

Radical-mediated degradation mechanisms of tribromo- and other trihalogenated acetic acids in oxygen-free solutions as studied by radiation chemistry methods



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$\cdot\text{CBr}_2\text{CO}_2^-$ and $\cdot\text{CCl}_2\text{CO}_2^-$ radicals, generated upon one electron reduction of tribromo- and trichloroacetic acids and $\cdot\text{CF}_2\text{CO}_2^-$ radicals produced from difluoroacetic acid by reaction with $\cdot\text{OH}$, exhibit optical absorptions in the UV with λ_{max} at 290 nm ($\epsilon = 2580 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 330 nm ($\epsilon = 3000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 310 nm ($\epsilon \approx 660 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), respectively. Mechanistically, the present report focuses on the free-radical-induced degradation of tribromoacetic acid. Absolute rate constants have been determined for the reactions of $\text{CBr}_3\text{CO}_2^-$ with e_{aq}^- , $\text{H}\cdot$, $\text{CO}_2^{\cdot-}$, $\cdot\text{CH}_2\text{OH}$, $\text{CH}_3\cdot\text{CHOH}$, $(\text{CH}_3)_2\cdot\text{COH}$ and $\cdot\text{CH}_3$ radicals to be $k = 1.8 \times 10^{10}$, 1.5×10^{10} , 2.8×10^9 , 1.6×10^9 , 2.3×10^9 , 3.0×10^9 and $3.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The major fate of $\cdot\text{CBr}_2\text{CO}_2^-$ is self-termination to yield tetrabromosuccinic acid which, however, is unstable and thermally decomposes to HBr , CO_2 and tribromoacrylic acid. Dibromofumaric acid, dibromomaleic acid and carbon monoxide were found as minor secondary products, formation of which is explained by a small yield of reductive decomposition of the transient tetrabromosuccinic acid. A complete and mechanistically satisfying material balance is provided for several systems in which $\text{CBr}_3\text{CO}_2^-$ has been degraded *via* a variety of radicals under various conditions. $\cdot\text{OH}$ Radicals do not react directly with $\text{CBr}_3\text{CO}_2^-$. They have been shown, however, to contribute indirectly to the degradation of this acid *via* their reaction with reductively liberated bromide ions. The $\text{Br}\cdot$ atoms formed in this process are considered to abstract a bromine atom from $\text{CBr}_3\text{CO}_2^-$ or oxidize the carboxyl function in a one-electron transfer process. The formation of free $\text{Br}\cdot$ atoms has been recognized by pulse radiolysis through their conjugate dimer radical anions $\text{Br}_2^{\cdot-}$. With respect to the other trihalogenated acids it is noteworthy that $\text{CCl}_3\text{CO}_2^-$ is efficiently reduced by $\text{CO}_2^{\cdot-}$ radicals and that CF_3CO_2^- exhibits a high stability toward γ -irradiation and practically resists any reductive attack.

Introduction

Halogenated hydrocarbons, although generally known as toxic and ecologically hazardous compounds, are nevertheless still in widespread use in various important fields of civilization. It has been shown that their degradation in the environment may eventually lead to complete mineralization, *i.e.* to CO_2 and the respective hydrogen halide acids.¹ Several molecular organic intermediates such as halogenated alcohols, aldehydes, ketones and organic acids have been identified *en route* to these inorganic substrates. As demonstrated by many radiation chemical and photocatalytic studies, most of the degradation steps involve the formation and reactions of free radicals. Two important initial steps have been identified in particular: (i) a reductive cleavage of a C–X bond and (ii) an oxidative cleavage of a C–H bond. Both processes lead to carbon-centred radicals which, under aerobic conditions, rapidly add molecular oxygen to yield peroxy radicals. Under anaerobic conditions most studies have just been concerned to demonstrate the liberation of halide ions with little attention being paid to the other products, particularly with respect to a satisfactory material balance. Also, the majority of the studies dealing with the mineralization process in an oxygen containing environment still lack a detailed mechanistic insight into the degradation of the above mentioned molecular organic intermediates, particularly the organic acids.

Nevertheless, there are examples which illustrate the importance and the need for such investigations. One of the environmentally crucial compounds is trifluoroacetic acid, $\text{CF}_3\text{CO}_2\text{H}$.

This carboxylic acid is the main product resulting from degradation of 1,1,1,2-tetrafluoroethane which is considered to be one of the more ozone-friendly alternatives to fully halogenated freons for applications as refrigeration, air conditioning and pharmaceutical aerosols and certain types of insulating foams.^{2,3} Yet, there is hardly any knowledge about the reactivity of $\text{CF}_3\text{CO}_2\text{H}$ toward free radicals, and whatever information is available from radiation chemistry and photocatalytic studies indicates an almost absolute inertness of this acid towards radical and redox attack. In fact, until now only two absolute rate constants have been reported, namely, an upper limit for its reaction with hydrated electrons ($k < 1.4 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)⁴ and for a reaction with NO_3^{\cdot} radicals ($k = 3.9 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).⁵ In the latter case it was shown that the reaction proceeds *via* an electron-transfer mechanism to yield $\text{CF}_3\text{CO}_2^{\cdot}$, followed by decarboxylation. However, since both e_{aq}^- and NO_3^{\cdot} are naturally not very abundant, this leaves $\text{CF}_3\text{CO}_2\text{H}$ as a chemically almost undegradable, long lasting environmental sink in fluorocarbon chemistry.

Considerably more information is available on the degradation mechanisms of $\text{CCl}_3\text{CO}_2\text{H}$ and other less chlorinated acetic acids. A general possibility involves reductive degradation *via* a C–Cl cleavage as a first step, while any significant contribution of an oxidative abstraction mechanism, *e.g.* by $\cdot\text{OH}$ radicals, is restricted to the presence of abstractable C–H bonds. Some studies,^{6,7} concerning the photocatalytic degradation of trichloroacetic acid on TiO_2 surfaces, reveal that the oxidative process may, however, be induced *via* valence band holes generated in a light-exposed semiconductor. In this case, the reaction proceeds *via* the photo-Kolbe mechanism, *i.e.* oxidation of the carboxylate group and subsequent decarboxylation.

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Practically no information is available, so far, on the degradation of brominated acetic acids. Although a qualitatively similar behaviour can be anticipated for all halogenated acids certain individual features are expected on the basis of, for example, the differences in the respective C–F, C–Cl and C–Br bond energies. In the present work we, therefore, focus on a pulse and steady-state radiolysis investigation of tribromoacetic acid, $\text{CBr}_3\text{CO}_2\text{H}$, with emphasis on the formation and properties of radical intermediates and a complete material balance for the molecular products. The study also includes some relevant information on the transients and products formed from the chlorine and fluorine analogue acids.

Experimental

All chemicals were laboratory reagent grade and used without further purification. They were supplied by Aldrich ($\text{CBr}_3\text{CO}_2\text{H}$, $\text{CF}_3\text{CO}_2\text{H}$, $\text{CHF}_2\text{CO}_2\text{H}$, $\text{CH}_2\text{BrCH}_2\text{CO}_2\text{H}$, $\text{CH}_3\text{CHBrCO}_2\text{H}$, 1,2- $\text{C}_2\text{H}_4\text{Br}_2$ and CBr_4) or by Merck ($\text{CCl}_3\text{CO}_2\text{H}$, $\text{C}_2\text{H}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$, NaCl , NaBr , NaF , $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$, 2-methylpropan-2-ol, methanol and ethanol).

The following abbreviations are used for the derivatives of acetic acid: TBAA (tribromoacetic acid), TCAA (trichloroacetic acid), TFAA (trifluoroacetic acid) and DFAA (difluoroacetic acid). The other acids, namely, tribromoacrylic, dibromofumaric, dibromomaleic, tetrabromosuccinic, tetrachlorosuccinic and tetrafluorosuccinic acids are abbreviated as TBAAcrA, DBFuA, DBMaA, TetBSA, TetCSA and TetFSA, respectively, while 1,2-dibromoethane is denoted as 1,2-DBE.

Tribromoacrylic acid was synthesized in analogy to the synthesis of 3-bromo-2,3-diiodoacrylic acid⁸ and has been characterized by electron impact mass spectrometry (70 eV). The observed $^{79/81}\text{Br}$ isotope pattern was obtained as expected from the natural abundance of the two isotopes. The spectrum in terms of m/z of the most intensive ion of the isotope clusters (relative intensity % and elemental composition) was as follows (signals below 5% rel. intensity have been omitted): 312 (70.6%, $\text{C}_3^{79}\text{Br}_2^{81}\text{BrO}_2\text{H}^+$); 263 (8.3, $\text{C}_2^{79}\text{Br}_2^{81}\text{Br}^+$); 229 (100, $\text{C}_3^{79}\text{Br}^{81}\text{BrO}_2\text{H}^+$); 185 (29.5, $\text{C}_2^{79}\text{Br}^{81}\text{BrH}^+$); 184 (72.8, $\text{C}_2^{79}\text{Br}^{81}\text{Br}^+$); 149 (10.9, $\text{C}_3^{81}\text{BrO}_2^+$); 131 (23.7, $\text{C}_3^{79}\text{BrO}^+$); 120 (6.0, $\text{C}_2^{79}\text{BrOH}^+$); 104 (35.2, $\text{C}_2^{79}\text{BrH}^+$); 103 (25.4, $\text{C}_2^{79}\text{Br}^+$); 91 (9.5, C^{79}Br^+); 79 (12.5, $^{79}\text{Br}^+$). Dibromofumaric acid was synthesized according to a literature reference.⁹

Solutions were always freshly prepared. The solvent was deionized millipore-filtered water the quality of which corresponded to triply distilled water (>18 M Ω). The desirable pH values of solutions were adjusted by the addition of corresponding amounts of 0.1 mol dm⁻³ HClO_4 or NaOH .

The pulse radiolysis experiments were performed by utilizing either 500 ns pulses of 1.55 MeV electrons from a Van de Graaff accelerator facility, or 50 ns pulses of 8 MeV electrons from a linear electron accelerator (LINAC). Basic details of the equipment and the analysis of data have been described already.^{10,11} Dosimetry was based on the oxidation of SCN^- to $(\text{SCN})_2^{\cdot-}$, which in aqueous N_2O -saturated solutions takes place with $G \approx 6$. (G denotes the number of species per 100 eV, or the approximate μmol concentration per 10 Joule absorbed energy.) The radical concentration generated per pulse typically amounts to $(1\text{--}3) \times 10^{-6}$ mol dm⁻³ for all the systems investigated in this study. Experimental error limits are estimated to be $\pm 10\%$ unless specifically noted.

γ -Radiolysis was carried out in the field of a ^{60}Co γ -source with total adsorbed doses in the range 50–300 Gy (1 Gy = 1 J kg⁻¹ = 100 rad) as determined by Fricke dosimetry.

The concentrations of the halogenated acids (TBAA, TCAA and TFAA as their respective anions) as well as ionic radiation products (Br^- , Cl^- , F^- , $\text{CHBr}_2\text{CO}_2^-$, $\text{CHCl}_2\text{CO}_2^-$, $\text{CHF}_2\text{CO}_2^-$, $\text{C}_2\text{O}_4^{2-}$, $\text{CBr}_2=\text{CBrCO}_2^-$ and $^-\text{O}_2\text{CCBr}=\text{CBrCO}_2^-$) were determined by high-performance ion chromatography employing a Dionex 2010i machine. The ion chromatography was equipped

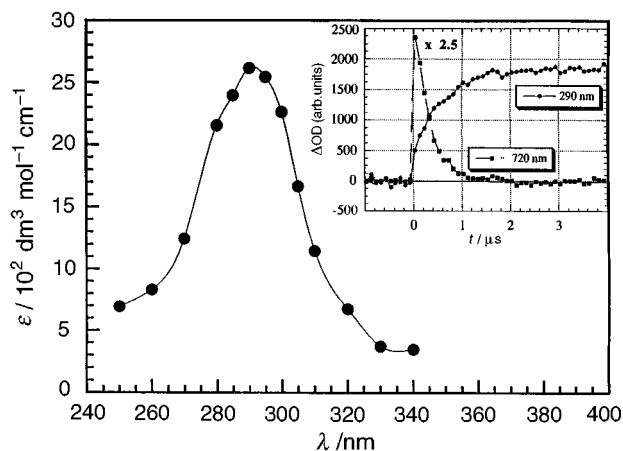


Fig. 1 Differential UV absorption spectrum of $\cdot\text{CBr}_2\text{CO}_2^-$ recorded 5 μs after the pulse upon pulse radiolysis of an aqueous, N_2 -saturated, pH 10, solution of 1.3×10^{-4} mol dm⁻³ TBAA and 1% (v/v) propan-2-ol. Extinction coefficients are average values evaluated from various systems on the basis of $G(e_{\text{aq}}^-) = 2.8$, $G(\cdot\text{OH}) = 2.8$ and $G(\text{H}\cdot) = 0.6$. Insert: Absorption–time traces recorded at 720 nm (decay of e_{aq}^-) and 290 nm (formation of $\cdot\text{CBr}_2\text{CO}_2^-$).

with a 20 cm Ion Pac AS4A-SC column protected by an Ion Pac AG-4 guard-column. The eluent generally consisted of an aqueous solution from a mixture of NaHCO_3 and Na_2CO_3 , 1.7×10^{-3} and 1.8×10^{-3} mol dm⁻³, respectively. For the separation of TBAA and oxalic acids a diluted eluent of 8.5×10^{-4} mol dm⁻³ NaHCO_3 and 9×10^{-4} mol dm⁻³ Na_2CO_3 was used. A borate eluent (5×10^{-3} mol dm⁻³ $\text{Na}_2\text{B}_4\text{O}_7$) was employed in the investigation of fluorinated acetic acids. The flow rate of the eluent was generally 2 ml min⁻¹. The background conductivity was suppressed by a Dionex Anion-Micro-Membrane-Suppressor, AMMS-1, using 0.025 mol dm⁻³ H_2SO_4 in counter flow. Identification of ionic products was achieved with a conductivity detector by comparison with authentic compounds wherever possible. CO_2 was determined in the form of HCO_3^- ions by ion chromatography using an Ion Pac ICE-ASI column. Experimental details on this have already been published.¹²

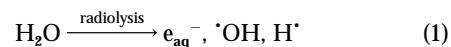
The yields of CO were analysed by GC, using a Molecular Sieve 5A column, helium as a carrier gas and thermoconductivity detector. Methylbromide was determined by GC with FID on the 15 m capillary column RTx-1. Carbon tetrabromide was analysed by means of reversed-phased HPLC, employing a mixture of $\text{CH}_3\text{OH-H}_2\text{O}$ (1 : 1) as eluent and UV-detection at 224 nm. The lower detection limit was equal to 1×10^{-6} mol dm⁻³.

All experiments were carried out at room temperature, 22 ± 2 °C.

Results and discussion

Time-resolved measurements

Reduction of TBAA by e_{aq}^- and $\text{H}\cdot$. Radiolysis of an aqueous solution, saturated with N_2 , is known to lead to the production of the radicals given in reaction (1) (besides the non-radical



products H^+_{aq} , H_2O_2 and H_2). These species are formed with radiation chemical yields of $G = 2.8$, 2.8 and 0.6 ($\approx \mu\text{mol}/10 \text{ J}$),¹³ respectively, and have to be considered for possible reaction with solutes. An actual pulse radiolysis experiment conducted in an N_2 -saturated solution of 1.3×10^{-4} mol dm⁻³ TBAA and 1% (v/v) propan-2-ol at pH 10 shows the formation of a transient absorption in the UV range. The differential absorption spectrum, monitored after 5 μs , is displayed in Fig. 1 and exhibits a maximum at λ 290 nm. The insert shows absorption–time traces

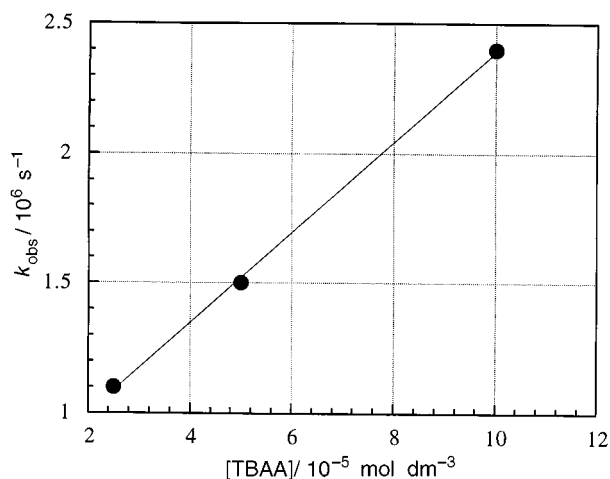
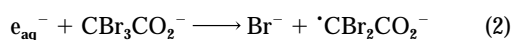


Fig. 2 Plot of first-order rate constants k_{obs} vs. TBAA concentration for the reaction of the hydrated electron with TBAA measured in pulse-irradiated, N_2 -saturated, pH 10 solutions

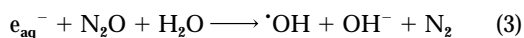
recorded at λ 720 nm, the maximum of the e_{aq}^- absorption, and at 290 nm. Identical kinetics of the respective exponential decay and growth curves ($t_2 = 300$ ns) identify the 290 nm species as a direct product from the e_{aq}^- -induced reduction of TBAA. In analogy to the generally observed dissociative electron capture by halogenated hydrocarbons the spectrum displayed in Fig. 1 is, therefore, assigned to the $^{\cdot}\text{CBr}_2\text{CO}_2^-$ radical formed in reaction (2). Kinetic analysis of the absorption-time traces and



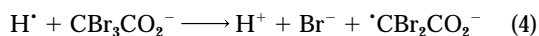
corresponding ones recorded from solutions of various TBAA concentrations, revealed a linear relationship between the observed first-order rate constant, k_{obs} , and [TBAA], as shown in Fig. 2. From this the bimolecular rate constant $k_2 = (1.8 \pm 0.3) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was obtained. Such fast reactions between the hydrated electron (as well as other reducing radical anions) with negatively charged substrates are well known, particularly when the process involves an electrophilic reaction site remote from the negative charge.¹³

Extending the timescale into the lower millisecond range indicates that the decay of $^{\cdot}\text{CBr}_2\text{CO}_2^-$ mainly follows a second-order rate law. It appears, however, that various steps are involved in the overall decay kinetics. A detailed analysis for this process is described further below.

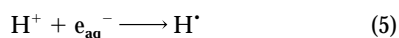
Pulse radiolysis of the same solution ($1.3 \times 10^{-4} \text{ mol dm}^{-3}$ TBAA, pH 10), but saturated with N_2O instead of N_2 , *i.e.* under conditions where the hydrated electrons are converted into hydroxyl radicals according to reaction (3), qualitatively leads



to the same spectrum as displayed in Fig. 1. The intensity of absorption is, however, reduced by a factor of about five. Since this lower yield corresponds to that of hydrogen atoms it is reasonable to assign this yield of $^{\cdot}\text{CBr}_2\text{CO}_2^-$ to the reduction of TBAA by H^{\cdot} atoms [reaction (4)].



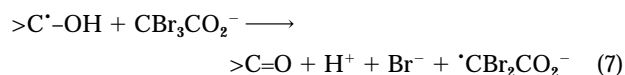
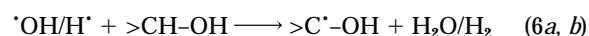
Further support for reaction (4) is provided by the pH dependence of this transient's yield in N_2O -saturated solutions. It increased with decreasing pH owing to an increasing conversion of hydrated electrons into hydrated atoms *via* reaction (5)



in competition with reaction (3). At pH 1, *e.g.* the $^{\cdot}\text{CBr}_2\text{CO}_2^-$ yield (in terms of G_{ε}) was about five times higher than at pH 10.

The rate constant for the H^{\cdot} -induced formation of TBAA radicals has been determined to be $k_5 = 1.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from a TBAA concentration dependence at pH 1. This rate constant is practically as high as that for the e_{aq}^- -induced process. On the basis that both e_{aq}^- and H^{\cdot} generate $^{\cdot}\text{CBr}_2\text{CO}_2^-$ with a combined $G = 3.4$ the extinction coefficient of this radical at 290 nm is calculated to be $\varepsilon = 2650 \pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (see Table 1).

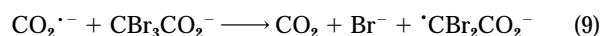
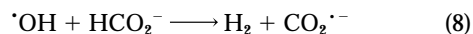
Reduction of $\text{CBr}_3\text{CO}_2^-$ by α -hydroxyalkyl radicals. Almost double the yields of $^{\cdot}\text{CBr}_2\text{CO}_2^-$ have been obtained in the presence of propan-2-ol, ethanol or methanol. Addition of the alcohols to the N_2 -saturated solution, furthermore revealed a two-step formation with the first process referring to the reduction of TBAA by e_{aq}^- . The second, slower process becomes the only one in N_2O -saturated solutions but at double yield. Accordingly, it is attributed to the reduction of TBAA by α -hydroxyalkyl radicals in the overall sequence of reactions (6) and (7). The actual yields of α -hydroxyalkyl radicals



generated in reaction (6a) amount to about 85%, 89% and 93% for propan-2-ol, ethanol and methanol, respectively, and the same percentages are assumed for the H^{\cdot} -atom reaction. (The remainder accounts for β -hydrogen abstraction and O-H cleavage.)¹⁴ With the conventionally used G values (*vide supra*) the maximal yields of $^{\cdot}\text{CBr}_2\text{CO}_2^-$ from reactions (4) and/or (6a/b) and (7) are 5.2, 5.5 and 5.8 for the three alcohols, respectively. With measured $G_{\varepsilon} = 13\,700$, 14\,500 and 14\,000, extinction coefficients of 2630, 2640 and 2410 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ are calculated, well in accord with that derived from the $e_{\text{aq}}^-/\text{H}^{\cdot}$ -induced reactions.

Absolute rate constants for reaction (7) have been evaluated from the pseudo-first-order build-up of the $^{\cdot}\text{CBr}_2\text{CO}_2^-$ absorption measured at various TBAA concentrations. They are 3.0×10^9 , 2.3×10^9 and $1.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($\pm 10\%$) for the reaction of $(\text{CH}_3)_2\text{COH}^{\cdot}$, $\text{CH}_3\text{CHOH}^{\cdot}$ and $\text{CH}_2\text{OH}^{\cdot}$, respectively. The slight decrease is in the order of the respective redox potentials.¹⁵ Rate constants, yields and extinction coefficients are summarized in Table 1.

Reduction of TBAA by $\text{CO}_2^{\cdot-}$. TBAA is also reduced by $\text{CO}_2^{\cdot-}$ [reactions (8) and (9)] as demonstrated with a N_2O -



saturated solution of 0.1 mol dm^{-3} sodium formate and 10^{-4} mol dm^{-3} TBAA. The yield of $^{\cdot}\text{CBr}_2\text{CO}_2^-$ formed upon reduction by $\text{CO}_2^{\cdot-}$ amounts to $G_{\varepsilon} = 15\,000$. The $\text{CO}_2^{\cdot-}$ -induced reduction accounts for 100% of the reacting $^{\cdot}\text{OH}$ radicals.¹⁴ From a TBAA concentration dependence experiment an absolute rate constant for reaction (9) of $k_9 = (2.8 \pm 1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has been derived.

Under the above conditions $^{\cdot}\text{CBr}_2\text{CO}_2^-$ is also produced from H^{\cdot} atoms; about 93% of H^{\cdot} atoms react *via* a sequence analogous to reactions (8) and (9), while only 7% react directly with TBAA.

The extinction coefficient for $^{\cdot}\text{CBr}_2\text{CO}_2^-$, calculated for the $\text{CO}_2^{\cdot-}$ -induced process, amounts to $\varepsilon = 2420 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. From this and all the other data listed in Table 1 an overall average $\varepsilon = 2580 \pm 200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ is evaluated. In connection with an alternative yield calculation [see eqn. (24)] for irradiated N_2O -saturated systems this extinction coefficient may, however, just represent an upper limit with the actual average value possibly being lower by about 10%.

Table 1 Yields (in terms of G), extinction coefficients and formation rate constants of $\cdot\text{CBr}_2\text{CO}_2^-$ radicals. Solution for yield measurements: 1×10^{-4} mol dm $^{-3}$ TBAA

System	Reactive species	G^a $\approx 10^{-7}$ mol dm $^{-3}$ J $^{-1}$	$G\varepsilon$	ε/dm^3 mol $^{-1}$ cm $^{-1}$	k (TBAA + reactive species)/ dm 3 mol $^{-1}$ s $^{-1}$ b
10^{-1} mol dm $^{-3}$ HCO $_2^-$ N $_2$ O-sat., pH 10	CO $_2^{\cdot-}$	6.2	15 000	2 420	2.8×10^9
1% (v/v) Propan-2-ol N $_2$ O-sat., pH 10	(CH $_3$) $_2\cdot\text{C}(\text{OH})$	5.2	13 700	2 630	3.0×10^9
1% (v/v) Ethanol N $_2$ O-sat., pH 10	CH $_3\cdot\text{CH}(\text{OH})$	5.5	14 500	2 650	2.3×10^9
1% (v/v) Methanol N $_2$ O-sat., pH 10	$\cdot\text{CH}_2(\text{OH})$	5.8	14 000	2 420	1.6×10^9
N $_2$ O- or N $_2$ -sat., pH 1	H $^{\cdot}$	3.4	8 800	2 610	1.5×10^{10}
N $_2$ -sat., pH 3.7–10	$e_{\text{aq}}^-/\text{H}^{\cdot}$ ($\approx 5:1$)	3.4	9 360	2 750	1.8×10^{10}
1% (v/v) Dimethyl sulfoxide N $_2$ O-sat., pH 10	$\cdot\text{CH}_3$		nd	nd	3.0×10^{7c}
1% (v/v) 2-Methylpropan-2-ol N $_2$ O-sat., pH 10	$\cdot\text{CH}_2\text{C}(\text{CH}_3)_2(\text{OH})$		nd	nd	$\approx 10^6$

^a Based on $G(e_{\text{aq}}^-)$ 2.8, $G(\cdot\text{OH})$ 2.8, $G(\text{H}^{\cdot})$ 0.6 and, in the case of the alcohols, efficiency of α -hydroxyalkyl radical formation.¹⁴ ^b Variation of TBAA concentration between 10^{-4} and 10^{-3} mol dm $^{-3}$. ^c Variation of TBAA concentration between 1×10^{-2} and 5×10^{-2} mol dm $^{-3}$.

Degradation of TBAA induced by the alkyl radicals. The generation of $\cdot\text{CBr}_2\text{CO}_2^-$ species from the TBAA can be achieved not only *via* a reductive process but also through non-reducing alkyl radicals such as methyl radicals. The latter are conveniently produced *via* reaction (10) in an N $_2$ O-saturated, aqueous

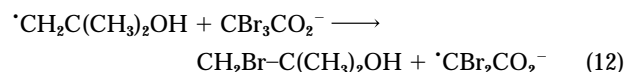


solution of dimethyl sulfoxide. The yield of $\cdot\text{CH}_3$ radicals generated this way amounts to 92% of the initially available $\cdot\text{OH}$ radicals.¹⁶ In this system the formation kinetics of the $\cdot\text{CBr}_2\text{CO}_2^-$ absorption reveals two distinct contributions. A small, fast initial growth is attributed to a direct reaction of TBAA with practically all H $^{\cdot}$ -atoms. The second slower component is much larger in yield and reflects a bromine abstraction according to reaction (11). From TBAA concentration



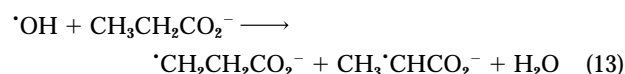
dependence experiments the rate constant was determined to be $k_{11} = (3.0 \pm 0.5) \times 10^7$ dm 3 mol $^{-1}$ s $^{-1}$.

The same picture, in principle, was observed for the $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ radicals generated in the reaction of $\cdot\text{OH}$ with 2-methylpropan-2-ol and which, like $\cdot\text{CH}_3$, have no reductive power. They also seem to abstract bromine from TBAA as can be deduced from the formation of the $\cdot\text{CBr}_2\text{CO}_2^-$ absorption. Evaluation of the rate constant for reaction (12) was, however,

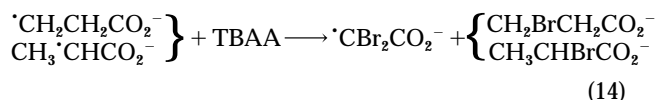


not possible within reasonable limits since the slow increase in the optical absorbance at 290 nm was interfered already significantly by the subsequent second-order disappearance of $\cdot\text{CBr}_2\text{CO}_2^-$ radicals and the total yield of the radical is not known. Only an estimate of $k_{12} \approx 10^6$ dm 3 mol $^{-1}$ s $^{-1}$ can be given.

Additional experimental proof that C-centred radicals may, indeed, undergo efficient bromine abstraction from TBAA was provided by using propionic acid as $\cdot\text{OH}$ scavenger (N $_2$ O-saturated, pH 10 solution of 2×10^{-3} mol dm $^{-3}$ propionic acid and 2×10^{-4} mol dm $^{-3}$ TBAA). In this case two different primary radicals are generated [reaction (13)], which in

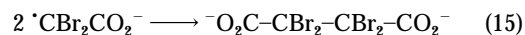


their subsequent reaction with TBAA not only produced the $\cdot\text{CBr}_2\text{CO}_2^-$ radical, detectable by pulse radiolysis, but also generated two different products [reaction (14)]. Both,



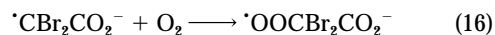
(\pm) 2-bromopropionic acid and 1-bromopropionic acid were identified by ion chromatographic analysis.

Second-order decay of $\cdot\text{CBr}_2\text{CO}_2^-$. In the absence of suitable molecular reaction partners the $\cdot\text{CBr}_2\text{CO}_2^-$ radicals decay by a second-order process. From the dose dependence a bimolecular rate constant of $2k/\varepsilon = 1.1 \times 10^6$ was derived. With $\varepsilon = 2580$ dm 3 mol $^{-1}$ cm $^{-1}$, $2k = 2.8 \times 10^9$ dm 3 mol $^{-1}$ s $^{-1}$ is derived. The under-



lying process is considered to be, in the first instance, a dimerization. Note that the rate constant is relatively high considering that it refers to a reaction between two species carrying the same charge. The absolute value is, however, below the diffusion limit and thus includes some activation energy. The tetrabromosuccinic acid (TetBSA) could not be identified as such, mainly because it is not stable in aqueous solution. Further aspects of this will be discussed in a different context later in this paper.

Reaction of $\cdot\text{CBr}_2\text{CO}_2^-$ with oxygen. Further evidence supporting our assignment that the observed absorption with a maximum at 290 nm has to be attributed to the carbon-centred radical is provided by experiments in air-saturated solution. Here, the second-order decay of the initially formed radical changes into a faster exponential decay, attributable to a reaction with molecular oxygen, to yield the respective peroxy radical [reaction (16)]. From the half-life of 2 μ s and the oxygen



concentration of 2.8×10^{-4} mol dm $^{-3}$ a rate constant $k_{16} = 1.2 \times 10^9$ dm 3 mol $^{-1}$ cm $^{-1}$ is calculated. This rate constant is of the same order of magnitude as for analogous reactions with other halogenated alkyl radicals.¹⁷

Formation of $\cdot\text{CCl}_2\text{CO}_2^-$ and $\cdot\text{CF}_2\text{CO}_2^-$. Having established that $\cdot\text{CBr}_2\text{CO}_2^-$ exhibits quite a reasonable and thus detectable optical absorption a corresponding investigation was conducted on the analogue chlorine and fluorine substituted species, $\cdot\text{CCl}_2\text{CO}_2^-$ and $\cdot\text{CF}_2\text{CO}_2^-$, for which also no spectral data were available so far.

Reduction of $\text{CCl}_3\text{CO}_2^-$ (10^{-2} mol dm $^{-3}$) by hydrated electrons ($k = 8.5 \times 10^9$ dm 3 mol $^{-1}$ s $^{-1}$)¹⁸ in N $_2$ -saturated solution yielded, indeed, a transient differential absorption spectrum attributable to $\cdot\text{CCl}_2\text{CO}_2^-$ with λ_{max} around 330 nm [Fig. 3(a)]. The intensity of this absorption is in the same range as that for $\cdot\text{CBr}_2\text{CO}_2^-$, and the extinction coefficient is estimated to be $\varepsilon_{330} = 3000$ dm 3 mol $^{-1}$ cm $^{-1}$.

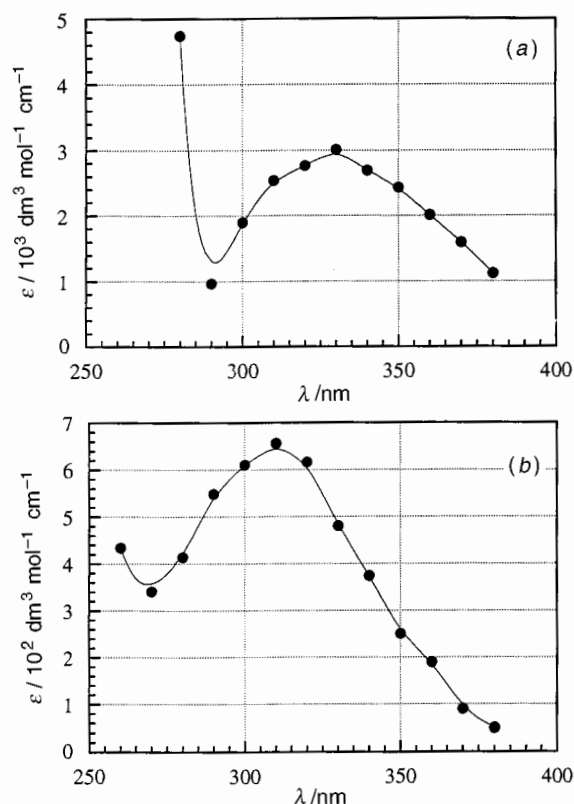
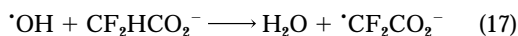


Fig. 3 Differential UV absorption spectra of (a) $\text{CCl}_2\text{CO}_2^-$ obtained upon pulse irradiation of an N_2 -saturated, pH 10, solution containing 0.01 mol dm^{-3} TCAA and 1% (v/v) propan-2-ol; (b) CF_2CO_2^- obtained upon pulse radiolysis of an N_2O -saturated, pH 10, solution containing 0.1 mol dm^{-3} DFAA

The CF_2CO_2^- radical could not be generated reductively since the reaction of CF_3CO_2^- with e_{aq}^- or reducing radicals is too slow, if occurring at all. A transient with a maximum absorption at 310 nm, as shown in Fig. 3(b), and attributable to CF_2CO_2^- could, however, be detected, for example, upon pulse radiolysis of an N_2O -saturated solution of $10^{-1} \text{ mol dm}^{-3}$ $\text{CF}_2\text{HCO}_2^-$. It is believed to result from hydrogen abstraction [reaction (17)]. Note that, on the basis of an assumed quantita-



tive reaction, the calculated extinction coefficient, $\epsilon_{\text{max}} \approx 660 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, is much lower than that for $\text{CBr}_2\text{CO}_2^-$ and $\text{CCl}_2\text{CO}_2^-$. This could have an electronic reason but may also reflect an incomplete reaction due to a low rate constant for the abstraction process.

γ -Radiolysis of $\text{CBr}_2\text{CO}_2^-$ solutions

Products and material balance. Six different systems were subjected to a detailed product study, all of them consisting of $2 \times 10^{-4} \text{ mol dm}^{-3}$ aqueous TBAA solutions at pH 10. The first two were N_2O -saturated and, in addition, contained either formate (system I) or ethanol (system II) as OH scavenger. The major radicals available for reductive initiation of TBAA degradation accordingly were $\text{CO}_2^{\cdot-}$ and CH_3CHOH , respectively [reactions (8)/(9) and (6)/(7)]. In systems III and IV, also N_2O -saturated, the OH scavengers were 2-methylpropan-2-ol and dimethyl sulfoxide which, in their respective reactions with OH , generate the redox-inert radicals $\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ and CH_3 [reaction (10)]. In these cases TBAA degradation is initiated by bromine abstraction. System V is an N_2O -saturated TBAA solution containing no OH scavenger. This is a particularly interesting system since it shows considerable TBAA degradation despite the fact that the major reactive species, namely, OH does not directly react with TBAA.

System VI, finally, was N_2 -saturated and provided OH radicals ($G \approx 2.8$) and reducing species, namely e_{aq}^- ($G \approx 2.8$) and H^\cdot ($G \approx 0.6$), at almost equal yield. For these latter two systems it will be shown that TBAA degradation may also be initiated via Br^\cdot -atoms generated in the reaction of OH with reductively liberated bromide ions.

The products obtained upon γ -radiolysis of the above systems are summarized in Table 2. The main products were hydrogen bromide (measured as Br^-), tribromoacrylic acid and CO_2 . In system IV also appreciable yields of CH_3Br were formed. In all systems, some small amounts of CO, dibromofumaric and dibromomaleic acid were detected with yields accounting, however, for only $\leq 5\%$ of the overall TBAA degradation.

The data listed in Table 2 actually represent the yields obtained after heating the irradiated sample for 20 min at 55°C or being measured as limiting values after leaving the room temperature samples for longer periods ($\geq 24 \text{ h}$) before analysis. Analysis of room temperature samples conducted immediately after irradiation gave significantly lower Br^- , TBAA and CO_2 yields which kept increasing with time. Heating or waiting had no effect, however, on the yield of the overall TBAA degradation, of CH_3Br from system IV and all the minor products. This indicates that the delayed, post-irradiation formation of some of the products is not due to a thermal decomposition of TBAA itself but from a product generated in the irradiation process. (See also section on 'Origin of tribromoacrylic acid' below.)

One common finding for all systems is a complete material balance for the results obtained after heating the samples. With $\{\text{Br}\}$ denoting the total yield of bromine products (Br^- , CH_3Br , TBAA, DBFuA, DBMaA), $\{\text{C}\}$ that of the carbon products (CO_2 , CO, TBAA, DBFuA, DBMaA) and $\{-\text{TBAA}\}$ the measured degradation of tribromoacetic acid, the ratios of $\{\text{Br}\}/\{-\text{TBAA}\}$ and $\{\text{C}\}/\{-\text{TBAA}\}$ in all systems match the theoretically predicted values of 3.0 and 2.0, respectively, within an error margin of $\leq 5\%$. This is an excellent agreement considering that the TBAA degradation is measured as a difference between two relatively large concentrations.

The $\{\text{Br}\}/\{-\text{TBAA}\}$ and $\{\text{C}\}/\{-\text{TBAA}\}$ ratios are considerably lower for the immediate room temperature results indicating that certain products indeed escape, at least partially, detection under these circumstances. Before discussing the absolute yields and the details of the individual systems we shall first focus, however, on the common features of TBAA, DBFuA and DBMaA and CO formation.

Origin of tribromoacrylic acid (TBAA). The yields of Br^- , TBAA and CO_2 measured in the immediate analysis of the room temperature samples always fell short from the maximum values by an approximate 1:1:1 ratio. This observation suggests that all these three products originate from a common precursor formed as a result of the irradiation but not directly detectable in the analysis. The stoichiometric sum of Br^- , TBAA and CO_2 constitutes tetrabromosuccinic acid which formally results from combination of two $\text{CBr}_2\text{CO}_2^-$ radicals [reaction (18)]. Accordingly, we assign the formation of the final products to the subsequent decomposition of TetBSA [reaction (19)]. A similar mechanism has been forwarded for



tetrachlorosuccinic acid (TetCSA) which, in a process analogous to [reaction (19)], was found to decay into trichloroacrylic acid.¹⁹ The brominated TetBSA appears, however, to be much less stable than the chlorinated analogue for which a half-life of 9 min at 80°C has been reported.¹⁹ Our present investigation shows that TetBSA, on the other hand, is already completely decomposed after heating the sample for 20 min at 55°C . For comparison, we also generated tetrafluorosuccinic acid from

Table 2 Yields of products from γ -irradiated, pH 10, solutions of 2×10^{-4} mol dm $^{-3}$ under various conditions. All yields are given in terms of G values (molecules per 100 eV, or μ moles per 10 J absorbed energy).

System	-TBAA	Br $^{-}$	TBACrA	CO $_2$	CO	DBFuA	CH $_3$ Br	Total Br	Total C
						+ DBMaA		-TBAA	-TBAA
I: 10^{-3} mol dm $^{-3}$ HCO $_2^{-}$ /N $_2$ O									
20 min/55 °C or 24 h/room temperature	6.25	9.65	3.0	3.1 ^a	0.1	0.2	na	3.05	2.08
Calculated <i>via</i> eqn. (24) ^b	6.2								
Classical calculation	6.4								
II: 1% (v/v) C $_2$ H $_5$ OH/N $_2$ O									
20 min/55 °C or 24 h/room temp.	6.45	10.5	3.2	3.4	0.1	0.1	na	3.15	2.09
Calculated <i>via</i> eqn. (24) ^b	6.15 (only reductive contribution)								
Classical calculation	5.35 (only reductive contribution)								
III: 1% (v/v) (CH $_3$) $_3$ COH/N $_2$ O									
20 min/55 °C or 24 h/room temp.	6.0	9.1	2.75	3.4	0.1	0.1	na	2.93	2.03
Calculated <i>via</i> eqn. (24) ^b	6.45								
Classical calculation	5.95								
IV: 1% (v/v) (CH $_3$) $_2$ SO/N $_2$ O									
20 min/55 °C or 24 h/room temp.	6.1	3.7	2.8	3.1	0.2	0.1	5.5	2.92	1.98
Calculated <i>via</i> eqn. (24) ^b	6.95								
Classical calculation	5.85								
V: N $_2$ O									
20 min/55 °C or 24 h/room temp.	3.4	7.5	0.9	3.9	0.2	≤ 0.1	na	3.00	2.00
+ 10^{-4} mol dm $^{-3}$ Br $^{-}$	2.7		0.3						
+ 10^{-3} mol dm $^{-3}$ Br $^{-}$	1.5		0.0						
VI: N $_2$									
20 min/55 °C or 24 h/room temp.	3.9	9.0	0.9	4.2	0.3	0.1	na	3.05	1.95

^a Difference between measured total $G(\text{CO}_2) = 9.1$ and $G(\text{CO}_2) \approx 6.0$ formed from formate through 100% of $\cdot\text{OH}$ and 40% of $\text{H}\cdot$. ^b Includes H-atom and Br-atom contributions.

dimerization of $\cdot\text{CF}_2\text{CO}_2^{-}$ radicals in N $_2$ O-saturated solutions of CHF $_2\text{CO}_2^{-}$. In this case no traces of fluoride (lower detection limit was in the range of 1×10^{-6} mol dm $^{-3}$) could be detected in the irradiated sample, even after heating at 90 °C for 7 h. TetFSA appears to be absolutely stable in aqueous solution, well in line with the expected trend.

The high degree of instability of tetrabromosuccinic acids is also reflected in the chromatographic analysis. A clean ion chromatogram of TBACrA with a band of narrow and symmetric shape is only obtained with authentic TBACrA [as shown in Fig. 4(b)] or in case of the irradiated sample after heating or long-time standing. The room temperature sample analysed immediately after the irradiation, on the other hand, always resulted in a much broader and asymmetric band for TBACrA [as displayed in Fig. 4(a)]. Furthermore, this asymmetry is entirely attributable to a tailing while the front section of the chromatographic band exhibits the undisturbed classical shape. Such a picture is indicative of at least a partial formation of TBACrA during the chromatographic process on the column, *i.e.* a column material assisted decay of the presumed precursor TetBSA. Accordingly, the observed TBACrA signal may include an unspecifiable contribution by correspondingly delayed bromide formation [reaction (19)], rendering any determination of the initially available TBACrA yield from the peak area unfeasible.

Further support for our assignment can be derived from the retention times of the various halogenated succinic acids. It is shortest for the fluorinated one, TetFSA, which eluted after 8 min from a short pre-column. Under the same conditions the chlorinated acid, TetCSA, appeared after 15 min while no direct chromatographic evidence could be produced for the bromo derivative, TetBSA. It is suspected, however, to elute at even longer times if it were stable enough. Under the chromatographic conditions referred to in Fig. 4 a much longer column

was applied resulting in correspondingly longer retention times, and any TetBSA, even if present, may then simply become undetectable because of band broadening. In any case, the fact that TetBSA escapes direct analytical detection, even with the short pre-column, is understandable and does not rule out its formation in the irradiation process.

The mechanism suggested in reactions (18) and (19) theoretically requests a 1:1 ratio between TBACrA and CO $_2$, and a 2:1 ratio between TBAA degradation and TBACrA (or CO $_2$) formation. For systems I–IV this is, indeed, the case within an error limit of $\pm 5\%$ for most of the yields. A larger discrepancy is noted only for the CO $_2$ yield in system III ($G = 3.4$) which deviates from half of the TBAA degradation ($G = 3.0$) by a little over 10%. The reader is reminded, however, that the accuracy of both the TBAA degradation (as a differential measurement) and the CO $_2$ determination are associated with the highest uncertainties of all our experimental data. The fact that the CO $_2$ yields are slightly higher than the TBACrA yields, on average by 0.2 G units (0.15 without system III), can, however, be rationalized by a small contribution of Br $^{-}$ -induced TBAA degradation. As will be shown in detail later, this process leads to complete conversion of TBAA into CO $_2$ and can be accounted for by the combined DBFuA and DBMaA yields ($G \approx 0.15 \pm 0.05$).

In connection with the formation of TBACrA still another aspect is worth mentioning. As has been pointed out in the Experimental section this acid, which is necessary for initial chromatographic reference, was not available commercially but had to be synthesized by a two-stage procedure in analogy to a patent literature for diiodobromoacrylic acid. It is certainly interesting to note that γ -irradiation of an aqueous solution of tribromoacetic acid provides a fast, one-step pathway to TBACrA which can conveniently be obtained in good quantities by appropriate preparative chromatography.

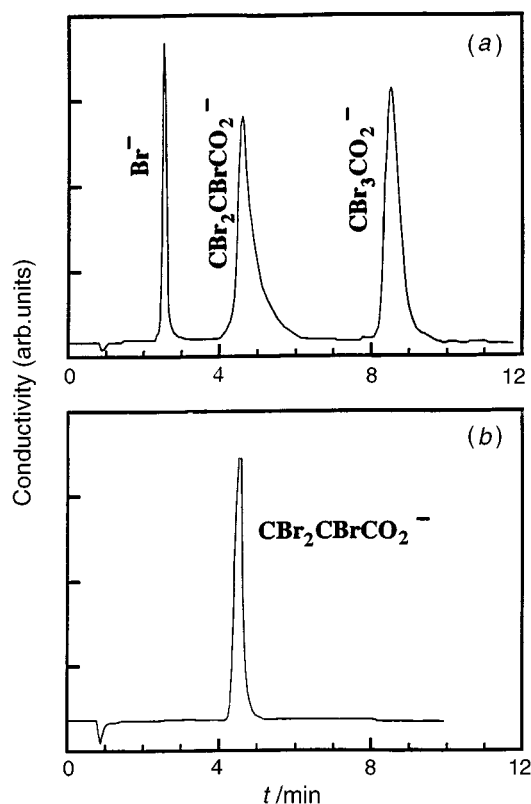
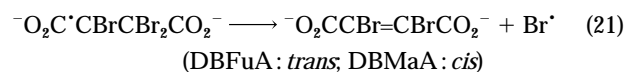
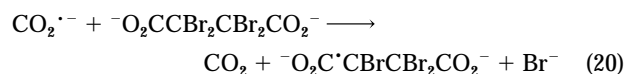


Fig. 4 (a) Ion chromatogram obtained immediately after γ -irradiation (absorbed dose: 50 Gy) of an N_2O -saturated, pH 10, solution containing $1 \times 10^{-4} \text{ mol dm}^{-3}$ TBAA and 1% (v/v) ethanol. (b) Ion chromatogram of an aqueous solution containing $5 \times 10^{-5} \text{ mol dm}^{-3}$ of authentic TBAA.

Origin of dibromofumaric and dibromomaleic acid and CO.

Although DBFuA, DBMaA and CO are only formed in very small quantities there seems no ambiguity about their formation not being associated with the above described TBAA formation and thermal TetBSA decomposition.

Since in our experiments the TBAA conversion amounted to about 20% a reasonable rationale for the generation of DBFuA and DBMaA would be through a secondary process in which the transient product TetBSA begins to compete with the original solute TBAA for the reducing radicals. In such a process, *e.g.* *via* reactions (20) and (21), both unsaturated acids would



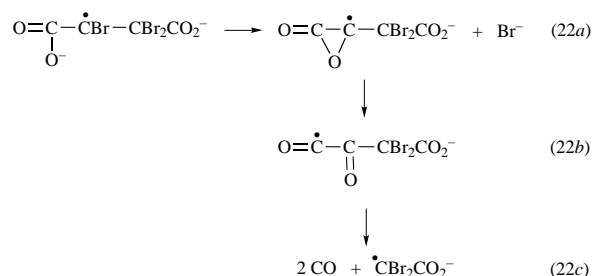
directly be formed *via* β -bromine cleavage from the TetBSA- $(-\text{Br})^{\cdot}$ radical. Such β -elimination processes are known to occur quickly, with rate constants in the order of 10^6 s^{-1} .²⁰ It is noted that reaction (21) predominantly yields the *trans*-isomer, *i.e.* DBFuA, while the *cis*-isomer, DBMaA, is generated only in trace amounts ($G \leq 0.05$). This was verified by ion chromatography with reference to the respective authentic compounds.

A test for this kind of reaction sequence with the more stable and thus easier to handle tetrachloro- and tetrafluoro-succinic acids is, unfortunately, not possible since chlorine or fluorine atoms cannot be cleaved by analogous β -eliminations. Our assumption that DBFuA and DBMaA originate from a secondary degradation process is, however, further supported by the suppression of their formation under conditions where TetBSA cannot significantly compete anymore with TBAA for the reducing radicals, *e.g.* in solutions containing higher TBAA

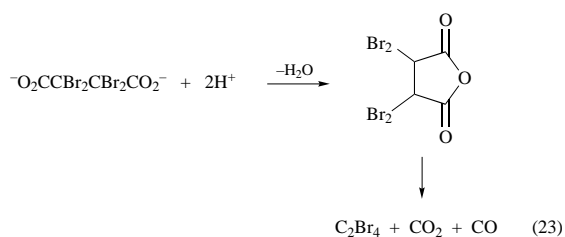
concentrations ($10^{-2} \text{ mol dm}^{-3}$) but irradiated with the same total dose as the low concentration ($2 \times 10^{-4} \text{ mol dm}^{-3}$) samples.

The origin of CO is less clear. Since we observed significantly higher CO yields upon radiolysis of air-saturated solutions of TBAA one suspicion would be a remaining oxygen impurity and an involvement of peroxy and/or oxyl radicals ($^{\cdot}\text{OOCBr}_2\text{CO}_2^-$ and $^{\cdot}\text{OCBr}_2\text{CO}_2^-$, respectively). However, since no CO was detected in solutions containing propan-2-ol as $^{\cdot}\text{OH}$ scavenger (under otherwise identical experimental conditions) an oxygen-free pathway should also be envisaged. One such possibility may involve rearrangement of the radical formed upon reduction of TetBSA in competition with the bromine elimination reaction [reaction (21)].

Oxiranyl radicals similar to the type suggested to be formed in reaction (22a) are known to rearrange as shown in reaction (22b)²¹ and the radical generated this way can easily be envisaged to lose CO according to the overall process (22c). There is,



however, no direct precedence for the formation of an oxiranyl radical *via* a fast intramolecular $\text{S}_{\text{N}}2$ reaction involving two neighbouring carbon atoms. A carboxylate induced halide (chloride) elimination has only been reported within a 1,3 mechanism (*i.e.* over one additional carbon) in connection with the hydrolysis of tetrasuccinyl dichloride.¹⁹ Another possibility would be reaction (23) with the analytically undetectable



anhydride of tetrabromosuccinic acid and tetrabromoethene as intermediates. All these mechanisms fail, however, to explain the lack of CO in propan-2-ol containing solutions leaving the question on the origin of this product indeed an open one.

It is, however, also noted that no CO formation was detectable in irradiated solutions of tetrafluorosuccinic acid where reductive fluoride liberation indicates formation of the analogue $^-\text{O}_2\text{C}^{\cdot}\text{CFCF}_2\text{CO}_2^-$ radical. This does not necessarily contradict the mechanism forwarded above for the brominated systems since C-Br bonds are distinctly different in nature than C-F bonds and the fluoride elimination necessary to yield the oxiranyl radical may not be possible. In essence, however, we feel that the mechanism of the CO formation still remains more of an open problem.

Absolute degradation yields

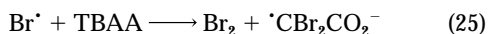
The material balance presented above showed an excellent agreement between the yield of TBAA degradation and the product yields. It is, however, also interesting to compare the absolute TBAA degradation yields with those expected on the basis of commonly used yields for scavangeable e_{aq}^- ($G \approx 2.8$),

$\cdot\text{OH}$ ($G \approx 2.8$) and H^\cdot ($G \approx 0.6$), further denoted as classical yields, or those predicted by a more sophisticated formula [eqn. (24)] evaluated by Schuler *et al.*²² for the scavenging

$$G(S) = 5.2 + 3.0 \frac{(k_s[S]/\lambda)^{\frac{1}{2}}}{1 + (k_s[S]/\lambda)^{\frac{1}{2}}} \quad (24)$$

of $\cdot\text{OH}$ radicals in N_2O -saturated solutions. In this equation $G(S)$ denotes the radiation chemical yield of $\cdot\text{OH}$ radicals available for reaction with the scavenger S, while the product $k_s[S]$ represents the pseudo-first-order rate constant for this process and λ is a so-called track recombination frequency of $4.7 \times 10^8 \text{ s}^{-1}$.

Mechanistically the simplest of all systems is I with $\text{S} = \text{HCO}_2^-$ for which the measured degradation yield amounts to $G(-\text{TBAA})_{\text{exp}} = 6.25 \pm 0.2$. The classical calculation, as they will be referred to in the following, takes into account that all primary species (e_{aq}^- , $\cdot\text{OH}$, H^\cdot) quantitatively lead to TBAA reduction, either directly or indirectly *via* $\text{CO}_2^{\cdot-}$, *i.e.* $G(-\text{TBAA}) = G(e_{\text{aq}}^- + \cdot\text{OH} + \text{H}^\cdot) = (2.8 + 2.8 + 0.6) = 6.2$. As will be shown below there is good evidence that Br^\cdot atoms, which are suggested to be formed in the secondary degradation of TetBSA *via* reaction (21), will initiate some additional TBAA degradation, either *via* direct bromine abstraction [reaction (25)] or generation of additional $\text{CO}_2^{\cdot-}$ by reaction



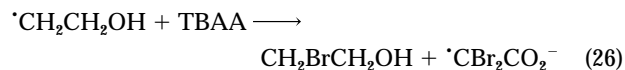
with formate. The yield of this secondary TBAA degradation is accounted for by the combined yields of dibromofumaric and dibromomaleic acid, *i.e.* $G = 0.2$. The conventionally calculated yield of TBAA destruction thus amounts to a total of $G(-\text{TBAA}) = 6.4$.

Evaluation of the degradation yield on the basis of the Schuler formula [(24)] results in $G(S) = 5.4$ for the $\cdot\text{OH}$ -induced process, based on the listed rate constant of $3.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction of $\cdot\text{OH}$ with formate¹³ and the experimentally applied formate concentration of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$. It can be assumed that similar considerations apply to the scavenging of hydrogen atoms but so far no quantitative assessment is available. Given the experimental conditions, any contribution from a corresponding 'square root' dependent parameter should, however, be very small and it seems, therefore, reasonable to account for the additional H^\cdot atom contribution just by its standard $G(\text{H}^\cdot) = 0.6$ value. Adding further the Br^\cdot atom contribution the combined yield calculated *via* this more sophisticated method amounts to $G = 6.2$. This not only means that both methods of calculation provide almost the same result for this system, but the calculations are also seen to be in excellent agreement with the experimental result.

In system II with ethanol as $\cdot\text{OH}$ scavenger the yield calculated *via* eqn. (24) for the reductive degradation of TBAA by $\text{CH}_3\cdot\text{CHOH}$ amounts to $G = 6.05$. This takes into account that $\text{CH}_3\cdot\text{CHOH}$ radicals are generated with an 84.3% efficiency in this process¹⁴ and with the assumption that the same percentage prevails for the reaction of H^\cdot with ethanol. Together with the presumed Br^\cdot -induced contribution this makes a total $G(-\text{TBAA}) = 6.15$. The classical calculation, on the other hand, would give a total of $G(-\text{TBAA}) = 0.843 \times G(\cdot\text{OH} + e_{\text{aq}}^- + \text{H}^\cdot) + G(\text{DBFuA} + \text{DBMaA}) = 5.35$. The actually measured $G(-\text{TBAA})_{\text{exp}} = (6.45 \pm 0.10)$ in this system exceeds this latter value significantly and is even slightly higher than the yield calculated on the basis of eqn. (24).

A reasonable rationale for a higher degradation yield in this system is the fact that in the reaction of $\cdot\text{OH}$ and H^\cdot with ethanol not only reducing radicals are formed but also redox-inert $\cdot\text{CH}_2\text{CH}_2\text{OH}$ radicals. This type of radical has also been shown to react with TBAA, namely, *via* bromine abstraction. The total yield of $\cdot\text{CH}_2\text{CH}_2\text{OH}$ radicals amounts to 13.2% yield in the $\cdot\text{OH} + \text{ethanol}$ reaction.¹⁴ Assuming a quantitative

reaction of $\cdot\text{CH}_2\text{CH}_2\text{OH}$ with TBAA the total yields of TBAA degradation would then increase to $G(-\text{TBAA}) = 6.15$ and 7.05 for the classical calculations and those based on eqn. (24), respectively. One conclusion which can be drawn from these figures is that the classical calculation appears to give too low yields even if the $\cdot\text{CH}_2\text{CH}_2\text{OH}$ -induced reaction was quantitative. This is, however, to be expected for all systems with high $\cdot\text{OH}$ scavenger concentrations because of the radiation chemistry specific track events and which led, in fact, to the development of eqn. (24). The fact that the measured TBAA degradation yield is lower (0.6 G units) than the maximum, but higher (0.3 G units) than the minimum calculated by eqn. (24) is taken as evidence for reaction (26) having taken place to some extent.



Given these latter figures, the yield of this reaction accounts for about one third of the $\cdot\text{CH}_2\text{CH}_2\text{OH}$ radicals. This low efficiency is explained by the low rate constants for these abstraction processes. Unfortunately, it was not possible to analyse for the possibly formed 2-bromoethanol. It should be recognized, in any case, that for these small contributions we are operating within the limits of experimental uncertainty and deviations from theoretically calculated yields, therefore, bear the risk of overinterpretation.

The above considerations find further support by the results obtained from systems III and IV with 2-methylpropan-2-ol and dimethyl sulfoxide, respectively, as $\cdot\text{OH}$ scavengers. In system III, the yield of β -hydroxyalkyl radicals, $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ radicals, calculated *via* the Schuler formula amounts to $G = 5.75$, taking into account that these radicals are formed with 95.7% efficiency from $\cdot\text{OH}$.¹⁴ With the contributions by H^\cdot and Br^\cdot atoms, all of which reduce TBAA directly, a total of $G(-\text{TBAA}) = 6.45$ is expected. The experimental $G(-\text{TBAA})_{\text{exp}} = (6.0 \pm 0.3)$ would thus again indicate an incompleteness of the β -hydroxyalkyl radical reaction with TBAA due to the low rate constant. It is noted that in this case the experimental result, presumably by coincidence, matches the classical calculation of $G(-\text{TBAA}) = 5.95$.

In system IV the corresponding G values are 6.95 [calculated on basis of eqn. (24)] plus the H^\cdot and Br^\cdot contribution, 5.85 (classical calculation), and (6.3 ± 0.4) (experimental). The deficit between experimental and maximum calculated yield reflects again the low rate constant for the bromine abstraction process by, in this case, $\cdot\text{CH}_3$ radicals. Clearly, the classical calculation provides too low yields, however.

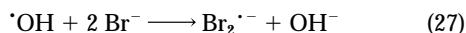
In summary, at higher $\cdot\text{OH}$ scavenger concentrations the Schuler equation appears to describe the scavenging efficiency more accurately than the classical calculation, while at low scavenger concentrations the difference becomes negligible.

Considering the absolute data it is further noted that in both systems in which β -hydroxyl radical reactions are invoked a $G\{\text{Br}^\cdot\}/G(-\text{TBAA}) = 3$ ratio is obtained, indicating that the products from the bromine abstraction processes lose their bromine as Br^- . This is known to occur for $\text{CH}_2\text{BrC}(\text{CH}_3)_2\text{OH}$ (system III) as a result of hydrolysis¹² but surprising for the 2-bromoethanol suggested to be generated in system II since this compound appears to be relatively stable in water. However, as mentioned before, the potential yield of $\text{CH}_2\text{BrCH}_2\text{OH}$ is only very small and any data related to its formation may be obscured in the experimental error limits.

Another indication for a good material balance, finally, is the excellent agreement between $G(\text{Br}^-)$ and the sum of $G(-\text{TBAA}) + G(\text{TBAcrA}) + 2 G(\text{DBFuA})$, where each of the components represents a process in which one or two bromide ions are liberated. The corresponding ratios in systems I, II and III are 9.65:9.65, 10.5:9.85 and 9.1:8.95, respectively. In system IV, where the yield of CH_3Br has to be added to that of Br^- , an equally satisfying 9.2:8.9 ratio is obtained.

Reaction of Br[•] atoms with TBAA. A completely new aspect has to be entered into the interpretation of the results in systems V and VI where no [•]OH scavenger is present. Our pulse radiolysis experiments have shown that there is no [•]CBr₂CO₂⁻ formation associable with a direct reaction between [•]OH and TBAA. Yet the yield of TBAA degradation in the γ -radiolysis in the N₂O-saturated system V is $G = 3.4$ while that of the available reducing species (H[•]) is only 0.6. Under N₂-saturated conditions in system VI, the respective numbers are $G = 3.9$ vs. 3.3, *i.e.* the TBAA degradation again exceeds, although to a smaller extent, the combined yield of reducing species (here e_{aq}⁻ and H[•]). These findings suggest that [•]OH radicals at least indirectly participate in the degradation mechanism. The most likely scenario involves the [•]OH-induced oxidation of the bromide liberated in the H[•] and e_{aq}⁻-induced processes.

The individual steps in the overall reaction (27) are diffusion



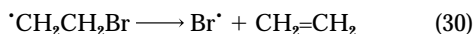
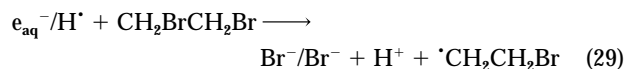
controlled^{23,24} and, at the 5×10^{-6} mol dm⁻³ [•]OH radical concentration of a typical pulse radiolysis experiment, Br₂^{•-} would be formed with t_f in the order of about 20 μs . Indeed, a transient absorption with all characteristic features of Br₂^{•-} is observed to grow in after the pulse. Measurements conducted at 360 nm (λ_{max} of Br₂^{•-})²⁵ reveal mostly second-order kinetics for this slow process, as expected, and a total growth period of about 50 μs . Further evidence for the formation of Br₂^{•-} emerges from its subsequent decay which occurs by second-order kinetics and a rate constant known for Br₂^{•-} dismutation, $2k = 1.7 \times 10^9$ dm³ mol⁻¹ s⁻¹.²⁶ This absorption is not present upon addition of any [•]OH scavenger in excess to Br⁻.

The yield of TBAA degradation in the γ -radiolysis is thus likely to be associated with a reaction of Br₂^{•-} or Br[•] atoms which exist in equilibrium (28). Of these two radical species the



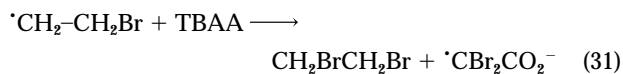
free Br[•] is expected to be the more reactive one. The experimental finding that the TBAA degradation yield decreases upon shifting the equilibrium to the left hand side by addition of excess bromide (see Table 2) not only supports this scheme but also suggests that it is indeed the Br[•] atom which predominantly reacts with TBAA as postulated in reaction (25).

The feasibility of this reaction is corroborated by pulse and γ -radiolysis experiments in which free bromine atoms have been generated *via* reduction of 1,2-dibromoethane (1,2-DBE) and subsequent β -elimination from the resulting radical.²⁰ In our



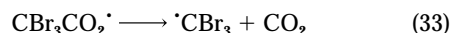
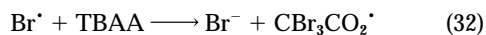
pulse radiolysis experiment, conducted at a 1,2-DBE concentration of 10^{-3} mol dm⁻³, reaction (30) becomes the rate determining process for Br[•] formation and the entire two-step process is completed within about 1- μs .²⁰ Addition of 10^{-4} mol dm⁻³ TBAA to this solution indicated a slow formation of a transient with absorption characteristics of the [•]CBr₂CO₂⁻ radical in support of reaction (25). It was not possible to extract an absolute rate constant from these experiments. A rough estimate, however, puts it in the order of those for the other abstraction reactions mentioned earlier. γ -Radiolysis evidence for a Br[•]-induced reaction was obtained with N₂-saturated, pH 10, solutions containing 2×10^{-3} mol dm⁻³ 1,2-DBE and 2×10^{-4} mol dm⁻³ TBAA. Under these conditions the calculated yield of TBAA degradation through direct reduction by e_{aq}⁻ and H[•] amounts to $G = 0.5$. The much higher experimental yield of $G(-\text{TBAA}) = 2.0$, therefore, clearly indicates an additional process.

In principle, both the pulse and γ -radiolysis results may also be attributable to an abstraction reaction initiated by [•]CH₂CH₂Br, the precursor of the bromine atom. However, in order to beat the β -elimination [reaction (30)], reaction (31)



would have to occur with a rate constant of $>10^{10}$ dm³ mol⁻¹ s⁻¹ which is at least three orders of magnitude higher than measured for such processes. Consequently, reaction (31) can be discarded.

Although our results clearly demand a Br[•]-induced degradation of TBAA they also request that this may not exclusively proceed *via* the abstraction reaction formulated in reaction (25). Looking at the yields listed in Table 2, it is noted that in the two systems of concern, namely V and VI, the measured CO₂ yields are higher than the TBAA degradation yields. This is quite in contrast to the other four systems where $G(\text{CO}_2) < G(-\text{TBAA})$ and in which only very few if any Br[•] atoms are available. This indicates some mechanism by which both carbon atoms of TBAA eventually are converted into CO₂. One possibility is an oxidation of the carboxyl function according to reaction (32) followed by fast decarboxylation [reaction (33)]. Such a redox

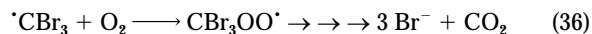


process is feasible considering that the redox potential of Br[•] should be higher than that of its conjugate equilibrium partner Br₂^{•-} for which $E^{\circ} = 1.63$ V (vs. NHE) has been determined.²⁷ Furthermore, it has been found in a separate experiment with oxalate that even Br₂^{•-} itself very efficiently oxidizes carboxyl groups in a one-electron transfer process.²⁸

The [•]CBr₃ radical generated in reaction (33) has various possibilities to end up as CO₂. One would be a combination of [•]CBr₃ with [•]OH followed by hydrolysis of the brominated alcohol. The probability of reaction (34) occurring will be about the same as for the initiating reaction of [•]OH with Br⁻ in the systems of concern.



A more likely pathway from [•]CBr₃ to CO₂, however, would involve molecular oxygen which may be present as a small impurity but which is also known to be formed in aqueous solutions containing Br₂, Br[•] and H₂O₂ (with hypobromite and O₂^{•-} as possible intermediates).²⁹ Hydrogen peroxide is present in all irradiated aqueous systems with a minimum $G \approx 0.7$.³⁰ The anticipated reaction of [•]CBr₃ with oxygen proceeds *via* a peroxy radical which, in analogy to the chlorine analogue CCl₃OO[•], is expected to mineralize completely to CO₂ and halide.³¹



If oxygen was present the initial [•]CBr₂CO₂⁻ radical would, of course, also generate a peroxy radical, namely, [•]OOCBr₂CO₂⁻ which ultimately breaks down into its inorganic components. In any case, all these processes and also the ultimate fate of Br₂ would provide enough additional bromide for reaction with [•]OH to ensure TBAA degradation beyond the initial reductive initiation.

The maximum yield of reaction (32) may be estimated from the total amount of TBAA degradation minus double the combined yields of TBAAcrA, DBFuA and DBMaA, all of which require two [•]CBr₂CO₂⁻ radicals for their formation. G [reaction

(32)] would consequently amount to $[3.4 - (2 \times 0.9)] = 1.6$ and $[3.9 - (2 \times 1.0)] = 1.9$ for systems V and VI, respectively. These yields account for almost half of the total TBAA degradation. With any of the TBAA molecules degraded this way giving two molecules of CO_2 and any TBAA formation being accompanied by liberation of one molecule of CO_2 [reaction (20)] the total $G(\text{CO}_2)$ yields expected on this basis would be $[(2 \times 1.6) + 0.9] = 4.1$ (system V) and $[(2 \times 1.9) + 0.9] = 4.7$ (system VI). Considering that some small amount of carbon shows up as CO these calculated yields agree very well with the experimental $G(\text{CO}_2 + \text{CO}) = 4.1$ (system V) and 4.5 (system VI) lending further credibility to the suggested mechanism.

γ -Radiolysis of $\text{CCl}_3\text{CO}_2^-$, CF_3CO_2^- and $\text{CHF}_2\text{CO}_2^-$ solutions

No attempt shall be made here to provide an equally detailed account of the radical-induced chemistry involving chlorinated and fluorinated analogues of TBAA. Only some aspects will be reported which emphasize certain differences relative to the brominated acid.

Trichloroacetic acid (TCAA). The radiolytical degradation of trichloroacetic acid generally shows a large degree of similarity to the TBAA degradation. In N_2 - and N_2O -saturated, pH 10, 2×10^{-4} mol dm^{-3} aqueous solutions of TCAA, for example, the respective degradation yields ($G = 3.9$ and 0.9 , respectively) also exceed the yield of reducing equivalents, e_{aq}^- and H^\cdot , ($G = 3.4$ and 0.6), although to a lesser extent than in the TBAA system. The excess may, therefore, be due to a reaction of Cl^\cdot atoms with TCAA, in analogy to reaction (25). The chlorine atoms are suggested to be formed in a reaction of Cl^- with $^\cdot\text{OH}$, possibly *via* an intermediate $\text{Cl}(\text{OH})^\cdot$ adduct radical anion. Any contribution of the Cl^\cdot -conjugate Cl_2^\cdot can probably be disregarded since it is only stable in very acid solutions.

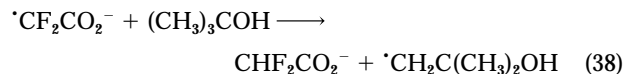
The $G(\text{Cl}^\cdot)/G(\text{TCAA})$ ratio, measured immediately after the irradiation, amounts to $1.0 (\pm 0.1)$. This is considered to reflect the relative stability of the tetrachlorosuccinic acid (TetCSA) as compared to the tetrabromo analogue, with TetCSA being formed upon dimerization of primarily generated $^\cdot\text{CCl}_2\text{CO}_2^-$ radicals.



Besides e_{aq}^- and H^\cdot , the reductive TCAA degradation process can also effectively be induced by $\text{CO}_2^{\cdot-}$, *e.g.* upon irradiation of N_2O -saturated, pH 10, 2×10^{-4} mol dm^{-3} aqueous solutions of TCAA containing also 2×10^{-4} mol dm^{-3} formate. This is interesting since $\text{CO}_2^{\cdot-}$ is not able to reduce the most highly chlorinated organic compound, namely, CCl_4 .³² Another noticeable result is that, in contrast to the easy bromine atom abstraction from TBAA, no indication has been observed for any chlorine abstraction from TCAA by alkyl radicals as tested, for example, with $^\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$. This does, of course, not mean that such a reaction is not possible but it is presumably too slow to compete with other radical processes. The reason for the comparatively low reactivity is considered to be the larger bond energy within a C–Cl as compared to a C–Br bond.

Trifluoro- and difluoro-acetic acid (TFAA and DFAA). TFAA shows an extremely high stability against any reactive radical which can be generated upon irradiation of its aqueous solutions (2×10^{-4} mol dm^{-3}).³³ Radiolysis with doses up to 1000 Gy under air, oxygen, N_2O or $\text{N}_2\text{O}-\text{O}_2(4:1)$, with added scavengers, and over a wide pH range did not indicate any degradation of TFAA or formation of new products, suggesting that this acid is practically inert towards e_{aq}^- , H^\cdot , $^\cdot\text{OH}$, $\text{O}_2^{\cdot-}$ and HO_2^\cdot . Only in very basic solutions (pH > 10) and in the presence of 2-methylpropan-2-ol a small yield of F^- ($G \approx 0.25$) was observed. This may indicate some low reactivity of TFAA towards e_{aq}^- under these conditions. The fact that traces of $\text{CHF}_2\text{CO}_2^-$ were detectable in the same solutions would indeed be indicative of $^\cdot\text{CF}_2\text{CO}_2^-$ radicals formed in this reaction of

e_{aq}^- with TFAA and of a subsequent H-atom abstraction from the alcohol as formulated in reaction (38). The yield of



$^\cdot\text{CF}_2\text{CO}_2^-$ radicals is almost quantitative, on the other hand, if difluoroacetic acid (DFAA) was subjected to reaction with $^\cdot\text{OH}$ radicals. This is deduced from the yield of tetrafluoro succinic acid, $G(\text{TetFSA}) = 2.6$, obtained in γ -irradiated N_2O -saturated 1×10^{-3} mol dm^{-3} solution of DFAA at pH 10. The major fate of the $^\cdot\text{CF}_2\text{CO}_2^-$ radicals formed in reaction (17) appears to be dimerization giving tetrafluorosuccinic acid [reaction (39)]. As



mentioned before this compound is absolutely stable in aqueous solutions and can conveniently be analysed for by ion chromatography.

On the whole, our experiments confirmed, however, the inertness of TFAA towards radical and redox initiated degradation. This is of environmental significance since TFAA is an important degradation product of many trifluoromethyl substituted compounds which have been utilized as substitutes for chlorine containing refrigerator liquids, propellants, anaesthetics and solvents.²

Conclusions

This study provides a detailed mechanistic and quantitative account for the free-radical and redox-induced degradation of tribromoacetic acids including analysis of products as well as absolute kinetic data on elementary reaction steps. It elaborates on certain principles applicable to the reactions of halogenated organic acids, in general, but also addresses a number of points specifically. With halogenated organic acids being important molecular intermediates in the degradation of many environmentally hazardous compounds *en route* to mineralization (conversion into CO_2 and inorganic halide ions) our results are considered to be of value for a quantitative understanding of detoxification and water remediation processes.

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