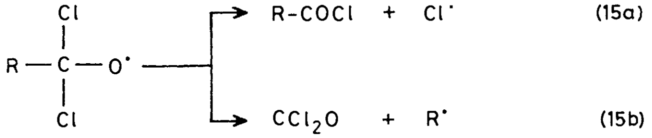
The oxyl radicals have various possibilities to react further. In the presence of t-butyl alcohol reaction (12) should be envisaged. For oxyl radicals such hydrogen abstraction is known to be a reasonably fast process.[23] Subsequently the α-chloro alcohol can be expected to eliminate HCl [reaction (13)] and the acid chloride to hydrolyse to the free organic acid [reaction (14)].

$$R\text{-}C(Cl_2)O^{\bullet} + (CH_3)_3COH$$
$$\downarrow$$
$$R\text{-}C(Cl_2)OH + \dot{C}H_2C(CH_3)_2OH \qquad (12)$$

$$R\text{-}C(Cl_2)OH \dashrightarrow R\text{-}COCl + HCl \qquad (13)$$

$$R\text{-}COCl + H_2O \dashrightarrow R\text{-}COOH + HCl \qquad (14)$$

Competitively, and in the absence of t-butyl alcohol probably exclusively, the oxyl radical may suffer radical cleavage [reaction (15)].[24] Two pathways can be envisaged with the molecular products being subject to fast hydrolysis, thereby yielding acetic acid from R–COCl *via* reaction (14) or CO_2 *via* (16). Interestingly, free $Cl^{\bullet}$ atoms have been trapped during the metabolism of CCl_4[25] (*i.e.* where R = Cl) and it was suggested that they are formed from the $CCl_3OO^{\bullet}$ peroxyl radical or a



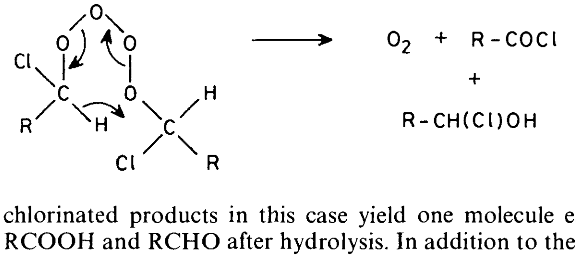
$$CCl_2O + H_2O \longrightarrow CO_2 + 2\,HCl \qquad (16)$$

radical derived therefrom. Since phosgene is also a metabolic product of CCl_4[26] we now suggest that it is in fact the $C(Cl_3)O^{\bullet}$ alkoxyl radical which cleaves these $Cl^{\bullet}$ atoms.

Acid formation from secondary peroxyl radicals $R{-}CH(Cl)OO^{\bullet}$ can also be envisaged to occur by various routes.[27–29] They are also based on an initial combination of two peroxyl radicals to an intermediate tetraoxide. A well known concerted mechanism (17)[27,28] would yield two molecules of acid chloride

$$R{-}CH(Cl)OOOOCH(Cl){-}R \longrightarrow 2\ R{-}COCl + H_2O_2 \qquad (17)$$

which would hydrolyse to the corresponding acid. Another possible rearrangement proceeds *via* a six-membered ring in the transition state[29] (Russell mechanism) [reaction (18)]. The



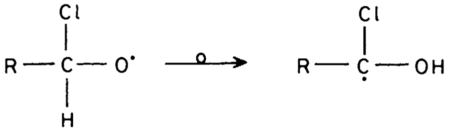
(18)

chlorinated products in this case yield one molecule each of RCOOH and RCHO after hydrolysis. In addition to these two molecular pathways the tetraoxide could also break down to O_2 and two $RCH(Cl)O^{\bullet}$ alkoxyl radicals [corresponding to reaction (10)]. The decay of such alkoxyl radicals *via* hydrogen abstraction (19) and hydrolysis (20) would, however, only lead

$$RCH(Cl)O^{\bullet} + (CH_3)_3COH \longrightarrow RCH(Cl)OH + \dot{C}H_2C(CH_3)_2OH \qquad (19)$$

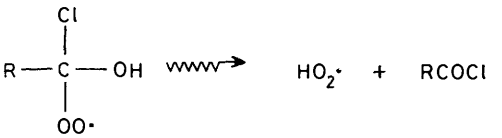
$$RCH(Cl)OH \longrightarrow RCHO + HCl \qquad (20)$$

to aldehyde. This does nevertheless not eliminate the oxyl radicals as a possible source of acid since such radicals have been reported to undergo a fast 1,2-hydrogen shift (21)[30] to



$$R{-}\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}{-}O^{\bullet} \xrightarrow{o} R{-}\overset{\displaystyle Cl}{\dot{C}}{-}OH \qquad (21)$$

yield a carbon-centred α-hydroxy radical. Oxygen addition to this carbon-centred radical, for example, would lead to an α-hydroxy peroxyl radical. Such configuration is prone to $HO_2^{\bullet}$ cleavage (22) and subsequent hydrolysis of RCOCl would yield the acid.



$$R{-}\overset{\displaystyle Cl}{\underset{\displaystyle OO^{\bullet}}{C}}{-}OH \rightsquigarrow HO_2^{\bullet} + RCOCl \qquad (22)$$

In any case, all possible reaction routes for secondary peroxyl radicals are characterized by a complete chlorine elimination from the initial radical carbon atom. Depending on the pathways the yields of organic acid relative to the peroxyl radicals would be either 1:1 or 0.5:1. The experimental results show, in fact, ratios between these limits, suggesting that the various routes are competitive.

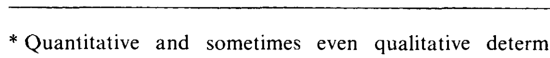
No acetic acids are formed from $R{-}CH_2OO^{\bullet}$ radicals. In principle, these peroxyl radicals undergo the same type of reactions as described above. Acid formation is always associated with a hydrolysis process of a chlorine which must still be present at the carbonyl carbon. Degradation of $R{-}CH_2OO^{\bullet}$ can, therefore, only lead to aldehydes as highest oxidation product. Aldehydes were indeed found to be formed from $R{-}CH_2OO^{\bullet}$ as well as from $R{-}CHClOO^{\bullet}$ and qualitatively identified, *e.g.* CH_3CHO from $CH_3CHClOO^{\bullet}$ or CH_2ClCHO from $CH_2ClCHClOO^{\bullet}$ (quantitative determination is still difficult*).

A very interesting result is the formation of considerable amounts of chloride ions in the $^{\bullet}OH$ radical reaction with the various substrates in the absence of oxygen. One possible explanation would be a β-chlorine elimination from the primary ethyl radical. A corresponding process has very recently been directly observed, namely $Br^{\bullet}$ elimination from $\dot{C}H_2{-}CH_2Br$.[12] The $Cl^{\bullet}$ atom thus formed could subsequently abstract hydrogen from the chlorinated ethane and thereby initiate a chain reaction (23) and (24) (R = H or Cl) which would be in

$$R_2\dot{C}{-}CR_2Cl \longrightarrow Cl^{\bullet} + R_2C{=}CR_2 \qquad (23)$$

$$Cl^{\bullet} + R_2CH{-}CR_2Cl \longrightarrow HCl + R_2\dot{C}{-}CR_2Cl \qquad (24)$$

accord with the slight dose rate effect observed on the Cl^- yield. However, two arguments can be put forward which contradict this reaction sequence. First, the energy required for a β-chlorine elimination from such radicals was calculated as 30 kJ mol^{-1}.[19] This cannot be compensated by solvation energies since no ions are formed in reaction (23). Secondly, Koltzenburg *et al.*[31] did not observe any olefinic product formed from very similar species carrying a leaving group X at the carbon in a β-position to the radical site. They unambiguously assigned the observed HX acid formation to an S_N1-type solvolysis (25) of the incipient radical.



(25)

The rate constants for reaction (25) were found to depend very strongly on both the nature of the leaving group X and the structure of the carbon skeleton. For unbranched alkyl radicals with a terminal chlorine substituent in β-position to the tervalent carbon this process is relatively slow ($k < 10^2$ mol^{-1} dm^3 s^{-1}). Applying this mechanism to our system the chloride

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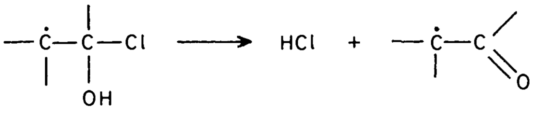
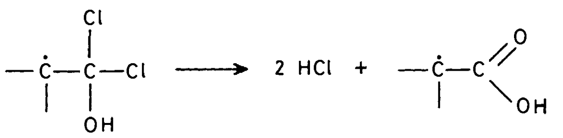
* Quantitative and sometimes even qualitative determination of aldehydes in our solutions is still difficult owing mainly to their polarity and their very small concentrations ($< 10^{-5}$ mol dm^{-3}). G.c.-identification from aqueous solutions is hardly possible and extraction into an organic phase would not be quantitative. Spectroscopic determination *via* derivatization to form a coloured product is also seriously hampered. For example, the specific derivatization of formaldehyde using chromotropic acid is strongly retarded in the presence of acetaldehyde, acetic acids, *etc.* (B. Katzac and Z. J. Vejdelek 'Handbuch der photometrischen Analyse Organischer Verbindungen, Vol. 1,' Verlag Chemie, Weinheim, 1974). Selective derivatizations of various acetaldehydes are not even known. A better approach seems to be an unselective derivatization which is followed by a chromatographic separation of the products. Such a method (A. Henglein, M. Gutièrrez, and Ch.-H. Fischer, *Ber. Bunsenges. Phys. Chem.*, 1984, **88**, 170) which involves the derivatization of aldehydes with 2,4-dinitrophenylhydrazine and analysis of the resulting hydrazones by h.p.l.c. after extraction did indeed strongly indicate the formation of aldehyde products in our solutions. However, we are not yet able to determine *G* values, since the derivatization of halogenated aldehydes may not be quantitative. For example, chloral hydrate ($CCl_3CHO{\cdot}H_2O$) does not seem to react with 2,4-dinitrophenylhydrazine at all.

yields obtained in oxygen-free solutions can accordingly be explained by a very slow solvolysis of the various β-chlorinated radicals. Since this process is in competition with the bimolecular deactivation of two alkyl radicals it also provides a rationale for the small dose rate effect.

Multiple chlorine substitution at the β-position would, of course, lead to further hydrolysis after the first hydroxyl group has been introduced, *e.g.* reactions (26) and (27). Looking at the nature of the primary radicals formed from the halogenated ethanes (column 2 of Table 2) this consideration would be in excellent accord with the observed Cl^- yields (column 3 of Table 2). The latter clearly increase with increasing chlorine substitution in the β-position to the radical site.


(26)


(27)

β-Chloro radicals are also produced upon one-electron reduction of 1,2-DCE and 1,1,2-TCE, respectively. However, Table 1 reveals that hardly any chloride is formed in addition to the initial yield derived from one-electron reduction [$G(Cl^-) \sim G(e_{aq}^-) = 2.9$]. It is therefore concluded that t-butyl alcohol which was always present in these solutions intercepted the alkyl radicals prior to their solvolysis. This in turn agrees with the low rate constant of the latter reaction as suggested by Koltzenburg *et al.*[31]

Solvolysis reactions such as (25) cannot occur in N_2O–O_2-saturated solutions, because they cannot compete with the fast oxygen addition to alkyl radicals ($k > 10^8$ mol^{-1} dm^3 s^{-1}). $G(Cl^-)$ in such solutions were nevertheless also greater than expected on the basis of the organic acid yields. Furthermore, products were detected which resulted from carbon–carbon cleavage, *e.g.* HCOOH, CO_2, and HCHO. This can only be accounted for by additional reactions of the peroxyl radicals competing with the main decay pathway outlined in reactions (10)—(22). Several possibilities such as γ-hydrolysis of the peroxyl and alkoxyl radicals, or γ-chlorine elimination from the alkoxyl radicals associated with dioxethane formation may be envisaged among others. However, we are currently not able to attribute any mechanism to this very interesting side reaction. A necessary prerequisite for a conclusive consideration would be a complete material balance. The most important non-ionic products are aldehydes but so far they have evaded unambiguous quantitative determination. Studies are under way to unravel the mechanism of the carbon–carbon bond cleavage.

Conclusions.—The present systematic radiation chemical study on simple chlorinated ethanes was focused on the generation of organic acids as a major product in radical-mediated processes. The results corroborate a number of earlier findings on some individual halogenated alkanes. The only structural prerequisite is that the primary radical carries at least one further halide at the site of the unpaired electron, *i.e.* its structure has to be either $\mathrm{R\dot{C}(Hal)_2}$ or $\mathrm{R\dot{C}H(Hal)}$. The key intermediates for the acid formation (H–Hal and R–COOH) are the corresponding peroxyl radicals which result from fast oxygen addition to the carbon-centred radicals. The formation of organic acids requires the presence of water as hydrolysing agent and is associated with the generation of inorganic acids (hydrogen halide).

Our experiments can be taken as a model for any event leading to such halogenated alkyl radicals. The latter may be formed from the saturated compounds *via*, for example, reaction with other free radicals, *via* one-electron uptake from enzymatic systems such as cytochrome P-450, or *via* reduction at light-exposed semiconductor particles, *etc.* The fact that, after the initial formation of the alkyl radicals, it needs only oxygen and water to generate the acids, is considered to be of great significance for the environmental and toxicological hazards of such halogenated alkane derivatives.

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