Electron Transfer Reactions of Halogenated Aliphatic Peroxyl Radicals: Measurement of Absolute Rate Constants by Pulse Radiolysis

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The peroxyl radicals $Cl_3COO\cdot$, $Cl_2CHOO\cdot$, $ClCH_2OO\cdot$, CH_3OO; $\cdot OOCCl_2CO_2^-$, $\cdot OOCHClCO_2^-$, $\cdot OOCH_2CO_2^-$, $\cdot OOCF_2CO_2^-$, and $(CH_3)_2C(OH)CH_2OO\cdot$ have been generated in aqueous alcohol solutions by pulse radiolysis using the Brunel and Hahn-Meitner accelerators. The absolute rate constants of the one-electron transfer reactions of related aliphatic peroxyl radicals with ascorbate, promethazine, phenol, and tyrosine have been found to increase with increasing substitution of chlorine atoms. For the reaction of the radical $Cl_3CO_2\cdot$ and promethazine, at pH 6, k $6.0 \pm 0.4 \times 10^8$ l mol^{-1} s^{-1} has been measured. For the analogous reaction of the radical $ClCH_2O_2\cdot$, k $3.3 \pm 0.2 \times 10^7$ l mol^{-1} s^{-1} has been determined.

ALTHOUGH an extensive literature on simple alkylperoxyl radicals exists [1] there appears to be little information available concerning the properties of their halogen-substituted analogues, particularly at room temperature. Compared with many aromatic or heterocyclic organic radicals, alkylperoxyl radicals absorb only weakly in the near-u.v. or visible region: direct observation of their reactions by kinetic absorption spectroscopy is therefore difficult unless the other reactant or a reaction product itself absorbs strongly. The trifluoromethylperoxyl radical $F_3CO_2\cdot$ has been identified by i.r. spectroscopy in an argon matrix containing CF_3O_2F exposed to u.v. light at 8 K [2] and by e.s.r. in rotating cryostat experiments.[3] The related trichloroperoxyl radical $Cl_3CO_2\cdot$ has also been identified by e.s.r. spectroscopy in γ-irradiated carbon tetrachloride–oxygen matrices at 208 K: changes in the absorption spectra observed on warming from 77 K were attributed [4] to reaction (1). It has been suggested that the radical

$$Cl_3\dot{C} + O_2 \longrightarrow Cl_3CO_2\cdot \tag{1}$$

$Cl_3CO_2\cdot$ formed in this way is the chain-propagating intermediate responsible for the extreme sensitivity of oxygenated aqueous chloroform solutions exposed to X- and γ-radiation [reaction (2)].[5,6] The hydroperoxide

$$Cl_3CO_2\cdot + CHCl_3 \longrightarrow Cl_3CO_2H + Cl_3\dot{C} \tag{2}$$

Cl_3CO_2H has been tentatively identified in rigorously dried chloroform irradiated in the presence of oxygen.[7,8] In the presence of water it is thought to decompose according to the overall reaction (3).

$$CCl_3O_2H + H_2O \longrightarrow CO_2 + 1/2O_2 + 3Cl^- + 3H^+ \tag{3}$$

Recent studies indicate that the radical $Cl_3CO_2\cdot$ can be generated in aerated aqueous–alcohol carbon tetrachloride solutions by pulse radiolysis.[9-11] Systems containing propan-2-ol–acetone or t-butyl alcohol can be used. Under the experimental conditions (a) and (b) hydroxyl radicals ($OH\cdot$), hydrogen atoms ($H\cdot$), and solvated electrons (e_{aq}^-) formed on radiolysis of water react *via* [9-14] reactions (4)—(7) and (8)—(11):

(a) propan-2-ol ($\geqslant$1M), acetone ($\geqslant$1M), carbon tetrachloride (*ca.* 10^{-2}M), air saturated

$$OH\cdot + (CH_3)_2CHOH \longrightarrow H_2O + (CH_3)_2\dot{C}OH \tag{4}$$

$$H\cdot + (CH_3)_2CHOH \longrightarrow H_2 + (CH_3)_2\dot{C}OH \tag{5}$$

$$e_{aq}^- + (CH_3)_2CO \longrightarrow (CH_3)_2CO^{\cdot -} \xrightleftharpoons{H^+} (CH_3)_2\dot{C}OH \tag{6}$$

$$(CH_3)_2\dot{C}OH + CCl_4 \longrightarrow (CH_3)_2CO + Cl_3C\cdot + H^+ + Cl^- \tag{7}$$

(b) t-butyl alcohol ($\geqslant$1M), carbon tetrachloride (*ca.* 10^{-2}M), air saturated

$$OH\cdot + (CH_3)_3COH \longrightarrow H_2O + \dot{C}H_2(CH_3)_2COH \tag{8}$$

$$\dot{C}H_2(CH_3)_2COH + O_2 \longrightarrow \cdot O_2CH_2(CH_3)_2COH \tag{9}$$

$$H\cdot + O_2 \longrightarrow HO_2\cdot \rightleftharpoons H^+ + O_2^{\cdot -} \tag{10}$$

$$e_{aq}^- + CCl_4 \longrightarrow Cl_3C\cdot + Cl^- \tag{11}$$

respectively. The trichloromethyl radicals $Cl_3C\cdot$ so formed can subsequently react with oxygen to form $Cl_3CO_2\cdot$ according to reaction (1). Early experiments indicated that the radical $Cl_3C\cdot$ reacts rapidly with several nucleophilic compounds.[9] It was pointed out, however, that the systems studied were not rigorously deoxygenated and the observed oxidation reactions might be due to the radical $Cl_3CO_2\cdot$ and not $Cl_3C\cdot$. Subsequent investigations have confirmed that the radical $Cl_3C\cdot$ does not in fact undergo one-electron transfer reactions readily.[10,11] In contrast the radical $Cl_3CO_2\cdot$ reacts rapidly with several nucleophiles. A preliminary report concerning its reactions with tyrosine has been published.[10] We now report further studies concerning this and related reactions in which we have sought to assess the importance of the three chlorine substituents. Ascorbic acid, the phenothiazine promethazine, tyrosine, and phenol have been used as readily oxidisable substrates.

EXPERIMENTAL

Free radical reactions with first-order half-lives $\geqslant 3$ μs were studied using the Brunel University 4 MeV 200 ns electron pulse linear accelerator and associated equipment for kinetic spectroscopy.[15] Reactions with first-order half-lives in the range 500 ns—3 μs were undertaken using the 4 MeV 5 ns Van de Graaff accelerator at the Hahn-Meitner-Institut. The path lengths of the optical cells were 1.5 and 1 cm at Brunel and the Hahn-Meitner-Institut, respectively, and the radiation doses per pulse 0.5—1 krad. Except where stated the pH of the solutions was adjusted by the addition of perchloric acid or sodium hydroxide. First-order rate constants were generally measured in duplicate at three different substrate concentrations. Solutions were exposed to the minimum amount of light to prevent photolysis and were used as quickly as possible after preparation to limit the extent of auto-oxidation. Even so it is inevitable that under the oxygenated neutral or alkaline conditions used some degradation of substrate occurred and the value of the rate constants obtained must be viewed accordingly.

TABLE 1

Absolute rate constants (l mol^{-1} s^{-1}) for the reactions of aliphatic peroxyl radicals with ascorbic acid and promethazine (0.01M-phosphate buffer)

	Ascorbic acid	Promethazine	
	pH 7	pH 6	pH 7
$Cl_3CO_2\cdot$	$2.0 \pm 0.2 \times 10^8$ $(1.6 \pm 0.2 \times 10^8)$ *	$6.0 \pm 0.4 \times 10^8$ *	$4.5 \pm 0.2 \times 10^8$
$Cl_2CHO_2\cdot$	$2.6 \pm 0.4 \times 10^8$ $(1.8 \pm 0.2 \times 10^8)$ *	$1.4 \pm 0.1 \times 10^8$ *	$6.7 \pm 1.1 \times 10^7$
$ClCH_2O_2\cdot$	$9.2 \pm 1.5 \times 10^7$	$3.3 \pm 0.2 \times 10^7$ *	$3.6 \pm 0.4 \times 10^7$
$\cdot O_2CCl_2CO_2^-$	$9.0 \pm 0.7 \times 10^7$	$7.6 \pm 1.2 \times 10^7$ *	$5.7 \pm 1.2 \times 10^7$
$\cdot O_2CHClCO_2^-$	$5.1 \pm 0.7 \times 10^7$	$3.0 \pm 0.1 \times 10^7$ *	$2.7 \pm 0.2 \times 10^7$
$\cdot O_2CF_2CO_2^-$		$5.6 \pm 1.1 \times 10^7$ *	
$CH_3O_2\cdot$	$2.2 \pm 0.3 \times 10^6$		
$(CH_3)_2C(OH)CH_2O_2\cdot$	$2.1 \pm 0.2 \times 10^6$		No reaction

* Measured on the Hahn-Meitner accelerator where owing to the higher time resolution larger solute concentration ranges could be covered than with the Brunel accelerator.

RESULTS

Ascorbic Acid.—On pulse radiolysis of air-saturated aqueous solutions containing t-butyl alcohol (3M), one of the organic halides, CCl_4, $CHCl_3$, CH_2Cl_2, $Cl_3CCO_2^-$, $Cl_2CHCO_2^-$, or $ClF_2CCO_2^-$ (0.04—0.1M) and ascorbic acid (pH 6—8) the formation of a strongly absorbing transient species ($\lambda_{max.}$ 360 nm) was observed. The absorption spectrum of the species was similar to that previously reported [16-19] for the ascorbic acid radical anion, $A^{\bullet -}$. The rate of appearance of the absorption was exponential and first order in ascorbate concentration, attributable to the reactions where $XRO_2\cdot$ represents an alkylperoxyl radical

$$e_{aq}^- + X_2R \longrightarrow XR\cdot + X^- \quad (12)$$

$$XR\cdot + O_2 \longrightarrow XRO_2\cdot \quad (13)$$

$$XRO_2\cdot + AH^- \longrightarrow XRO_2H + A^{\bullet -} \quad (14)$$

containing one, two, or three halogen atoms. The yields of $A^{\bullet -}$ taking $\varepsilon_{360\,nm}$ 3 300 l mol^{-1} cm^{-1} corresponded to G 2.7. equivalent to $G(e_{aq}^-)$. Values for the absolute rate constants *k* are shown in Table 1. The absorption due to $A^{\bullet -}$ was not observed when similar solutions were irradiated at pH 2. With monohalogen-substituted radicals, but only when high ascorbate concentrations were used, a small additional slowly forming absorption component with a similar spectrum was observed after the initial rapid formation. This was tentatively attributed to some of the 2-hydroxy-2-methylpropylperoxyl radicals formed according to (9) subsequently reacting with ascorbate to yield a further small amount of $A^{\bullet -}$. To confirm this an aqueous solution containing t-butyl alcohol (3M) and ascorbate was saturated with nitrous oxide–oxygen gas mixtures and pulse irradiated. The exponential formation of a transient species with an absorption spectrum characteristic of $A^{\bullet -}$ was again observed. The rate of formation was first order in ascorbate concentration attributable to reactions (15)—(18) and for reaction (18) $k = 2.1 \times 10^6$ l mol^{-1} s^{-1}.

$$e_{aq}^- + N_2O \longrightarrow N_2 + OH^- + OH\cdot \quad (15)$$

$$OH\cdot + (CH_3)_2COH \longrightarrow \dot{C}H_2(CH_3)_2COH \quad (16)$$

$$\dot{C}H_2(CH_3)_2COH + O_2 \longrightarrow \dot{O}_2CH_2(CH_3)_2COH \quad (17)$$

$$\cdot O_2CH_2(CH_3)_2COH + AH^- \longrightarrow HO_2CH_2(CH_3)_2COH + A^{\bullet -} \quad (18)$$

At very low ascorbate concentrations the decay of the absorption due to $A^{\bullet -}$ occurred more rapidly and the additional slowly forming component was absent. This is attributed to the absence of reaction (18) under these conditions and the occurrence of the alternative reaction (19). In order to assess the reactivity of the unsubstituted

$$\cdot O_2CH_2(CH_3)_2COH + A^{\bullet -} \longrightarrow \text{products} \quad (19)$$

methylperoxyl radical towards ascorbic acid solutions containing dimethyl sulphoxide (1M) and ascorbate (0.8—3.2×10^{-2}M) were saturated with a nitrous oxide–oxygen mixture (4 : 1) and pulse irradiated. The exponential formation of the characteristic $A^{\bullet -}$ absorption was again observed, the rate of appearance was first order in ascorbate concentration to the reaction sequence [20] (15) and (20)—(22)

$$OH\cdot + (CH_3)_2SO \longrightarrow CH_3\cdot + CH_3SO_2^- + H^+ \quad (20)$$

$$CH_3\cdot + O_2 \longrightarrow CH_3O_2\cdot \quad (21)$$

$$CH_3O_2\cdot + AH^- \longrightarrow CH_3O_2H + A^{\bullet -} \quad (22)$$

and for the reaction (22) $k = 2.2 \pm 0.3 \times 10^6$ l mol^{-1} s^{-1}.

When solutions containing t-butyl alcohol, $ClCH_2CO_2^-$ and ascorbate were pulse irradiated the $A^{\bullet -}$ absorption was also apparent. However, its magnitude was lower. Its rate of formation corresponded only to the reaction of 2-hydroxy-2-methylpropylperoxyl radicals with ascorbate [reaction (18)] and it was concluded that compared with the other peroxyl radicals studied the reaction of the radical $\cdot O_2CH_2CO_2^-$ with ascorbate is very slow.

Promethazine.—When promethazine was used instead of ascorbate in the above pulse radiolysis systems containing di- and tri-halogen compounds the exponential formation of a strongly absorbing species was observed. Its spectrum

($\lambda_{max.}$ 510 nm) was similar to that previously attributed [9,21–24] to the phenothiazine radical cation $PZ^{\bullet +}$. Its rate of formation was first order in promethazine concentration corresponding to reaction (23). Values of the respective absolute

$$XRO_2\cdot + PZ \longrightarrow PZ^{\bullet +} + XRO_2^- \qquad (23)$$

rate constants k are shown in Table 1. The absorption was not observed on pulse radiolysis of promethazine the t-butyl alcohol–nitrous oxide–oxygen, the t-butyl alcohol–chloroacetic acid, or the dimethyl sulphoxide–nitrous oxide–oxygen systems, indicating that the non-halogenated peroxyl radicals formed in these systems react only slowly if at all with the phenothiazine.

Phenol and Tyrosine.—When phenol or tyrosine were used instead of ascorbate at neutral pH no formation of transient absorbing species could be observed. At pH 12, however, the exponential formation of strong transient absorptions characteristic of phenoxyl radicals were apparent in systems containing di- and tri-halogenated compounds. The rates of formation were first order in phenol or tyrosine concentrations corresponding to reaction (24). Values for

$$XRO_2\cdot + RO^- \longrightarrow RO\cdot + XRO_2^- \qquad (24)$$

the respective absolute rate constants k are shown in Table 2. As in the case of promethazine no absorption was observed in the other systems studied.

TABLE 2

Absolute rate constants ($l\ mol^{-1}\ s^{-1}$) for the reaction of aliphatic peroxyl radicals with phenol and tyrosine (pH 12)

Radical	Phenol *	Tyrosine
$Cl_3CO_2\cdot$	$2.3 \pm 0.2 \times 10^8$	$1.3 \pm 0.2 \times 10^8$
$Cl_2CHO_2\cdot$	$1.1 \pm 0.1 \times 10^8$	$1.0 \pm 0.1 \times 10^8$
$ClCH_2O_2\cdot$	$1.1 \pm 0.1 \times 10^7$	$2.1 \pm 0.1 \times 10^7$
$\cdot O_2CCl_2CO_2^-$	$1.4 \pm 0.1 \times 10^7$	$1.6 \pm 0.2 \times 10^7$
$\cdot O_2CHClCO_2^-$	$7.1 \pm 1.0 \times 10^6$	$1.2 \pm 0.1 \times 10^7$
$\cdot O_2CF_2CO_2^-$	$1.5 \pm 0.1 \times 10^7$	$3.0 \pm 0.3 \times 10^7$
$CH_3O_2\cdot$	$<10^6$	$<10^6$
$(CH_3)_2C(OH)CH_2O_2\cdot$		

* See Table 1.

DISCUSSION

Pulse radiolysis and e.s.r. experiments [16–19,25] have shown that in neutral and alkaline solution ascorbic acid (pK_a 4.1) is rapidly oxidised by several oxidising radicals to the long-lived trioxo radical anion $A^{\bullet -}$ which exists in the pH range 0—14 and has an absorption spectrum similar to that observed in these studies. The fact that we observe the absorption only in neutral solution shows the peroxyl radicals produced in the present systems are oxidising but are not sufficiently so to oxidise unionised ascorbic acid. A yield of ascorbate radical anion equal to that of e_{aq}^- supports the theory that the radicals are derived from the chloro-compounds. The transient products from tyrosine, phenol, and promethazine further illustrate the oxidising nature of the precursor radicals and strongly indicate that electron transfer from substrate to the radical occurs.

It has been suggested that under some conditions the radicals $Cl_3CO_2\cdot$ may break down to form chlorine monoxide radicals which are themselves electrophilic [reaction (25)]. In the case of the radiolysis of aqueous chloroform solutions [7] containing Fe^{2+} the yields of Fe^{3+} can be explained by involvement of either reaction (26) or (27). However, in the present studies the rates

$$Cl_3CO_2\cdot \longrightarrow COCl_2 + OCl\cdot \qquad (25)$$

$$Cl_3CO_2\cdot + Fe^{2+} \xrightarrow{H^+} Cl_3CO_2H + Fe^{3+} \qquad (26)$$

$$OCl\cdot + Fe^{2+} \xrightarrow{H^+} HOCl + Fe^{3+} \qquad (27)$$

of formation of the transient products observed were first order in their parent substrate. Thus if the peroxyl radicals undergo further reactions to yield different oxidising radicals, these reactions must be very rapid. Furthermore, the values of the respective rate constants vary with the nature of the chloro-compound in agreement with the formation of different oxidising radicals. In the case of carbon tetrachloride, the concentrations of promethazine or phenol studied were such that the shortest half-life measured was *ca.* 500 ns. Preliminary experiments at higher substrate concentrations indicate that reaction (13) becomes rate determining and the formation of the absorbing products is no longer first order in substrate concentration. The oxygen concentration in these air saturated aqueous–organic solutions is not known with accuracy. If it is assumed, however, that it is 3×10^{-4}M this implies a value for reaction (1) $k \geqslant 10^9\ l\ mol^{-1}\ s^{-1}$. The absolute rate constants for the reaction of oxygen with several aliphatic alcohol radicals are of the order of $1—5 \times 10^9\ l\ mol^{-1}\ s^{-1}$.[26] Although non-halogenated alkylperoxyl radicals can act as oxidising agents, they are much less reactive than other electrophilic radicals such as $OH\cdot$ and $Br_2^{\bullet -}$. The enhanced reactivity of halogen-substituted radicals can be attributed to the electronegative halogen atoms exerting an inductive effect. It is perhaps surprising, however, that the substitution of just one chlorine atom and even that β to the radical centre causes at least a ten-fold increase in reaction rate constant. Under the conditions used in these studies the unsubstituted alkylperoxyl radicals reacted only with ascorbate, while the monochloro-radicals $ClCH_2OO\cdot$ and $\cdot OOCHClCO_2^-$ reacted with all three substrates with rate constants $>10^7\ l\ mol^{-1}\ s^{-1}$. Introduction of a second chlorine atom increases the reaction rate constant further, but a third atom has little additional effect. The effect of two fluoro-groups appears to be similar to two chloro-groups as seen from the experiments with trichloroacetic acid and chlorodifluoroacetic acid. Assuming that at the pH of these experiments, the carboxy-groups of the peroxyl radicals are ionised as in the parent acids, the rate constants for the reactions of $Cl_2CHOO\cdot$ and $\cdot OOCCl_2CO_2^-$, and $ClCH_2OO\cdot$ and $\cdot OOCHClCO_2^-$ indicate that the CO_2^- group has a slight deactivating effect.

In those experiments where reactions of a peroxyl radical with a particular nucleophile was not observed it is likely that the radicals decay bimolecularly according to reaction (28). Although α-hydroxy-substituted organic peroxyl radicals have been shown [27] to react with

$$2RO_2\cdot \longrightarrow \text{products} \qquad (28)$$

the hydrogen phosphate anion to yield the superoxide radical anion O_2^- [reaction (29)], similar reactions

$$R_2C(OH)O_2^{\cdot} + HPO_4^{2-} \longrightarrow R_2CO + H_2PO_4^- + O_2^{\cdot -} \quad (29)$$

with the α-chloro-substituted radicals in those solutions containing phosphate buffer are considered unlikely.

In conclusion it is clear that halogenated peroxyl radicals readily enter into reactions with nucleophiles. The fact that just one α-chloro-substituent considerably enhances the reactivity of an alkylperoxyl radical as a one-electron oxidising agent may be of particular significance when the biochemistry and toxicology of these compounds are considered.

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