PERKIN 2

# The reaction of the OH radical with pentafluoro-, pentachloro-, pentabromo- and 2,4,6-triiodophenol in water: electron transfer *vs.* addition to the ring

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The OH-radical-induced dehalogenation of pentafluorophenol ($F_5C_6OH$), pentachlorophenol ($Cl_5C_6OH$), pentabromophenol ($Br_5C_6OH$) and 2,4,6-triiodophenol ($I_3H_2C_6OH$) in water has been studied by pulse radiolysis in basic solution where these compounds are deprotonated and hence slightly water soluble. Hydroxyl radicals react with these phenolates both by electron transfer and by addition. Electron transfer yields hydroxide ions and the corresponding phenoxyl radicals ($X_5C_6O^•$ and $I_3H_2C_6O^•$); these were also generated independently, to the exclusion of OH-adduct radicals, by reacting the phenolates with $N_3$ radicals [$k(N_3^• + F_5C_6O^-) = 4.9 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, $\lambda_{max}(F_5C_6O^•) = 395$ nm; $k(N_3^• + Cl_5C_6O^-) = 5.7 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, $\lambda_{max}(Cl_5C_6O^•) = 452$ nm; $k(N_3^• + Br_5C_6O^-) = 6.5 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, $\lambda_{max}(Br_5C_6O^•) = 476$ nm; $k(N_3^• + I_3H_2C_6O^-) = 5.6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, $\lambda_{max}(I_3H_2C_6O^•) = 540$ nm]. Hydroxyl radical addition to the pentahalophenolates is followed by rapid halide elimination, giving rise to hydroxytetrahalophenoxyl radical anions ($X_4O^-C_6O^•$). The latter exhibit absorption maxima near those of the pentahalophenoxyl radicals. This prevents a proper determination of the relative importance of the two processes by optical detection. However, these two processes distinguish themselves by their behaviour with respect to the stoichiometry and kinetics of the production of ionic conducting species. In basic solution, electron transfer causes a conductivity increase due to the formation of $OH^-$ whereas addition followed by HX elimination and deprotonation of the $X_4OHC_6O^•$ radical results in a conductivity drop. The evaluation of the conductivity change at 8 μs after the radiolytic pulse has ended, reveals that about 27%, 53%, 73%, and 97% of the OH radicals react by electron transfer with $F_5C_6O^-$, $Cl_5C_6O^-$, $Br_5C_6O^-$ and $I_3H_2C_6O^-$, respectively. Further conductivity change occurs during the bimolecular termination of the halophenol-derived radicals ($t_{1/2} < 1$ ms, $2k$ range between $1.2 \times 10^9$ and $4 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$) and continues into progressively longer times, owing to the hydrolysis of unstable HX-releasing products, on account of the replacement of $OH^-$ by halide/halophenolate ions. Additionally, further halide is released on a time scale of minutes and hours. The rates of the conductivity change in the time range from a few ms to several tens of seconds are proportional to the $OH^-$ concentration.

The free-radical-induced degradation reactions of halogenated phenols, which have become wide-spread anthropogenic environmental pollutants, are a topic of interest as characterizing their behaviour helps to devise strategies to minimize their impact. For instance in the seventies, pentachlorophenol was widely used in China as a molluscicide and herbicide. Its biodegradation is slow, and thus it is not surprising that it is still observed in many drinking-water resources (for a review on the degradation of pentachlorophenol under environmental conditions, see ref. 1). This situation has led to studies regarding the biological,[2] photochemical,[3–7] sonolytic[8] and oxidative[9–13] degradation of halogenated phenols. Since in these reactions quinone compounds are conceivable products, the hydrolytic degradation of tetrachloro-*p*-benzoquinone (*p*-chloranil) as a representative of these compounds, has also been investigated.[14] Some of the results discussed below regarding the radiolysis of pentachlorophenol have already been reported elsewhere.[15] The present work puts these in a wider perspective and focuses on the question as to how the different halogen substituents affect the reactivity of the halogenated phenol.

Hydroxyl radicals are among the most powerful oxidants, and in drinking-water purification they may be generated through the so-called *advanced oxidation processes*, *e.g.* by the combined action of ozone and hydrogen peroxide (*cf.* refs. 16,17). For the elucidation of the primary reactions of OH radicals with some pentahalophenols, pulse radiolysis with optical detection has been used in the past.[10,12,15] Pentahalophenols have p$K_a$ at or below 5.5,[18] and since their neutral forms are mostly insoluble, the experiments involve the pentahalophenolate anion. It was concluded that two processes must occur side by side, *i.e.* electron transfer as well as OH-addition to the ring.[12] For this reason, more than one type of intermediate is formed in these reactions. It turns out that the overlap of their UV spectra prevents a quantitative assignment. We have now resumed these studies by applying conductometric, as well as optical, detection. It will be seen that the combination of these two techniques allows us to obtain a much clearer picture.

## Experimental

The chemicals were of the highest purity commercially available [except for pentafluorophenol (Fluka) whose stated purity was 99% by GC] and were used without further purification; nevertheless some reactive impurity in the pentafluorophenol interfered with the experiments by a rapid reaction with the pentafluorophenoxyl radical. For this reason, pentafluorophenol was further purified by zone melting

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(Desaga, Heidelberg). After this purification, the impurity that gave rise to this effect was significantly reduced but not fully eliminated.

Solutions were made up in Milli-Q-filtered (Millipore) water. The concentrations of the phenolates were $10^{-4}$ mol dm$^{-3}$, and in the experiments with azide this was added in 20-fold excess. Prior to irradiation, the solutions were saturated with $O_2$-free $N_2O$ (Messer Griesheim) and adjusted to the desired pH with NaOH. The pulse radiolysis set-up with optical and conductivity detection has been described.[19] Thiocyanate dosimetry was employed in the optical measurements, and dimethyl sulfoxide dosimetry in the conductivity experiments.[20] γ-Radiolyses were carried out in a $^{60}$Co-γ-panorama source (Nuclear Engineering Ltd.) at a dose rate of 0.16 Gy s$^{-1}$. Halide ion yields were determined by ion chromatography (Dionex 2010i).

*o*-Chloranil (Fluka) and *p*-chloranil (Janssen), used as reference material, dissolve only slowly in water; this dissolution is accompanied by the release of about one molar equivalent of chloride ion (after 30 min). *o*-Chloranil dissolved in acetonitrile undergoes a UV spectral change within 2 min when injected into water (which becomes acidic as the hydrolysis proceeds), while the spectrum of *p*-chloranil in solution stays essentially the same for at least 10 min.

Some product studies were done by HPLC–MS (instrument, HP5989). $N_2O$-saturated solutions of pentachlorophenol were γ-irradiated at pH 7 (buffered with phosphate) for 30 min, rotary-evaporated to dryness, acidified, and extracted into diethyl ether to remove the phosphate. After evaporation of the ether, the residue was dissolved in the eluent (50% methanol in water). The quinones (*p*-chloranil and 2,3,5-trichloro-6-hydroxybenzoquinone) were assigned on the basis of the *m*/*z* of their radical anions. The products which have a pronounced phenolic character (tetrachlorodihydroxybenzenes, tetrachlorophenol and 2,5-dichloro-3,6-dihydroxybenzoquinone) were assigned on the basis of the *m*/*z* of the phenolates. The degree of chlorine substitution of a compound was calculated from the isotope ratios indicated by these MS peaks.

## Results and discussion

### The free-radical generating system

When dilute aqueous solutions are irradiated with ionizing radiation, the energy is absorbed mainly by the solvent water, giving rise to the production of OH radicals, hydrated electrons and H atoms as reactive free radicals and, in addition, to some $H_2O_2$ and $H_2$ [reaction (1)].[21] The radiation-chemical yields are

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H^+, H_2O_2, H_2 \qquad (1)$$

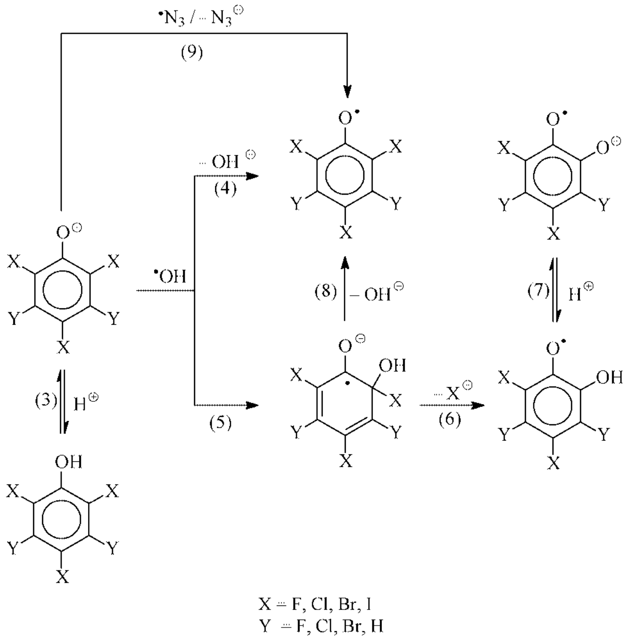
$G({}^{\bullet}OH) \approx G(e_{aq}^-) \approx 2.9 \times 10^{-7}$ mol J$^{-1}$ and $G(H) \approx 0.6 \times 10^{-7}$ mol J$^{-1}$. The hydrated electron may be converted with $N_2O$ into further hydroxyl radicals [reaction (2)]. The pentahalophenols

$$e_{aq}^- + N_2O + H_2O \longrightarrow {}^{\bullet}OH + OH^- + N_2 \qquad (2)$$

$X_5C_6OH$ have low p$K_a$ values [equilibrium (3)]; F 5.6, Cl 4.5;[18] Br 4.6 (estimated, see ref. 22). The p$K_a$ of triiodophenol is estimated at 6.6.[22]

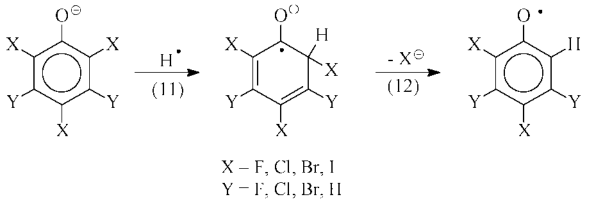
Under the experimental conditions used, these phenols are fully dissociated. The OH radical can react with the pentahalophenolates by electron transfer to form pentahalophenoxyl [reaction (4)], or add to the benzene ring whereby the electrophilic OH radical is preferentially directed into the *o*- and *p*-positions [*e.g.* reaction (5); for the sake of clarity, addition to the *p*-position and the reactions subsequent to this are not presented in the scheme]. The geminal halohydrins thus formed undergo rapid ($k > 10^5$ s$^{-1}$) HX elimination [*e.g.* reaction (6); *cf.* refs. 23–28]. Semiquinone-type radicals have low p$K_a$ [equilibrium (7)] even when unsubstituted (*cf.* refs. 29,30). Hence the hydroxytetrahalophenoxyl radicals exist as anions under these experimental conditions.

Hydroxyl radicals may convert $N_3^-$ into $N_3^{\bullet}$ radicals [reaction (10)] which react with phenolates to practically exclusively form phenoxyl radicals [*e.g.* reaction (9)].[31–33]



$$N_3^- + {}^{\bullet}OH \longrightarrow OH^- + N_3^{\bullet} \qquad (10)$$

The H atom also reacts with these substrates by addition to the ring in the *o*- and *p*-position with respect to the phenolate function [*e.g.* reaction (11)]. These H-adduct radicals are expected to re-aromatize by elimination of a halide ion [*e.g.* reaction (12)]. Thus in these reactions, phenoxyl-type radicals are formed as well.



### Optical measurements

The UV spectra of phenoxyl-type radicals usually show sharp absorption bands,[34] while those of the pentahalophenoxyl radicals were reported to be rather broad.[12] To clarify this apparent contradiction, the UV spectra of the ${}^{\bullet}$OH- and $N_3^{\bullet}$-induced intermediates have been redetermined using the smallest available (2 nm) monochromator slit width. These spectra are given in Figs. 1–3. Compared with the reported[12] ones, the pentafluoro- and pentachlorophenoxyl radicals in the present work show narrower peaks in the wavelength region that is typical for phenoxyl-type radicals.

The H-atom-generated phenoxyl-type radicals [*cf.* reactions (11) and (12)] can be observed in isolation by scavenging the OH radicals with 2-methylpropan-2-ol.[21] An example of the resulting spectrum is shown in Fig. 4. Since the H-atom yield is only 10% of the total water-radical yield, and since the rates of reaction of the major radicals, *i.e.* ${}^{\bullet}$OH or $N_3^{\bullet}$, are almost equally fast (see below), the subsequent interpretations are practically unaffected by the presence of the H-atom-adduct intermediates in these systems.

The bimolecular rate constants for the reactions of ${}^{\bullet}$OH and $N_3^{\bullet}$ with the pentahalophenolates have been determined from

**Table 1** Compilation of the rate constants of the formation and termination of some polyhalophenolate-derived radicals as determined by optical detection

| Reaction | Rate constant/ $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ | Source |
|---|---|---|
| $F_5C_6O^- + {}^\bullet OH \longrightarrow$ Products | 4.8 | Ref. 12 |
| | 7.6 | This work |
| $Cl_5C_6O^- + {}^\bullet OH \longrightarrow$ Products | 8.6 | This work |
| $Br_5C_6O^- + {}^\bullet OH \longrightarrow$ Products | 9.6 | This work |
| $I_3H_2C_6O^- + {}^\bullet OH \longrightarrow I_3H_2C_6O^\bullet + OH^-$ | 1.2 | This work |
| $F_5C_6O^- + N_3^\bullet \longrightarrow F_5C_6O^\bullet + N_3^-$ | Slow | Ref. 12 |
| | 4.9 | This work |
| $Cl_5C_6O^- + N_3^\bullet \longrightarrow Cl_5C_6O^\bullet + N_3^-$ | 3.4 | Ref. 12 |
| | 5.7 | This work |
| $Br_5C_6O^- + N_3^\bullet \longrightarrow Br_5C_6O^\bullet + N_3^-$ | 6.3 | Ref. 12 |
| | 6.5 | This work |
| $I_3H_2C_6O^- + N_3^\bullet \longrightarrow I_3H_2C_6O^\bullet + N_3^-$ | 5.6 | This work |
| $2\ F_5C_6O^\bullet \longrightarrow$ Products | 1.2 | This work |
| $2\ Cl_5C_6O^\bullet \longrightarrow$ Products | 1.5 | This work |
| $2\ Br_5C_6O^\bullet \longrightarrow$ Products | 4.0 | This work |
| $2\ I_3H_2C_6O^\bullet \longrightarrow$ Products | 3.4 | This work |

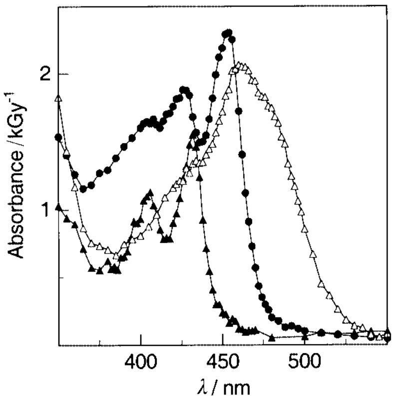


**Fig. 1** Pulse radiolysis of pentafluorophenolate (▲), pentachlorophenolate (●) and pentabromophenolate (△) in $N_2O$-saturated aqueous solutions. UV/Vis spectra of the intermediates produced by the OH radical and the H atom (the latter amounting to 10% of total radical yield).

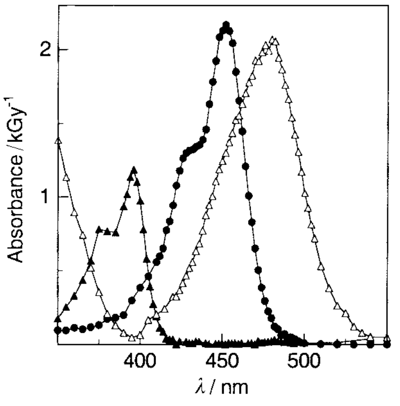


**Fig. 2** Pulse radiolysis of pentafluorophenolate (▲), pentachlorophenolate (●) and pentabromophenolate (△) in $N_2O$-saturated aqueous solutions containing an excess of *azide* ions. UV/Vis spectra are of the corresponding phenoxyl-type radicals. The spectra include a contribution from the intermediates formed [reactions (11) and (12)] *via* H-atom addition (10% of total radical yield).

the slope of the rate of the build-up of the intermediates as a function of the substrate concentration. These data are compiled in Table 1, together with relevant literature data. A purification of the commercially available pentafluorophenol in the present work results in an extended lifetime of the pentafluorophenoxyl radical. The value for the rate constant of the reaction of $N_3^\bullet$ with pentafluorophenol is in line with expectation. (It is conceivable that a similar contamination of the material used in the previous study[12] might have in some way led to the impression that this rate constant was relatively low.)

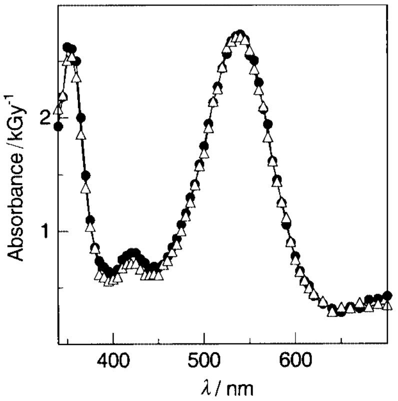


**Fig. 3** Pulse radiolysis of 2,4,6-triiodophenolate in $N_2O$-saturated aqueous solutions with an excess of (●), and without (△), azide ion. UV/Vis spectrum of the phenoxyl-type radical. The spectra include a contribution from the intermediates formed [reactions (11) and (12)] *via* H-atom addition (10% of total radical yield).

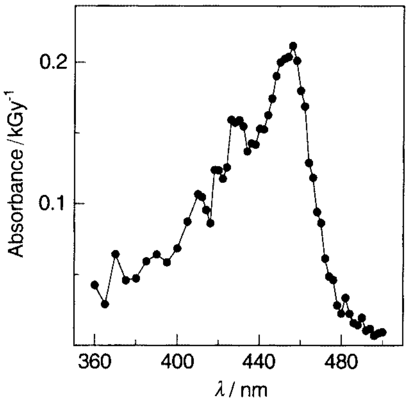


**Fig. 4** Pulse radiolysis of $N_2O$-saturated solutions of pentachlorophenolate in the presence of 0.2 mol dm$^{-3}$ 2-methylpropan-2-ol. Spectrum of the intermediates formed by the H atom (note that the scale of the ordinate is one tenth of that in Figs. 1 and 2).

It is seen from Figs. 1 and 2 that the spectra of the azide-radical-induced intermediates, *i.e.* the pentahalophenoxyl radicals, and those of the free-radical intermediates induced by the OH radical, are quite different, in contrast to the situation with 2,4,6-triiodophenolate. In this case, the spectra obtained with ${}^\bullet OH$ and $N_3^\bullet$ are identical (Fig. 3). This indicates that ${}^\bullet OH$ reacts with 2,4,6-triiodophenolate by electron transfer only,

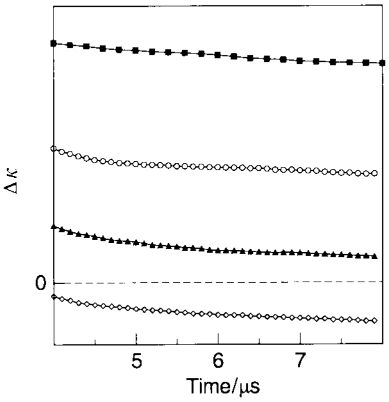


**Fig. 5** Pulse radiolysis of $N_2O$-saturated aqueous solutions (pH 10, no azide) of 2,4,6-triiodophenolate (■), pentabromophenolate (○), pentachlorophenolate (▲) and pentafluorophenolate (◇). Conductivity change after completion of the neutralization reaction [*i.e.* disappearance of the proton formed in reaction (1)]. Δκ in arbitrary units.

while with the other polyhalophenols OH-radical-addition must occur as well.

In principle, it should also be possible to produce in isolation the spectra of the hydroxytetrahalophenoxyl radical anions [*cf.* reactions (5)–(7)] by reacting the *o*- and *p*-tetrahalobenzoquinones with a reducing radical such as $CO_2^{\bullet -}$. However, this approach is impracticable since, as the examples of *o*- and *p*-chloranil show, these compounds undergo hydrolysis during dissolution in water (see also ref. 14) which is a lengthy process.

Since a spectrum is known of only one of the intermediates, *i.e.* the pentahalophenoxyl radical [*cf.* reaction (4)], the system remains incompletely characterized optically. However, it is helpful in the present case that the intermediates undergo transformation into hydrolytically active species. This enables the ratio of electron transfer to addition in these systems to be determined by conductometry.

## Primary reactions by conductometry

When $^\bullet OH$ or $N_3^\bullet$ reacts with the pentahalophenolates by electron transfer [*cf.* reaction (4); reaction (10) followed by reaction (9)], the conductivity of the solution changes because the pentahalophenolate ion which is consumed in this process has a lower equivalent conductivity (*ca.* 40 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, taking the picrate ion as a model) than the newly-formed hydroxide ion (170 $\Omega^{-1}$ cm$^2$ mol$^{-1}$). In basic solution this leads to an increase in conductivity. In contrast, upon addition of $^\bullet OH$ to the ring, a halide ion and a proton are eliminated [*cf.* reactions (5)–(7)]. The proton neutralizes a hydroxide ion, and since the halide ion left over has a relatively low equivalent conductivity (50–70 $\Omega^{-1}$ cm$^2$ mol$^{-1}$), there will be an overall reduction of the conductance. Fig. 5 shows that the four polyhalophenolates upon OH-radical attack yield conductometric signals that are quite different from each other. Upon azide radical attack on these substrates, the conductivity change points in all cases to a quantitative formation of the corresponding phenoxyl radicals (data not shown). For $^\bullet OH$, the respective ratios of electron transfer to addition (*cf.* Table 2) have been calculated from the OH-radical reaction data [*cf.* Fig. 5, at 8 μs; at this time, the initial conductance spike (not shown) due to radiolytic $H^+$ generated in reaction (1), has subsided through neutralization] on the basis of the stoichiometry of reactions (4)–(8) and the respective equivalent conductivities.

Genuine one-step electron transfer to the OH radical is encountered quite infrequently. Usually, the same overall chemical effect is arrived at *via* a very short-lived intermediate OH-radical adduct. Thus also in the present system, one might envisage the formation of the polyhalophenoxyl radicals to proceed by an addition–elimination process such as reaction (5) followed by reaction (8). However, one also expects that the rate of halide ion elimination from the adduct radical [reaction (6)] should increase from fluoride to iodide. Therefore if the only route to the phenoxyl radical was by reaction (8), the highest proportion of phenoxyl radical should occur in the case of the pentafluoro compound, *in contrast* to what is observed. When looking at the competition between reactions (4) and (5), steric effects should favour OH-radical addition in the case of the smaller halogens, *i.e.* this should be most favoured in the case of pentafluorophenolate, *in agreement* with observation. It follows that the major route to the pentahalophenoxyl radicals is in fact the electron transfer reaction (4). Nevertheless, it is quite possible that as in other aromatic systems,[35,36] here as well, the electron transfer reaction does not proceed by an outer-sphere-type reaction but *via* a short-lived π-complex formed in the first instance. Recently, experimental evidence has been reported which supports this concept.[37]

**Table 2** Reactions of OH radicals with some polyhalophenolates (pH 10). Percentage of electron transfer and addition as determined by pulse radiolysis with conductometric detection

| Substrate | % Addition | % Electron transfer |
|---|---|---|
| Pentafluorophenolate | 73 | 27 |
| Pentachlorophenolate | 47 | 53 |
| Pentabromophenolate | 27 | 73 |
| Triiodophenolate | 3 | 97 |

The electron transfer *vs.* OH-radical addition ratio may depend on the temperature. It has been observed that an increase in temperature in the pentachloro- and pentabromophenolate systems favours the electron-transfer reaction,[10] while this effect is not evident in pentafluorophenolate.

## Secondary reactions by conductometry

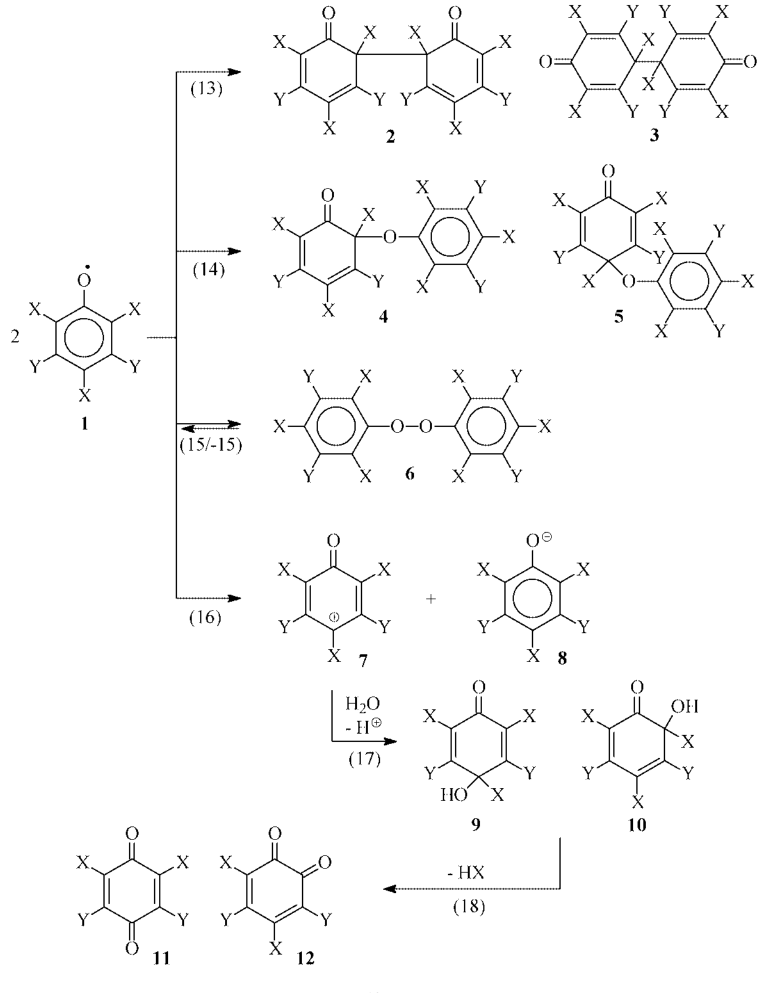
The final yields of halide ions are much higher than can be accounted for by reaction (6) (Table 3). This raises the question as to whether this additional halide release occurs earlier at the free-radical stage, or later as a consequence of the decomposition of the termination products. It has been mentioned above that tetrachloro-1,4-benzoquinone hydrolyzes quite rapidly in basic solution[14] with a high-enough rate (1.7 × $10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$) for it to be feasible to identify it kinetically, and also to study the hydrolysis of similar compounds by pulse radiolysis, using conductometric detection. For all of the other conceivable products, no reference data are available, and the mechanistic suggestions made below must remain tentative. We find that tetrachloro-1,2-benzoquinone hydrolyzes much faster than tetrachloro-1,4-benzoquinone, and one might infer that in general polyhalogenated compounds with an *ortho*-quinoid structure hydrolyze faster than the *para*-quinoid ones. It has been seen that pulse-conductometric experiments yield quantitative, besides kinetic, information (Table 3). In conjunction with the γ-radiolysis results (Table 3), this can be used to separately assess the halide release at the early and the later stages.

**2,4,6-Triiodophenol.** The simplest situation is encountered in the case of 2,4,6-triiodophenol. Here, one kind of radical strongly predominates, *i.e.* 2,4,6-triiodophenoxyl (≈87%). It has been seen above that these radicals decay bimolecularly at close to diffusion-controlled rates (*cf.* Table 1). After an initial steep rise, the conductivity drops again while the termination reactions proceed (Fig. 6). At still longer times (*i.e.* up to 10 s) no further conductance change of any importance is observed in this system. As can be seen from the inset of Fig. 6 where the inverse of the first half-life of the conductance change is plotted as a function of the dose per pulse, this change follows second-order kinetics and occurs on the time scale of the bimolecular termination of the radicals. This implies that the primary product(s) must decompose very rapidly ($k > 10^4$ s$^{-1}$; for some rate

**Table 3** Compilation of the *G* values of halide-ion release in the pulse radiolysis of polyhalogenated phenolates (pH 10, $N_2O$-saturated), as estimated[a] from the conductivity change, and some rate constants (in parentheses, units $dm^3\ mol^{-1}\ s^{-1}$). The rate of hydrogen halide release during the free-radical termination reaction must be faster than $10^4\ s^{-1}$. *G* values obtained after γ-radiolysis have been determined by ion chromatography

| | $G/10^{-7}$ mol $J^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| Substrate | Reacting radicals | At pulse end | During free-radical termination | Fast $OH^-$-induced | Slow $OH^-$-induced | Following γ-radiolysis[b] | 3 h after γ-radiolysis[c] |
| Pentafluorophenol | $^•OH$ (+10% $H^•$) | 4.8 | nd | nd | nd | 9.5 | 10.8 |
| | $N_3^•$ (+10% $H^•$) | 0.6 | nd | nd | nd | nd | nd |
| Pentachlorophenol | $^•OH$ (+10% $H^•$) | 3.2 | 1.5 | Absent | 1.1<br>(350) | 6.5 | 9.9 |
| | $N_3^•$ (+10% $H^•$) | 0.6 | Absent | 2.2<br>($3 \times 10^5$) | 1.3<br>(530) | 6.5 | 7.5 |
| Pentabromophenol | $^•OH$ (+10% $H^•$) | 2.2 | 1.0 | 1.0<br>($2.1 \times 10^5$) | 1.0<br>(820) | 5.8 | 7.0 |
| | $N_3^•$ (+10% $H^•$) | 0.6 | 0.6 | 2.0<br>($2.1 \times 10^5$) | 1.0<br>(820) | nd | nd |
| 2,4,6-Triiodophenol | $^•OH$ (+10% $H^•$) | 0.6 | 1.6 | Absent | Absent | 3.6 | 4.6 |
| | $N_3^•$ (+10% $H^•$) | 0.6 | 1.6 | Absent | Absent | nd | nd |

nd: not determined. [a] In the absence of azide, the instant conductance change is proportional to the sum *G*[reaction (4)] × [$\Lambda(OH^-) - \Lambda(PhO^-)$] + *G*[reaction (5)] × [$-\Lambda(OH^-) + \Lambda(X^-)$] + $G(H^•)$ × [$\Lambda(X^-) - \Lambda(PhO^-)$]. *G*[reaction (4)] + *G*[reaction (5)] = $G(^•OH)$. In the presence of azide, this conductance change is proportional to the sum $G(^•OH)$ × [$\Lambda(N_3^-) - \Lambda(PhO^-)$] + $G(H^•)$ × [$\Lambda(X^-) - \Lambda(PhO^-)$]. A basis of $0.6 \times 10^{-7}$ mol $J^{-1}$ for halide release which occurs in all of these systems follows from reactions (11) and (12); this process is silent conductivity-wise, as is the oxidation by $N_3^•$, reaction (9), since $\Lambda(N_3^-) \cong \Lambda(X^-) \cong \Lambda(PhO^-)$. [b] Analysis began immediately after γ-radiolysis. [c] Solution brought to pH 10.5 after radiolysis.



constants for the decay of such products see Table 3). Hydrogen iodide is released on this time scale with a *G* value of $1.6 \times 10^{-7}$ mol $J^{-1}$. The experiments shown in Fig. 6 have been done using $^•OH$ to generate 2,4,6-triiodophenoxyl. The same results are obtained when these intermediates are generated by $N_3^•$ (data not shown), as one expects on the basis of the data from the optical-detection experiments.

A *G* value of $1.6 \times 10^{-7}$ mol $J^{-1}$ for iodide release indicates that phenoxyl-radical disproportionation, reaction (16), cannot be the only termination route; this is expected to provide one

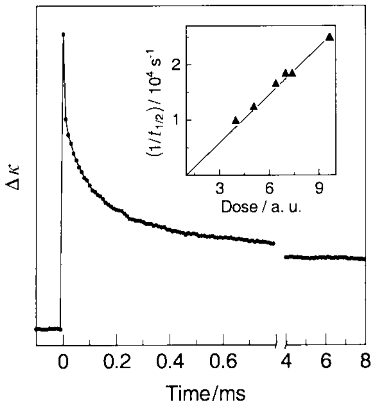


**Fig. 6** Pulse radiolysis of $N_2O$-saturated aqueous solutions of 2,4,6-triiodophenolate at pH 10 (no azide). Evolution of the conductivity within the time range of the termination of the 2,4,6-triiodophenoxyl radical. Inset: The inverse of the first half-life of the conductivity change as a function of the dose per pulse (1 arbitrary unit corresponds to about 1.2 Gy). Δκ in arbitrary units.

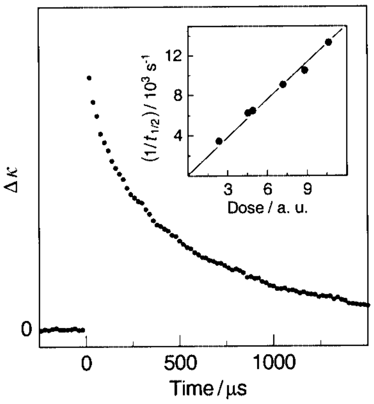


**Fig. 7** Pulse radiolysis of $N_2O$-saturated aqueous solutions of pentabromophenolate at pH 10 (no azide). Conductivity change within the time range of free-radical termination. Inset: The inverse of the first half-life of this conductivity change as a function of the dose per pulse. Δκ in arbitrary units.

iodide ion per two phenoxyl radicals, which would amount to about $3 \times 10^{-7}$ mol $J^{-1}$ if this route was followed exclusively. This suggests the occurrence of "silent" reactions such as (13)–(15). Such termination products are expected to be labile and should contribute to the release of further iodide over longer periods of time (see Table 3). The formation of a C–C-linked product such as from reaction (13) has been reported upon the oxidation of 2,4,6-triiodophenol in aqueous solution.[38]

**Pentabromophenol.** The $N_3$ radical produces pentabromophenoxyl, while the H atom (10% of the total primary radical yield) leads to the formation of HBr and tetrabromophenoxyl. As before, a loss of conductivity (not shown, but qualitatively similar to that observed in the case of the OH-radical-induced process, see Fig. 7) occurs with non-first-order kinetics during the termination of these phenoxyl radicals.

When the termination of the pentabromophenoxyl/tetrabromophenoxyl radicals (azide system) is over, the resulting products react with $OH^-$ in two distinctly separate processes (not shown but similar to what is observed upon OH-radical attack, see Figs. 8 and 9 below). Both are kinetically first-order, their rates depending on the $OH^-$ concentration. The faster of the two processes has a rate constant of $2.1 \times 10^5$ $dm^3$ $mol^{-1}$ $s^{-1}$ while the slower one occurs with 820 $dm^3$ $mol^{-1}$ $s^{-1}$ as is calculated from the slopes of the $k_{obs}$ *vs.* $[OH^-]$ plots.

A quantification of the conductance change in the azide system leads to the following picture. The H atom gives rise to $G(HBr) \approx 0.6 \times 10^{-7}$ mol $J^{-1}$. During the termination of the

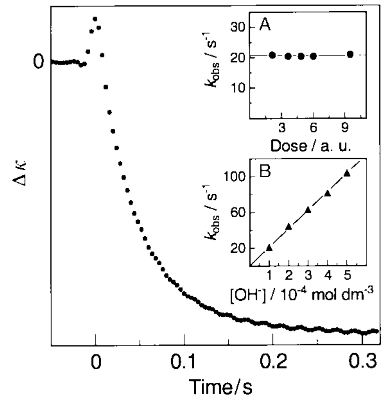


**Fig. 8** Pulse radiolysis of $N_2O$-saturated aqueous solutions of pentabromophenolate at pH 10 (no azide). The *faster* part of the biphasic conductivity change after the completion of the termination reactions, *i.e.* at the product stage. Inset A: rate of the conductivity change as a function of the dose per pulse at pH 10. Inset B: rate of the conductivity change as a function of the $OH^-$ concentration. Δκ in arbitrary units.

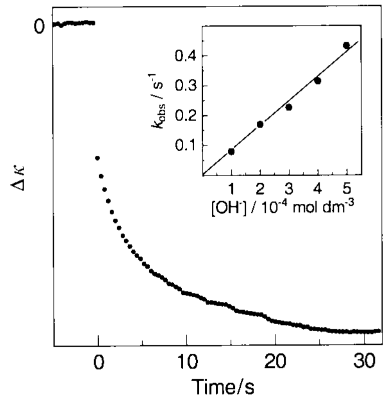


**Fig. 9** Pulse radiolysis of $N_2O$-saturated aqueous solutions of pentabromophenolate at pH 10 (no azide). The *slower* part of the conductivity change at the product stage. Inset: rate of the conductivity change as a function of the $OH^-$ concentration. Δκ in arbitrary units.

phenoxyl radicals, a further $0.6 \times 10^{-7}$ mol $J^{-1}$ HBr is released. After that, the major share of the halide is liberated by two subsequent $OH^-$-induced reactions, the faster one yielding $2.0 \times 10^{-7}$ mol $J^{-1}$ HBr, the slower one $1.0 \times 10^{-7}$ mol $J^{-1}$ HBr. Altogether, a total $G(HBr) = 4.2 \times 10^{-7}$ mol $J^{-1}$ is formed over these 20 s after the pulse. These *G* values are extracted from the pulse-radiolysis conductivity experiments. Owing to co-elution, it proved impossible by ion chromatography to determine bromide in the presence of azide, thus ruling out a comparison of the conductivity data with the product-analytical data.

In the *absence* of azide (Figs. 8 and 9), attack is by $^\bullet OH$ and $H^\bullet$, which give rise to $G(HBr) = 2.2 \times 10^{-7}$ mol $J^{-1}$ right after the pulse. During the time period of free-radical termination (the termination reactions now involve tetrabromosemiquinone as well as pentabromophenoxyl and tetrabromophenoxyl), $G(HBr) = 1.0 \times 10^{-7}$ mol $J^{-1}$ are liberated. The kinetics are necessarily more complex since the semiquinone radicals generated by $^\bullet OH$ addition–HBr elimination (see above) now play a non-negligible part (*cf.* Table 2), in contrast to the triiodophenol situation. This complexity may be the cause that, here, for a given dose, the apparent $t_{1/2}$ is distinctly smaller (Fig. 7, inset) than in the absence of semiquinone radicals (*cf.* Fig. 6, inset). This comparatively fast process is followed by two slower, $OH^-$-induced reactions, the faster one and the slower one each contributing HBr at $1.0 \times 10^{-7}$ mol $J^{-1}$ (the total $G(HBr)$ after a few seconds being $5.2 \times 10^{-7}$ mol $J^{-1}$). The bromide yield determined following γ-radiolysis is $5.8 \times 10^{-7}$ mol $J^{-1}$ (Table 3). Thus, most of the HBr is liberated within 40 s at pH 10.3. Additional HBr is released at still longer times (Table 3).

**Pentachlorophenol.** In the azide-containing system, pentachlorophenoxyl but no OH-adduct radicals are produced, while the addition of the H atom (10% of the total primary radical yield) leads to the formation of HCl and the tetrachlorophenoxyl radical. Initially, the intervention of the H atom gives rise to $G(\mathrm{HCl}) = 0.6 \times 10^{-7}$ mol J$^{-1}$. There is no halide release within the time range of the free-radical termination reactions, in contrast to the case of, *e.g.*, the pentabromo compound. After termination there is, as above, a biphasic OH$^-$-induced halide release (no diagrams shown; rate constants $3 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ and 530 dm$^3$ mol$^{-1}$ s$^{-1}$; *cf.* Table 3). On this longer time-scale, the two OH$^-$-induced processes release HCl in amounts of $2.2 \times 10^{-7}$ mol J$^{-1}$ and $1.3 \times 10^{-7}$ mol J$^{-1}$, respectively. Within 30 s, the total amount of HCl liberated rises to $4.1 \times 10^{-7}$ mol J$^{-1}$. Upon γ-irradiation, $G(\mathrm{HCl}) = 6.5 \times 10^{-7}$ mol J$^{-1}$ is observed which upon standing increases further to a value of $7.5 \times 10^{-7}$ mol J$^{-1}$ (Table 3). Thus, about half of the total HCl released is liberated at a late stage (minutes to hours).

With the OH radical instead of the azide radical reacting with pentachlorophenolate, the evolution of the conductance is somewhat different (data not shown). A conductivity change is observed during the period of free-radical termination. Further on, there is only a single OH$^-$-consuming process instead of two; this occurs with a rate constant of 350 dm$^3$ mol$^{-1}$ s$^{-1}$ (Table 3). Right after the end of the pulse, $^{\bullet}$OH and H$^{\bullet}$ have produced $G(\mathrm{HCl}) = 3.4 \times 10^{-7}$ mol J$^{-1}$. Subsequently, $G(\mathrm{HCl}) = 1.5 \times 10^{-7}$ mol J$^{-1}$ is formed during the time range of termination. Another $1.1 \times 10^{-7}$ mol J$^{-1}$ HCl appears on account of the OH$^-$-induced hydrolysis of the termination products. Eventually after about 30 s, a total of $G(\mathrm{HCl}) = 6.0 \times 10^{-7}$ mol J$^{-1}$ has been liberated. After γ-irradiation $G(\mathrm{HCl}) = 6.5 \times 10^{-7}$ mol J$^{-1}$ is found, which increases upon standing to a value of $9.9 \times 10^{-7}$ mol J$^{-1}$ (Table 3), *i.e.* about one third of the HCl is released at a late stage (minutes to hours).

**Pentafluorophenol.** It has been seen above that this compound could not be purified to a satisfactory degree. Thus in this case, those data that refer to the time range beyond a few microseconds might be erroneous from a quantitative point of view. Nevertheless, it is clear that in this system also, halide release proceeds in several stages.

## Product studies

Regarding the identification and quantification of the products, it is relatively easy to determine the amount of halide released; this has been done in most cases by ion chromatography. Moreover, applying the conductivity technique, it is possible to quantify the amount of halide even as it is released at various stages of the radiation-induced decomposition process (Table 3). It has proved more difficult to determine the organic products of this process. An attempt has been made to analyze these products by HPLC-MS, and by GC, in the case of the pentachlorophenolate. There is always the problem of the time elapsed between the irradiation and the analysis, which implies that only the more stable products can be detected.

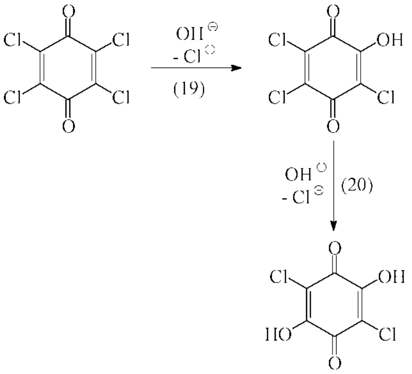
There is evidence for the production of 2,5-dichloro-3,6-dihydroxybenzoquinone, tetrachlorophenol, tetrachlorodihydroxybenzenes and some *p*-chloranil. It has been shown before[14] that tetrachloro-1,4-benzoquinone (*p*-chloranil) undergoes fast hydrolysis (OH$^-$-induced; $k = 1.7 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$) into 2,3,5-trichloro-6-hydroxybenzoquinone. This compound hydrolyses further, though more slowly (OH$^-$-induced; $k = 3.9$ dm$^3$ mol$^{-1}$ s$^{-1}$),[14] into 2,5-dichloro-3,6-dihydroxybenzoquinone. This suggests that these two products are not primary ones. In further HPLC experiments using optical detection, special attention has been paid to detect any dimeric material that should elute at longer retention times than the starting material. There was no evidence for such compounds being present, even after the shortest possible time required for such an analysis (30 min). The same conclusion was drawn from the result of a gas chromatographic analysis after trimethylsilylation of the irradiated sample (concentrated by rotary evaporation) and of a sample that had been reduced with $\mathrm{NaBH_4}$ prior to rotary evaporation.

## General considerations regarding the mechanistic features of polyhalophenol OH-radical-induced degradation

It has been seen above that the OH radical may react with these compounds by hydroxy-polyhalo-cyclohexadienyl radical and/or polyhalophenoxyl radical formation. On account of the very fast hydrogen halide elimination in the former [*cf.* reaction (6)], the free-radical system constitutes a mix of differently halogenated phenoxyl radicals (including, following H-atom addition, reaction (12) which makes a minor contribution consisting of phenoxyl radicals that carry one less halogen atom compared to the parent compound). Up to this stage, the reaction mechanism is quite clear. The mechanistic complexities arise as these polyhalophenoxyl radicals, *via* self-reaction and cross-reactions, give rise to various products by disproportionation and/or recombination. A feature common to many of these primary products is that they display quinoid functions which initiate hydrolytic dehalogenation; obviously, the rate of this process may vary depending on the details of each molecular structure. As dehalogenation proceeds, the rates for the continuation of this process may lessen. Reactions (13)–(18) reflect the general situation in the azide-radical-mediated system up to the end of the stage of the termination reactions (the OH-radical-mediated system is in the majority of cases necessarily more complicated owing to the additional presence of semiquinone radicals from reactions such as (6) and (7), and is not being discussed further at this point).

Phenoxyl radicals typically terminate by recombination at carbon [*cf.* reaction (13)], but mixed carbon–oxygen coupling [*cf.* reaction (14)] has also been observed.[39] The importance of a recombination at oxygen [*cf.* reaction (15)] is assumed to be small because of the low O–O binding energy of the resulting product which would tend to make this reaction reversible. Disproportionation [*cf.* reaction (16)] has not so far been observed in phenoxyl free-radical chemistry. We suggest however that this is the source of the conductivity changes during the bimolecular decay of the triiodophenoxyl and pentabromophenoxyl radicals [*cf.* reactions (16)–(18)]. As can be seen from Table 3, in the case of triiodophenoxyl the yield is high ($G = 1.6 \times 10^{-7}$ mol J$^{-1}$) compared to that of pentabromophenoxyl ($G = 0.6 \times 10^{-7}$ mol J$^{-1}$) and no HX elimination is observed with pentachlorophenoxyl. This we explain by steric effects. In the case of the triiodophenoxyl radicals steric hindrance by the bulky iodo substituents at the *o*- and *p*-positions will favour disproportionation *via* electron transfer. Steric hindrance by the bromo substituent occurs to a lesser extent and is absent with the still smaller chloro substituent. In these disproportionation reactions geminal halohydrins are formed [reaction (17)]. They are known to eliminate HX at a rate $>10^5$ s$^{-1}$.[23]

The kinetically visible OH$^-$-catalyzed processes (*cf.* Table 3) may be ascribed to a *fast* halide elimination from *o*-tetrahaloquinones **12** and *gem*-halohydrin-ether *o*-quinoid compounds such as **4** (and also **2**), and a *slow* halide elimination from *gem*-halohydrin-ether *p*-quinoids such as **5** (and also **3**) as well as from the *p*-tetrahaloquinones **11**, in so far as the latter are produced in reactions such as (18). Since *o*-tetrachlorobenzoquinone hydrolyzes faster than *p*-tetrachlorobenzoquinone, it is reasonable to assume that a similar trend should exist in these quasi-quinoid compounds. For our system, reference material is lacking. However, the hydrolysis of tetrachloro-1,4-benzoquinone is well established. In its first step [reaction (19)] it hydrolyses with a rate constant of $1.7 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$.[14] The second step is much slower [reaction (20), $k = 3.9$ dm$^3$



mol$^{-1}$ s$^{-1}$]. Apparently, following the first rapid decay processes, the HX-elimination slows down. Post irradiation HX-release is generally observed, but after several hours subsequent HX-release becomes so slow that no attempt has been made to follow it any further. In pentachlorophenol $G$(HCl) is $9.9 \times 10^{-7}$ mol J$^{-1}$ after several hours, *i.e.*, on average, only about 30% of the chlorine has been eliminated at this stage. Thus, rapid mineralization of the polyhalophenols is not achieved by their reaction with OH radicals. This also holds for a treatment with ozone (ref. 15,40 and Mvula and von Sonntag, unpublished).

It is likely that the halide release at the time of a few hours has not yet reached its end point and that a cascade of ever slower hydrolysis reactions would continue to unfold. Eventually, the hydrolysis products, which are of a polyphenolic nature, might undergo oxidation in the presence of atmospheric oxygen. This should lead to the fragmentation of the six-membered ring structures. At the present time, owing to the lack of quantitative product data, a more precise chemical mechanism is beyond reach.

## Acknowledgements

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