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On the Role of Superoxide in the Radical-Induced Degradation of Halogenated Organic Compounds. Evidence for Cross-Termination between $O_2^{\bullet-}$ and Halogenated Peroxyl Radicals

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γ-Radiolysis of aqueous, pH 6 solutions containing $CClF_2CO_2^-$ (1×10^{-3} to 2×10^{-2} M), HCO_2^- (2×10^{-3} M), and O_2 (20−100% O_2 saturation) or N_2O/O_2-(4:1 v/v)-saturated solutions of $CHF_2CO_2^-$ have been used as models to illustrate the high efficiency (70−100 %) of cross-termination between halogenated peroxyl radicals, here $^{\bullet}OOCF_2CO_2^-$ and $O_2^{\bullet-}$, as opposed to the self-termination of the respective radicals. Experiments have been conducted at various $[^{\bullet}OOCF_2CO_2^-]/[O_2^{\bullet-}]$ concentration ratios and with either of the two species in excess. The proposed mechanisms are supported by quantitative material balances. Since the final reaction products derived from $CClF_2CO_2^-$ are identical in nature (CO_2, Cl^-, F^-, H^+, oxalate) and yields are the same irrespective of cross- or self-termination, the conclusions were based on the H_2O_2 yields which are shown to differ significantly depending on the mechanism. The $^{\bullet}OOCF_2CO_2^- + O_2^{\bullet-}$ reaction is considered to proceed via an intermediate hydroperoxide, $HOOCF_2CO_2^-$, which predominantly decays via C−C cleavage into CF_2O and HCO_3^-. Only a minor fraction (about 10%) remains as C_2-compound and ends up as oxalate. Mechanistically, the results emphasize the significance of superoxide in all systems in which peroxyl radicals are generated. With respect to halogenated hydrocarbons this is considered to be particularly relevant in, for example, the radical- and redox-induced mineralization process under aerobic conditions and in the biological metabolism of such compounds.

Introduction

Halogenated hydrocarbons are known as potentially toxic and ecologically dangerous compounds. They are, nevertheless, still in widespread use in various important fields of human activity. Although their degradation in oxygenated environment eventually leads to the relatively harmless inorganic substrates CO_2 and the respective hydrogen halides, many of the reactive intermediates, generated in this so-called mineralization process *en route* to the final products, may harmfully interfere with the normal biochemistry of living organisms. Key radical intermediates in the chemistry of these systems are halogenated peroxyl radicals, $R(Hal)OO^{\bullet}$, formed upon rapid oxygen addition to those carbon-centered radicals which are generated, for example, via dissociative electron capture by the halogenated hydrocarbon.

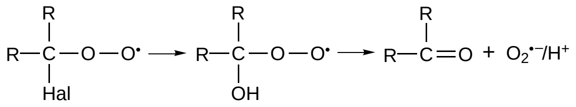
Halogenated peroxyl radicals are reasonably good oxidants and react with quite a number of donors, D, to yield the corresponding hydroperoxides and the one-electron oxidation products of the donor, denoted here as $D^{\bullet+}$ irrespective of its actual charge (eq 1).[1−6]

$$R(Hal)OO^{\bullet} + D + H^+ \rightarrow R(Hal)OOH + D^{\bullet+} \qquad (1)$$

Oxidations are, however, not necessarily limited to one-electron transfer mechanisms. Most interestingly, halogenated peroxyl radicals also engage in overall two-electron transfer reactions, e.g., with iodide ions or organic sulfides.[7,8] This type of mechanism (eq 2) passes by the hydroperoxide and leads directly to the reduced form of the latter, namely, the corresponding oxyl radicals, $R(Hal)O^{\bullet}$, and the two-electron oxidation products, here molecular iodine and sulfoxide, respectively. (The actual mechanisms are more complex than depicted in the overall stoichiometry of eq 2 and involve adduct intermediates.)

$$R(Hal)OO^{\bullet} + 2I^-/R_2S \rightarrow R(Hal)O^{\bullet} + I_2/R_2SO \qquad (2)$$

In the absence of suitable molecular reaction partners, one possibility to be considered would be hydrolysis of a halogen located on the peroxyl-carrying carbon, followed by superoxide elimination (eq 3).



$$R-\underset{Hal}{\overset{R}{C}}-O-O^{\bullet} \longrightarrow R-\underset{OH}{\overset{R}{C}}-O-O^{\bullet} \longrightarrow R-\overset{R}{C}{=}O + O_2^{\bullet-}/H^+ \qquad (3)$$

This appears to be a realistic option for a number of chlorine and bromine-containing species but not so much for fluorinated ones where hydrolysis seems to be a very slow, if at all, occurring process.

The most commonly considered fate of peroxyl radicals in case reactions 1−3 cannot be entered is that of self-termination, i.e., the reaction of two peroxyl radicals with each other (eq 4).

$$2R(Hal)OO^{\bullet} \rightarrow \text{products} \qquad (4)$$

This process typically proceeds via mechanisms which involve either H_2O_2 or O_2 elimination from a hypothetical tetroxide intermediate, generally referred to as concerted mechanism,[9] Russell mechanism,[10] and alkoxyl radical formation mechanism.[11] Whichever prevails depends on the degree of hydrogenation of the carbon atom carrying the peroxyl function. In the case that no hydrogen atom is left (referring to the example studied in this investigation) the latter is the only possibility. This is formulated in eq 5 for a dihalogenated

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carboperoxyl function, in general.

$$R'C(Hal)_2OO^{\bullet} \rightarrow R'C(Hal)_2O^{\bullet} + O_2 \quad (5)$$

Rate constants for these self-termination processes are typically below the value set by the diffusion of the reactants. For the self-termination of $CCl_3OO^{\bullet}$, for example, $2k_5 = 2 \times 10^8$ M^{-1} s^{-1} has been measured.[12]

In order to fully appreciate the chemistry of peroxyl radicals it has to be recognized that O_2 may not only serve as a necessary prerequisite for the peroxyl radical formation but, at the same time, is also the source of another radical, namely, $O_2^{\bullet -}$ or its conjugate acid $HO_2^{\bullet}$ (pK = 4.8).[13] These species emerge, for example, as elimination product from α-hydroxyperoxyl radicals (e.g., via eq 3 or formed in any irradiated solution containing primary and secondary alcohols) and also from scavenging of any available reducing entities, such as hydrated electrons or $CO_2^{\bullet -}$, by molecular oxygen. Chances are, therefore, high that both superoxide and peroxyl radicals are simultaneously present in any oxygenated system which is subjected to radical-generating conditions. Consequently, the chemical fate of superoxide must also be considered. Superoxide self-termination is, of course, one possibility, but this is generally a relatively slow process with a rate constant varying with pH. A maximum value of 1×10^8 M^{-1} s^{-1} [13] is attained only within a small pH range near the pK of $HO_2^{\bullet}$ where the internal superoxide cross-termination (eq 6) dominates the mutual $O_2^{\bullet -} + O_2^{\bullet -}$ or $HO_2^{\bullet} + HO_2^{\bullet}$ self-terminations.

$$O_2^{\bullet -} + HO_2^{\bullet} + H^+ \rightarrow H_2O_2 + O_2 \quad (6)$$

In neutral and basic environment, the lifetime of $O_2^{\bullet -}$ becomes considerably longer and renders this species as a not-to-be-neglected candidate for other reactions. In view of this and two (as only available examples) rate constants published for the reaction of $O_2^{\bullet -}$ with c-$C_6H_{11}OO^{\bullet}$ ($k = 2.5 \times 10^8$ M^{-1} s^{-1})[14] and $CH_3C(O)OO^{\bullet}$ ($k = 1 \times 10^9$ M^{-1} s^{-1})[15] it is, therefore, appropriate and necessary to also consider the cross-termination between superoxide and peroxyl radicals. This reaction probably proceeds via dismutation, possibly involving an intermediate adduct, to yield the corresponding hydroperoxide from the peroxyl radical as formulated for a halogenated peroxyl radical in eq 7.

$$R(Hal)OO^{\bullet} + O_2^{\bullet -} \rightarrow [R(Hal)OOOO^-] (+ H^+) \rightarrow R(Hal)OOH + O_2 \quad (7)$$

In order to investigate the relative importance of such cross-termination reactions, a model system has been chosen which (i) allows generation of all the radicals involved in a defined and quantifiable way, (ii) provides the least number of possibly competitive mechanistic alternatives, and (iii) allows an accurate and quantitative analysis of the reaction products for the establishment of a complete material balance. This has been achieved by applying radiolysis, which is one of the most convenient tools for radical generation, in general, and for the study of the chemistry of halogenated peroxyl radicals, in particular.[16] The specific system chosen was an oxygen-containing aqueous solution of $CClF_2CO_2^-$ which leads to the generation of $^{\bullet}OOCF_2CO_2^-$ peroxyl radicals and final molecular products which could conveniently be analyzed by ion chromatography (Cl^-, F^-, CO_2, oxalate) and a spectroscopic method (H_2O_2).

Experimental Section

All chemicals were laboratory reagent grade and were used without further purification. Chlorodifluoroacetic acid ($CClF_2CO_2H$ {CDFA}), difluoroacetic acid (CHF_2CO_2H {DFA}, oxalic acid ($C_2H_2O_4 \times 2H_2O$), NaCl, NaF, and HCO_2Na were supplied by Aldrich. Superoxide dismutase was obtained from Boehringer, Mannheim (Germany).

TABLE 1: Products and Their Radiation Yields (in Units of $G \approx 10^{-7}$ M J^{-1}) Obtained upon γ-Radiolysis of Air-Saturated, pH 6 Aqueous Solution of 2×10^{-2} M $CClF_2CO_2^-$ and 2×10^{-3} M HCO_2^- (Dose Rate 0.33 Gy s^{-1})

product	HCl	HF	CO_2	CO	(CO_2H_2)	H_2O_2
G-values	2.5	5.0	4.4[a] (7.2 total)	0.0	0.3	1.5

[a] Determined from the overall $G(CO_2)$ = 7.2, subtracting $G(CO_2)$ = 2.8 due to the reactions 13 and 14.

Solutions were always freshly prepared. The solvent was deionized millipore-filtered water, the quality of which corresponded to triply distilled water (≥18 MΩ). The desirable pHs of the solutions were adjusted by addition of appropriate amounts of 0.1 M NaOH or dilutions thereof.

Radiolysis was carried out in the field of a ^{60}Co γ-source with total adsorbed doses in the range of 50−160 Gy (1 Gy = 1 J kg^{-1} = 100 rad) as determined by Fricke dosimetry.[17]

Ionic products (Cl^-, F^-, $C_2O_4^{2-}$) were analyzed by high-performance ion chromatography. The Dionex 500 DX ion chromatograph used was equipped with a 20 cm Ion Pac AS12A-SC column protected by an Ion Pac AG12A guard-column. The eluent generally consisted of an aqueous solution containing a mixture of $NaHCO_3$ and Na_2CO_3 at concentrations of 0.3 and 2.7 mM, respectively. The flow rate of the eluent was generally 1.5 mL min^{-1}. Identification of ionic products was achieved with a conductivity detector and comparison with authentic compounds. CO_2 was also determined by ion chromatography, namely, in the form of HCO_3^- ions using an Ion Pac ICE-AS1 column. Experimental details on this determination have already been published.[18] Carbon monoxide was checked by GC, using a Molecular Sieve 5A column, helium as carrier gas, and a thermoconductivity detector. Analysis of hydrogen peroxide was based on the oxidation of I^- to I_2 and measurement through the optical absorbance of the I_3^- complex at 350 nm.[19] Using this method, it was also possible to distinguish between H_2O_2 and organic peroxide, namely, by adding catalase (≈160 U/mL, Boehringer, Mannheim) to irradiated solutions, which selectively removes H_2O_2.

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

Results and Discussion

Products and Material Balance. The $^{\bullet}OOCF_2CO_2^-$ radical under investigation in this study was generated via reductive initiation. γ-Radiolysis of an air-saturated, pH 6 solution containing 2×10^{-2} M $CClF_2CO_2^-$ (CDFA) and 2×10^{-3} M HCO_2^- showed the formation of Cl^-, F^-, CO_2, and small amounts of oxalate as products which can directly be related to the degradation of CDFA. In addition, H_2O_2 was formed in the irradiated solution. All the measured yields are listed in Table 1. Two further possible products, namely, CO and stable hydroperoxides, were also checked for, but neither was detectable under any experimental conditions in our present model system. This was done since (i) CO is a product formed in appreciable amounts from the chlorine and bromine analogues of $^{\bullet}OOCF_2CO_2^-$,[20] and (ii) hydroperoxides are actually postulated in our mechanism (see below) although only as short-lived molecular intermediates. The claim that no stable hydroperoxides (and/or peroxides) are formed is based on the fact that no $I^- \rightarrow I_2$ oxidation was observed anymore after treating the irradiated sample with catalase (160 U/mL), an enzyme which selectively destroys H_2O_2.

All the measured yields and the underlying mechanism have to be related to the primary reactive species formed upon radiolysis of an aqueous solution, namely, hydrated electrons (e_{aq}^-, $G = 2.8$), hydrogen atoms ($H^\bullet$, $G = 0.6$), hydroxyl radicals (${}^\bullet OH$, $G = 2.8$), and H_2O_2 ($G = 0.7$ in solutions with ${}^\bullet OH$ scavengers). The yields, given in terms of G-units, denote species per 100 eV or μM per 10 J of absorbed energy.

Initial Processes. The key initiating reaction is a reduction of CDFA by hydrated electrons (eq 8) leading to the formation of ${}^\bullet CF_2CO_2^-$ radicals. Subsequently, these react with oxygen to yield the corresponding ${}^\bullet OOCF_2CO_2^-$ peroxyl radical (eq 9).

$$e_{aq}^- + CClF_2CO_2^- \rightarrow Cl^- + {}^\bullet CF_2CO_2^- \qquad (8)$$

$${}^\bullet CF_2CO_2^- + O_2 \rightarrow {}^\bullet OOCF_2CO_2^- \qquad (9)$$

Rate constants for the oxygen addition to halogenated C-centered radicals are typically in the range of 10^9 M^{-1} s^{-1}.[4] This renders reaction 9 fast enough to attribute all products, except Cl^-, to the further decay of the ${}^\bullet OOCF_2CO_2^-$ radical.

Looking at the product yields, it is noted that the measured chloride yield ($G = 2.5$) falls short by about 10% from the e_{aq}^- yield. $G(Cl^-)$ appears, however, to be the reference yield for all other products. With $G(F^-) = 5.0$ and $G(\text{total carbon}) = G(CO_2 + 2\ \text{oxalate}) = 4.4 + 2 \times 0.3 = 5.0$, the stoichiometry of the original acid CDFA is quantitatively matched. It indicates that ${}^\bullet OOCF_2CO_2^-$ not only loses both fluorine atoms but also suffers, to a predominant extent, C-C bond cleavage.

The small fraction of hydrated electrons which does not appear to react with CDFA is scavenged by oxygen (eq 10), with this reaction serving as one source for superoxide.

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -} \qquad (10)$$

This competitive character of reactions 8 and 10 can, in fact, by quantified through the observed decrease in Cl^- and F^- yields with decreasing CDFA or increasing O_2 concentration. The corresponding mathematical equations (eq 11a for Cl^- and eq 11b for F^-) call for linear relationships between the reciprocal chloride and fluoride yields as a function of the $[O_2]/[CDFA]$ concentration ratio, and these are, indeed, obtained as shown in Figure 1.

$$\frac{1}{G(Cl^-)} = \frac{1}{G(e_{aq}^-)} + \frac{1}{G(e_{aq}^-)} \times \frac{k_{10}}{k_8} \times \frac{[O_2]}{[CDFA]} \qquad (11a)$$

$$\frac{1}{G(F^-)} = \frac{1}{2G(e_{aq}^-)} + \frac{1}{2G(e_{aq}^-)} \times \frac{k_{10}}{k_8} \times \frac{[O_2]}{[CDFA]} \qquad (11b)$$

Both intercepts of the least mean square analysis, i.e., $1/G(e_{aq}^-)$ for Cl^- and $(1/2)G(e_{aq}^-)$ for F^-, are compatible with the expected values of 0.36 and 0.18 (based on $G(e_{aq}^-) = 2.8$). Furthermore, the slopes differ exactly by the expected factor of 2, thus leading to the same rate constant ratio, k_{10}/k_8. With the known value of $k_{10} = 1.9 \times 10^{10}$ M^{-1} s^{-1},[21] k_8 is calculated to be 2.8×10^9 M^{-1} s^{-1}. It is noted that this rate constant for the reduction of $CClF_2CO_2^-$ by e_{aq}^- is more than 3 orders of magnitude higher than for the corresponding reduction of $CF_3CO_2^-$,[22] but still three times lower than that of 8.5×10^9 M^{-1} s^{-1} found for $CCl_3CO_2^-$.[22]

Hydrogen atoms, the other reducing primary species besides hydrated electrons, do not directly reduce CDFA. Not only is this evident from the intercepts in Figure 1 which do not indicate any $H^\bullet$ contribution, but a reaction between $H^\bullet$ and CDFA is also not expected because, by extrapolating from $k = 1 \times 10^6$ M^{-1} s^{-1} for the reaction of $H^\bullet + CF_3Cl$,[23] this process should have a very low rate constant and, therefore, no chance to compete with the $H^\bullet$-atom's reaction with oxygen ($k_{12} = 2.1 \times 10^{10}$ M^{-1} s^{-1})[21]

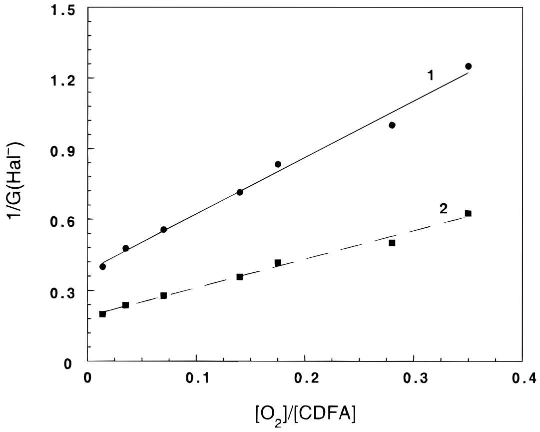


Figure 1. Plots of $1/G(Hal^-)$ versus $[O_2]/[CDFAA]$ according to eq 12. Data obtained, as listed in Table 1, from γ-radiolysis of oxygenated, pH 6 aqueous solutions containing $CClF_2COO^-$ (1×10^{-3} to 2×10^{-2} M) and 2×10^{-3} M HCO_2^-: (1) Cl^-, (2) F^-.

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \rightleftharpoons O_2^{\bullet -} + H^+ \qquad (12)$$

A very small fraction of $H^\bullet$ will (7%, $G = 0.04$) be scavenged by formate ($(k_{13,H^\bullet}) = 2.1 \times 10^8$ M^{-1} s^{-1}) (eq 13).[21]

Hydroxyl radicals, the other major reactive primary species besides hydrated electrons, do not react with either CDFA or oxygen and are quantitatively scavenged by formate ($k_{13,{}^\bullet OH} = 3.2 \times 10^9$ M^{-1} s^{-1} [21]) (eq 13).

$${}^\bullet OH/H^\bullet + HCO_2^- \rightarrow H_2O/H_2 + CO_2^{\bullet -} \qquad (13)$$

This reaction yields $CO_2^{\bullet -}$ which, in turn, is known to reduce oxygen with a rate constant of $k_{14} = 2.4 \times 10^9$ M^{-1} s^{-1} (eq 14).[24]

$$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -} \qquad (14)$$

Possible reduction of CDFA by $CO_2^{\bullet -}$ and $O_2^{\bullet -}$ (eqs 15 and 16) can be discarded.

$$CO_2^{\bullet -} + CClF_2CO_2^- \nrightarrow CO_2 + Cl^- + {}^\bullet CF_2CO_2^- \qquad (15)$$

$$O_2^{\bullet -} + CClF_2CO_2^- \nrightarrow O_2 + Cl^- + {}^\bullet CF_2CO_2^- \qquad (16)$$

In order to ascertain the inefficiency of reaction 15 in our system, we independently studied the possibility of this reaction in an N_2O-saturated, pH 6 solution containing 10 mM HCO_2^- and 1 mM $CClF_2CO_2^-$. Although CDFA is the only potential molecular reaction partner of $CO_2^{\bullet -}$ in this system, the observed chloride yield of $G(Cl^-) = 0.10$ corresponds to no more than 2% of the available $CO_2^{\bullet -}$. Therefore, any significant contribution of reaction 15 can, indeed, be neglected. Concerning reaction 16, so far no reactions are known between chloro- and fluoro-substituted organic compounds and $O_2^{\bullet -}$ in aqueous solutions.[13] This is in contrast to organic media where such reactions may occur, although not via one-electron reduction but nucleophilic substitution.[25,26] The absence of reaction 16 in our system is illustrated also experimentally by the fact that

G(Cl^-) is not increasing with enhancing the available $O_2^{\bullet-}$ yield. In conclusion, therefore, the entire initial yield of $H^\bullet$-atoms and $^\bullet OH$ radicals, either directly or indirectly via $CO_2^{\bullet-}$, ends up as $O_2^{\bullet-}$ which thus becomes a major player besides $^\bullet OOCF_2CO_2^-$ in the radical chemistry of our system.

Reactions of $^\bullet OOCF_2CO_2^-$. *Self-Termination.* One of the pathways by which $^\bullet OOCF_2CO_2^-$ radicals may decay is self-termination. Since the absence of hydrogen atoms at the α-carbon atom prevents any Russell type recombination[10] as well as H_2O_2 elimination via the so-called concerted mechanism,[9] the only mechanism left is the formation of oxyl radicals as formulated in eq 17.

$$2^\bullet OOCF_2CO_2^- \rightarrow 2^\bullet OCF_2CO_2^- + O_2 \qquad (17)$$

Subsequent C−C *β*-cleavage within the alkoxyl radicals (eq 18) would lead to the generation of $CO_2^{\bullet-}$ which, followed by reaction 14, not only ends up as CO_2 but also serves as a source of additional superoxide.

$$^\bullet OCF_2CO_2^- \rightarrow COF_2 + CO_2^{\bullet-} \qquad (18)$$

Hydrolysis of the carbonyl difluoride ($k_{19} < 0.05\ s^{-1}$)[27] will also lead to CO_2 as final product.

$$COF_2 + H_2O \rightarrow 2H^+ + 2F^- + CO_2 \qquad (19)$$

In principle, *β*-elimination from the oxyl radical could also result in the loss of a fluorine atom which in the aqueous environment would eventually give F^-. Such a mechanism would leave $F(O)CCO_2^-$ which, upon hydrolysis, would be a possible source for the small amount of oxalate observed. It should be emphasized, however, that such a fluorine elimination is not very favorable from the thermodynamic point of view. A possibly more likely source of oxalic acid may be a slow hydrolysis of the $^\bullet OOCF_2CO_2^-$ peroxyl radical (eq 20, in analogy to reaction 3).

$$^\bullet OOCF_2CO_2^- \xrightarrow{H_2O} {}^\bullet OOCF(OH)CO_2^- \rightarrow F(O)CCO_2^- + O_2^{\bullet-}/H^+ \qquad (20)$$

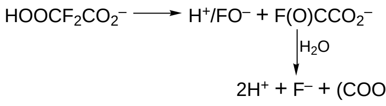
In summary, the self-termination mechanism would fully account for the observed products derived from the original organic compound CDFA. A problem arises, however, if one considers the H_2O_2 yield. If the decay of $^\bullet OOCF_2CO_2^-$ occurred exclusively via self-termination, the only possible fate of superoxide would then also be self-termination. Irrespective of whether the latter is formulated under participation of the conjugated $HO_2^\bullet$ as formulated in eq 6 ($k_6 = 1 \times 10^8\ M^{-1}\ s^{-1}$)[13] or as the much slower reaction of two $O_2^{\bullet-}$ (involving 2 H^+) with $2k < 0.35\ M^{-1}\ s^{-1}$),[13] the result is always the formation of 1 equiv of H_2O_2 from any two superoxide species. Considering that each of the primary species, namely e_{aq}^- (direct reaction with O_2 or via reaction sequence 8, 9, 17, 18, and 14, involving $^\bullet OOCF_2CO_2^-$), $H^\bullet$ (direct reaction with O_2 or via reaction sequence 13 and 4), and $^\bullet OH$ (via reaction sequence 13 and 14) produce one superoxide, the yield of $O_2^{\bullet-}$ formed in these processes is $G(O_2^{\bullet-}) = 6.2$. Consequently, this would result in $G(H_2O_2)_{self} = 3.1$ which together with the primary yield of $G(H_2O_2)_{w.r.} = 0.7$ from the water radiolysis would give a total maximum yield of $G(H_2O_2)_{max} = 3.8$ for the all-self-termination mechanism. The same numerical values would, incidentally, emerge if there was some hydrolysis of the halogen function in the peroxyl radical followed by unimolecular superoxide elimination (eq 20).

Comparison of the experimentally observed $G(H_2O_2)_{exp}$ with $G(H_2O_2)_{max}$ (see Table 1) clearly reveals a significant discrepancy, indicating that self-termination cannot be the exclusive pathway for the disappearance of the peroxyl radicals in our system.

Cross-Termination. Considering the above problem the only remaining alternative is invoked, namely, cross-termination between the peroxyl radical and superoxide (eq 21).

$$O_2^{\bullet-} + {}^\bullet OOCF_2CO_2^- + H^+ \rightarrow O_2 + HOOCF_2CO_2^- \qquad (21)$$

Irrespective of whether this reaction occurs via an electron transfer mechanism or involves a possible short-lived tetroxide adduct as intermediate (see eq 7), the results is an α-halogenated hydroperoxide. One possible fate of this hydroperoxide would be HOF elimination (reaction 22)



$$HOOCF_2CO_2^- \longrightarrow H^+/FO^- + F(O)CCO_2^- \qquad (22)$$

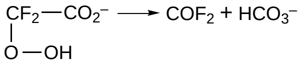
$$F(O)CCO_2^- \xrightarrow{H_2O} 2H^+ + F^- + (COO^-)_2 \qquad (23)$$

Hydrolysis of oxaloyl fluoride would then yield oxalate (eq 23). Since the latter is formed only in small quantities reaction 22 can, however, only be of minor importance. This statement also holds in view of a recent observation of ours that hydrolysis of oxalyl dibromide in diluted aqueous solutions does, in fact, not lead to oxalate but to stoichiometric amounts of bromide, carbon monoxide, and carbon dioxide (eq 24).[20]

$$Br(O)CC(O)Br \xrightarrow{H_2O} Br^- + Br(O)CCO_2^- \xrightarrow{H_2O} Br^- + CO + CO_2 \qquad (24)$$

Since in the first stage of this hydrolysis process, $Br(O)CCO_2^-$, an analogue of $F(O)CCO_2^-$, is likely to be formed, we have checked for the possible formation of CO in our CDFA system. However, not even traces of CO could be detected.

An alternative mechanism of the hydroperoxide decay would be a rearrangement coupled with C−C bond cleavage (reaction 25), in analogy to a similar process observed, for example, for alkyl hydroperoxides in a nonaqueous system.[28]



$$HO{-}O{-}CF_2{-}CO_2^- \longrightarrow COF_2 + HCO_3^- \qquad (25)$$

Hydrolysis of the carbonyldifluoride (eq 19) and the bicarbonate (the form in which CO_2 is anyway measured in ion chromatography) would then fully account for the experimentally observed CO_2 and F^- yields. In essence, self- and cross-termination routes are indistinguishable from the CDFA-derived products point of view.

The expected H_2O_2 yield from the $^\bullet OOCF_2CO_2^- + O_2^{\bullet-}$ cross-termination mechanism is, however, much lower as from the self-termination route. Not only is no $O_2^{\bullet-}$ generated from $^\bullet OOCF_2CO_2^-$ in this case (lack of reaction sequence 17, 18, 14), but in addition, an equal amount of $O_2^{\bullet-}$ is, in fact, consumed in the cross-termination via reaction 21 without yielding any H_2O_2.

A small further correction which may apply takes care of any possible consumption of H_2O_2 through the hypofluorite formed in reaction 22 (eq 26), with oxalate being a measure for this route (*G* = 0.3).

$$H^+/OF^- + H_2O_2 \rightarrow H^+/F^- + O_2 + H_2O \qquad (26)$$

TABLE 2: Radiation Chemical Yields of Products and Contributions of Self- and Cross-Termination Routes for ${}^{\bullet}OOCF_2CO_2^-$ Radicals. Data Obtained upon γ-Radiolysis of Oxygenated Aqueous, pH 6 Solutions Containing $CClF_2COO^-$ (1×10^{-3} to 2×10^{-2} M) and 2×10^{-3} M HCO_2^- (Dose Rate 0.33 Gy s^{-1})

CDFA (10^{-3} M)	20	8	4	2	1	4	4
vol % O_2[a]	20	20	20	20	20	50	100
$G(Cl^-) = G({}^{\bullet}OOCF_2CO_2^-)_{total}$	2.5 (2.6)	2.1 (2.3)	1.8 (1.9)	1.4 (1.4)	1.0 (1.0)	1.2 (1.3)	0.8 (0.8)
$G(F^-)$	5.0	4.2	3.6	2.8	2.0	2.4	1.6
G(oxalate)	0.3	0.2	0.2	0.1	0.1	0.2	0.1
$G(H_2O_2)_{experim}$	1.5	1.9	2.1	2.4	2.7	2.6	3.0
$G(H_2O_2)_{max}$[b]	3.8	3.8	3.8	3.8	3.8	3.8	3.8
$G(H_2O_2)_{min}$[b]	1.0	1.5	1.8	2.3	2.7	2.4	2.9
$G(O_2^{\bullet -})_{initial}$[b]	3.7	4.1	4.4	4.8	5.2	5.0	5.4
$G({}^{\bullet}OOCF_2CO_2^-)_{self}$[c]	0.5 (20%)	0.4 (19%)	0.3 (17%)	0.1 (7%)	0.0 (0%)	0.2 (17%)	0.1 (13%)
$G({}^{\bullet}OOCF_2CO_2^-)_{self}$[d]	*0.2 (8%)*	*0.2 (10%)*	*0.1 (6%)*	*0.0 (0%)*	*0.0 (0%)*	*0.0 (0%)*	*0.0 (0%)*
$G({}^{\bullet}OOCF_2CO_2^-)_{cross}$[c]	2.0 (80%)	1.7 (81%)	1.5 (83%)	1.3 (93%)	1.0 (100%)	1.0 (83%)	0.7 (97%)
$G({}^{\bullet}OOCF_2CO_2^-)_{cross}$[d]	*2.3 (92%)*	*1.9 (90%)*	*1.7 (94%)*	*1.4 (100%)*	*1.0 (100%)*	*1.2 (100%)*	*0.8 (100%)*

[a] Vol % of oxygen in N_2/O_2 gas mixture; 20% refers to air-saturated solutions. [b] Calculated yields. [c] Includes H_2O_2 consumption by hypofluorite. [d] Assuming no H_2O_2 loss through hypofluorite.

In summary, if cross-termination were the exclusive reaction route the peroxyl radicals got engaged in, the expected hydrogen peroxide yields would, by comparison with the self-termination mechanism, drop to a minimum value of

$$G(H_2O_2)_{min} = G(H_2O_2)_{w.r.} + 0.5\,[G(O_2^{\bullet -})_{initial} - G({}^{\bullet}OOCF_2CO_2^-)] - G(\text{oxalate})$$

with $G(O_2^{\bullet -})_{initial}$ denoting the superoxide yield generated through initiation by ${}^{\bullet}OH$ (eqs 13, 14) and $H^{\bullet}$ (eq 12) and the small amount of e_{aq}^- which directly reacted with oxygen (eq 10). The $O_2^{\bullet -}$-based contribution to $G(H_2O_2)_{min}$ thus includes only the remaining fraction of superoxide which does not become consumed in the cross-termination process. For our actual system this yield would amount to $G(H_2O_2)_{min} = 1.0$, a yield which is much closer to the experimental ($G = 1.5$) than to the self-termination value ($G = 3.8$). In case the oxalate yield was not representative for an additional loss of H_2O_2, i.e., reaction 20 would not occur or was inefficient, the calculated $G(H_2O_2)_{min} = 1.3$ would even be almost identical with the experimental value. In any case, the hydrogen peroxide yields indicate that peroxyl radical/superoxide cross-termination is indeed the dominating process.

Variation of $[{}^{\bullet}OCCF_2CO_2^-]/[O_2^{\bullet -}]$ Ratios. *Systems with Excess $O_2^{\bullet -}$.* In order to substantiate the proposed mechanism, a series of experiments have been carried out in which the ratio between the radiation chemically produced ${}^{\bullet}OOCF_2CO_2^-$ and $O_2^{\bullet -}$ was varied. In the formate-containing model systems it was possible to shift this ratio further in favor of superoxide by allowing a larger amount of hydrated electrons to react directly with oxygen. This was achieved by lowering the CDFA concentration and/or increasing the degree of oxygen saturation in the solution.

The respective experimental data, listed in Table 2, are in full accord with expectation. Thus the Cl^- yields, which also represent the yields of ${}^{\bullet}OOCF_2CO_2^-$ peroxyl radicals, decrease with decreasing [CDFA] and increasing $[O_2]$ concentration. The measured yields agree well, within error limits (±0.1 G-units), with those calculated on the basis of competition kinetics (values in parentheses). Furthermore, the F^- yields always amount to double the Cl^- yields. The trend for the oxalate data goes into the right direction but, owing to the very small yields, does not warrant any quantitative comment. The calculated $O_2^{\bullet -}$ yields have been listed to appreciate the experimentally covered $[{}^{\bullet}OOCF_2CO_2^-]/[O_2^{\bullet -}]$ ratios which varied from 1.0:1.5 to 1.0:6.75 (referring to initial $O_2^{\bullet -}$ yields).

The experimentally measured hydrogen peroxide yields are seen to vary significantly with the $[{}^{\bullet}OOCF_2CO_2^-]/[O_2^{\bullet -}]$ ratios as they should if cross-termination was involved. In the case of exclusive self-termination processes the H_2O_2 yield would instead remain at a constant $G(H_2O_2)_{max} = 3.8$. In fact, throughout all our experiments $G(H_2O_2)_{exp}$ is always very close to and just slightly above the minimal value $G(H_2O_2)_{min}$ expected if all the ${}^{\bullet}OOCF_2CO_2^-$ radicals reacted via cross-termination. The agreement would even be better (see values in *italics*) if the reactions leading to oxalate (eqs 22, 23) were not coupled to a corresponding loss in H_2O_2 (eq 26).

TABLE 3: Products and Their Radiation Chemical Yields (in Units of $G = 10^{-7}$ M J^{-1}) Obtained upon γ-Radiolysis of N_2O/O_2 (4:1 v/v)-Saturated, 2×10^{-2} M $CHF_2CO_2^-$ Aqueous Solutions at pH 6 (Dose Rate of 0.33 Gy s^{-1})

products	HF	CO_2	$(CO_2H)_2$	H_2O_2
G-values	10.6	10.3	0.15	1.3
	10.6[a]	10.6[a]	traces[a]	2.2[a]

[a] G-values for products in solution containing 25 mg/L SOD.

The difference $G(H_2O_2)_{exp} - G(H_2O_2)_{min}$ directly represents that yield of ${}^{\bullet}OOCF_2CO_2^-$ which escapes cross-termination (eq 21) and enters the self-termination channel (eq 17). This 1:1 relationship is based on the fact that the former process consumes one $O_2^{\bullet -}$ and the latter generates one $O_2^{\bullet -}$ per peroxyl radical; i.e., a total of two $O_2^{\bullet -}$ or one H_2O_2 is gained for any ${}^{\bullet}OOCF_2CO_2^-$ reacting via self-termination. The respective differences $G(H_2O_2)_{exp} - G(H_2O_2)_{min}$ are accordingly listed as $G({}^{\bullet}OOCF_2CO_2^-)_{self}$. The corresponding yields of the peroxyl radical reacting via cross-termination, $G({}^{\bullet}OOCF_2CO_2^-)_{cross}$, are then given by the difference between the total ${}^{\bullet}OOCF_2CO_2^-$ yield and the self-termination contribution. From all these figures it is finally possible to calculate the percentages of the two reaction routes (listed in parentheses). As can be seen, cross-termination accounts for at least 80% under all experimental conditions of this set of experiments and go up to at least 90% if the oxalate route had no effect on the H_2O_2 yields (% *values in italics*).

Systems with Excess ${}^{\bullet}OOCF_2CO_2^-$. In all the formate-containing solutions discussed so far, the yield of initially formed $O_2^{\bullet -}$ inherently exceeds that of ${}^{\bullet}OOCF_2CO_2^-$ radicals. Since the latter predominantly engage in cross-termination, the few $O_2^{\bullet -}$ formed through the small amount of ${}^{\bullet}OOCF_2CO_2^-$ self-termination in these systems have only a minor impact on the overall H_2O_2 yields. It was, therefore, interesting to conduct also a different kind of experiment in which the ${}^{\bullet}OOCF_2CO_2^-$ peroxyl radical was produced in excess over $O_2^{\bullet -}$. This was achieved with pH 6 solutions, saturated with a 4:1 (v/v) N_2O/O_2 mixture and containing 2×10^{-2} M $CHF_2CO_2^-$ (DFA). The final molecular products and their yields are listed in Table 3. As in the experiments with CDFA, F^- and CO_2 are the main products, generated at an almost 1:1 ratio, while the small remainder of the carbon balance again shows up as oxalic acid.

The underlying mechanism includes complete scavenging of all hydrated electrons by N_2O to yield $^\bullet$OH radicals (eq 27) which subsequently, together with the primary $^\bullet$OH radicals, react with DFA via hydrogen atom abstraction (eq 28).

$$e_{aq}^- + N_2O + H_2O \rightarrow {}^\bullet OH + OH^- + N_2 \qquad (27)$$

$$^\bullet OH + CHF_2CO_2^- \rightarrow H_2O + {}^\bullet CF_2CO_2^- \qquad (28)$$

The rate constant for this latter process has recently been determined to be 1.7×10^7 M^{-1} s^{-1} in pulse radiolysis experiments following the buildup of the $^\bullet CF_2CO_2^-$ absorption at 330 nm in N_2O-saturated solution of DFA at pH 10.[29] From the fluoride yield of $G(F^-) = 10.6$ and under the assumption that all $^\bullet CF_2CO_2^-$ are immediately converted into peroxyl radicals $G(^\bullet OOCF_2CO_2^-) = 5.3$ is deduced. This is close to the conventionally applied combined yield of primary hydroxyl radicals and hydrated electrons ($G = 5.6$). An even better agreement is achieved when calculating the effective yield of $^\bullet$OH scavenging in N_2O-saturated aqueous solutions via a more sophisticated formula (eq 29) developed by Schuler *et al.*[30]

$$G(S^\bullet) = 5.2 + 3.0\,\frac{(k_S[S]/\lambda)^{1/2}}{1 + (k_S[S]/\lambda)^{1/2}} \qquad (29)$$

In this equation $G(S^\bullet)$ denotes the radiation chemical yield for the radicals derived from the $^\bullet$OH scavenger, here DFA, 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 4.7×10^8 s^{-1}. This calculation gives $G = 5.3$, matching exactly the experimental value.

Hydrogen atoms in this system are expected to react exclusively with oxygen (eq 11), giving $G(O_2^{\bullet -}) = 0.6$. Any contribution of a possible reaction of $H^\bullet$ with DFA can be neglected, assuming that the rate constant for this process is about as low as for monofluoroacetate (6.5×10^5 M^{-1} s^{-1}).[21]

In conclusion, radiolysis of the DFA-containing systems results in the generation of $^\bullet OOCF_2CO_2^-$ peroxyl radicals in large excess over superoxide (ca. 9:1). This means that initially no more than 11% of $^\bullet OOCF_2CO_2^-$ may undergo cross-termination with $O_2^{\bullet -}$. The remaining $G = (5.3 - 0.6) = 4.7$ of the peroxyl radicals will have to enter self-termination (eqs 17, 18, 14) to produce one corresponding equivalent of $O_2^{\bullet -}$. If all these $O_2^{\bullet -}$ were to end up as hydrogen peroxide this would give a yield of $G(H_2O_2) = 2.35$. Together with the primary $G(H_2O_2)_{w.r.} = 0.7$ and with the correction reflected in the oxalate yields, a maximal $G(H_2O_2)_{max} = (2.35 + 0.7 - 0.15) = 2.9$ would emerge which is considerably higher than the experimental value. This disagreement is of course, expected since the $O_2^{\bullet -}$ generated in the peroxyl radical self-termination process will become available for cross-termination. If just half of the surplus peroxyl radicals reacted via self-termination they would, in fact, stoichiometrically produce enough $O_2^{\bullet -}$ to engage the other half in cross-termination. Accordingly, these peroxyl radicals would not contribute at all to the H_2O_2 yield and the hydrogen peroxide yield could then be as low as $G(H_2O_2)_{min} = 0.7 - 0.15 = 0.55$. The experimental yield of $G(H_2O_2)_{exp} = 1.3$ is higher than this minimal value but closer to it than to the fictional maximum. Basically this reconfirms that cross-termination is occurring also in this case. Numerically, the H_2O_2 formed in excess over the minimum, namely, $\Delta G(H_2O_2) = (1.3 - 0.55) = 0.75$ requires that a total of $G(O_2^{\bullet -}) = 1.5$ (i.e., $\approx$30%) of the surplus $^\bullet OOCF_2CO_2^-$ ($G = 4.7$) available in the first instance for self-termination do, indeed, enter this route. The majority of 70% engages, however, in cross-termination.

The fact that $O_2^{\bullet -}$ are indeed generated from these surplus peroxyl radicals, and from self-termination in general, is finally nicely demonstrated by the effect of added superoxide dismutase (SOD) which enhances the $O_2^{\bullet -}$ dismutation to H_2O_2 (with rate constants reported to be in the range from 1×10^8 M^{-1} s^{-1} to 1×10^9 M^{-1} s^{-1}).[13] In the presence of 25 mg/L SOD, for example, the measured H_2O_2 yield in our system substantially increases to $G = 2.2$.

Conclusion

In our present study it has been shown how important the cross-termination reaction between $^\bullet OOCF_2CO_2^-$ peroxyl radicals and superoxide may be. On a quantitative basis our results identify this reaction to be faster than the peroxyl radical self-termination. Although the bimolecular rate constant $2k$ is not explicitly known for this particularly halogenated peoxyl radical it should, however, not exceed that for the self-termination process of $CCl_3OO^\bullet$ which occurs with $2k = 2 \times 10^8$ M^{-1} s^{-1}, one of the highest recorded values.[12] ($^\bullet OOCF_2CO_2^-$ is not only larger in size than $CCl_3OO^\bullet$ but also carries a negative charge.) Accordingly, it seems reasonable to assign a rate constant for the $^\bullet OOCF_2CO_2^- + O_2^{\bullet -}$ cross-termination on the order of $10^8 - 10^9$ M^{-1} s^{-1}. This substantiates the two literature values for similar reactions[14,15] and thus probably allows extrapolation to cross-terminations between organic peroxyl radicals with $O_2^{\bullet -}$, in general.

In conclusion, we have made use of the H_2O_2 yield to evaluate the mechanism of free radical decay in a system where the product analysis from the compound of interest (here $CClF_2CO_2^-$ and $CHF_2CO_2^-$) would not have allowed one to distinguish between various possible routes. Furthermore, our study emphasizes the important role the inherently long-lived superoxide anion, $O_2^{\bullet -}$, may play in radical decay mechanisms. This aspect is considered to be of particular significance in the interpretation of free radical processes in systems where peroxyl radicals and superoxide are present simultaneously such as, for example, in biological environment or in the photocatalytic degradation of organic material.

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