JOURNAL OF Materials CHEMISTRY

EPR investigation of HO• radical initiated degradation reactions of sulfonated aromatics as model compounds for fuel cell proton conducting membranes

Gerold Hübner and Emil Roduner*

Institut für Physikalische Chemie, Universität Stuttgart Pfaffenwaldring 55, D-70569 Stuttgart, Germany. E-mail: Roduner@ipc.chemie.uni-stuttgart.de

Received 14th September 1998, Accepted 23rd November 1998

In order to predict hydroxy radical initiated degradation of new proton conducting polymer membranes based on polystyrene, polyethersulfone, polyetheretherketone, or on polymers obtained by radiation grafting of styrene on different fluoropolymers, eight sulfonated aromatics were chosen as model compounds for EPR experiments, aiming at the identification of products of HO• radical reactions with these polymers. Photolysis of H_2O_2 was employed as the source of hydroxyl radicals. A detailed investigation of the pH profile was carried out for *p*-toluenesulfonic acid. Besides benzyl- and hydroxy-cyclohexadienyl radicals at lower pH values, phenoxyl radicals were identified, predominating in the pH range 10.5–13.0. A large number of new radicals give evidence of multiple hydroxylation of the aromatic rings, confirming reaction mechanisms proposed on the grounds of product analysis, but no evidence of dimerisation was found. The result as regards stability of organic proton exchange membranes for fuel cells is, that all unsaturated bonds and weakly bound atoms are subject to immediate attack by HO•. Ether links open by HO• *ipso* addition. Strategies for the reduction of membrane degradation should focus on a minimisation of HO• formation and of its access to the interior of the membrane.

1 Introduction

Efforts to replace the most widely used perfluorinated Nafion® as proton conducting membranes in polymer electrolyte fuel cells (PEFC) by cheaper, ecologically more tolerable materials are presently undertaken by several research groups engaged in material research worldwide.[1–3] Partly fluorinated polymers like the trifluoro styrene containing membranes RAYMION®, the BAM3G membrane by Ballard,[4] or membranes based on fluorine back bone copolymers grafted with polystyrenesulfonic acid (ETFE or FEP-g-SPS type) [3,5] like R-1010, R-4010 by Pall RAI as well as polymers consisting of unfluorinated aromatic polymers like sulfonated polyethersulfone (PSU), polyether(ether)ketone (PEK),[6,7] or the polyethylene polystyrenesulfonic acid copolymers (PE/SPS) by DAIS [8] have proven almost comparable electrochemical properties.[1,3,8] As a common feature of all of these membrane materials the building block providing the essential acidic function consists of sulfonic acid substituted aromatic rings.

To ensure long term durability of the new materials, additional investigations are necessary about possible degradation mechanisms. HO• and HO_2• radicals originating from oxygen diffusion through the membrane and incomplete reduction at the fuel cell anode are held responsible for these degradation reactions.[5,3,9] Evidence for it is the formation of H_2O_2 as detected in product water.[2] Owing to their high oxidative potentials (2.8 and 1.7 V, respectively),[10,11] these radicals are often used in industrially applied advanced oxidation processes (AOPs) of organic compounds, as in waste water treatment,[12–18] or pulp lignification and bleaching [19–22] as well as for surface modifications of certain polymers.[23–29] They are thought to be responsible for cancer diseases, due to their ability to attack DNA molecules, and they play a role in atmospheric processes.[30] Degradation reactions of sulfonated aromatics as model compounds for detergents, medicines, agrochemicals and colouring agents have repeatedly been investigated in water treatment processes.[31–38] Sulfonated isopropylbenzene and *tert*-butylbenzene were investigated to model the long term stability of proton conducting membranes in oxidative media.[39] Reactions of HO• radicals with *p*- and *m*-toluenesulfonate, *p*-isopropylbenzenesulfonate and *m*-xylene-4-sulfonate were carried out in order to study radical intermediates in photochemical electron transfer reactions in poly(styrenesulfonate).[40,41] The products of sulfonic acid degradation have been analysed by different methods like HPLC,[33] GC–MS,[35] UV spectroscopy,[41] ^{13}C NMR[39] and electron paramagnetic resonance (EPR).[41,42] Apart from the intermediary benzyl and hydroxycyclohexadienyl radicals,[41,42] products resulting from a substitution of the $SO_3•^-$ group like *p*-cresol[33,35] and from a total mineralisation[33] of the molecules have been reported.

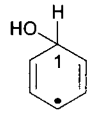
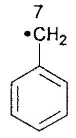
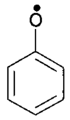
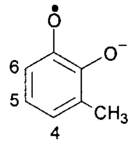
On an experimental scale, the generation of HO• or HOO• radicals can be achieved by a variety of different methods,[10,11,25,43] either by direct photochemical,[11,43–45] photocatalytic[46] or Fe^{2+} or Ti^{3+} catalysed (Analogous to Fenton's reaction)[43,45,47–49] degradation of H_2O_2. Moreover, HO• radicals are obtained by e^- irradiation[10,30,50–52] or sonolysis [53] of aqueous solutions or by photocatalytic oxidation of water on irradiated semiconductors like TiO_2.[54,55]

Different radical species are formed either by addition of HO• to the aromatic ring (acidic to neutral conditions) or by abstraction of H• from the side chains by $O•^-$ (alkaline conditions). Phenolate ions react with HO• by electron transfer so that phenoxyl radicals are formed.[56]

By means of EPR spectroscopy, radical intermediates of the HO• initiated degradation of the cyclohexadienyl,[41,42,57–59] benzyl,[41,42,60,61] or phenoxyl[41,62,63] type are experimentally distinguishable by means of their hyperfine splittings and *g*-values (see Table 1).

In the present study we investigate the degradation of *p*-toluenesulfonic acid in the pH range 0.1–13.9. Direct photolysis of H_2O_2 was chosen as the source of HO• radicals; this method works in a wide range of different pH values, moreover the resulting oxygen radicals are free and not bound to a catalyst. This study is extended to further sulfonated aromatics with ethyl, methoxy and hydroxy substituents (shown together with the results in Table 2, which also introduces the abbreviations used below) aiming at a more complete picture of the chemistry of HO• radicals in such systems. Methoxy substituted compounds mimic the ether bridges in the polymers with a PEK backbone. The study also included hydroxy substituted

Table 1 EPR hyperfine splittings in Gauss and *g*-values for radical intermediates of the reaction of hydroxyl radicals with aromatic hydrocarbons[64]

 Hydroxy cyclohexadienyl radical	 Benzyl radical	 Phenoxyl radical	 *ortho*-semiquinone anion radical
1 H(1): 36	2 H(7): 16.32	2 H(*o*): 6.65	3 H(CH_3): 0.63
2 H(*o*): 9.3	2 H(*o*): 5.15	2 H(*m*): 1.85	1 H(4): 2.85
2 H(*m*): 2.9	2 H(*m*): 1.78	1 H(*p*): 10.2	1 H(5): 4.13
1 H(*p*): 13.4	1 H(*p*): 6.2		1 H(6): 0.28
$g \approx 2.0022$–2.0026	$g = 2.0026$	$g = 2.0046$	$g \approx 2.0036$–2.0058

aromatics, because hydroxy groups turned out to be important intermediates in the degradation of TSA and the OCH_3 substituted compounds. Investigations at low pH are particularly relevant for understanding degradation in polymer electrolyte fuel cells.

2 Experimental

EPR spectra were recorded with a Varian E-Line X-band spectrometer. Microwave power was held at 1.5 mW. The aqueous solutions, with concentrations of 70 mmol l^{-1} sulfonic acid and 40 mmol l^{-1} H_2O_2 unless otherwise stated, were photolysed in a flow cell (quartz, 0.4 mm × 10 mm × 50 mm) at ambient temperature within the resonator. A 500 W Hg(Xe) high pressure mercury arc lamp (Oriel 66142) was used as an irradiation source. Wavelengths below 210 and above 400 nm were eliminated with a filter solution (1.14 mol l^{-1} $NiSO_4$/0.21 mol l^{-1} $CoSO_4$/0.01 mol l^{-1} H_2SO_4).[65] A constant flow (10–150 ml h^{-1}) of the solutions through the cell was maintained by a syringe pump. By changing the flow the residence time within the cavity is varied so that successive reaction products can separately be focused on.

g-Values were calculated relative to the Bruker® weak pitch sample ($g = 2.0028$). They are accurate to ± 0.0002 units. Second order effects are within this range of errors for the comparatively small coupling constants observed in our systems, and were neglected.

Doubly distilled water was used and the pH was adjusted with H_2SO_4 or KOH, using a Schott pH-meter (CG 817) calibrated with commercial buffer solutions. Before irradiation, solutions and sample cell were deoxygenated by bubbling with nitrogen. H_2O_2 (30% solution) was obtained from Merck, *p*-toluenesulfonic acid and 2,5-dihydroxybenzenesulfonic acid from Sigma-Aldrich in the purest available quality. *p*-ethylbenzenesulfonic acid was obtained from Aldrich, USA, and extracted with absolute alcohol before use.[66] *p*-Hydroxybenzenesulfonic acid was received as a 65% aqueous solution from Fluka. *p*-Methoxybenzenesulfonic acid was obtained by hydrolysing the corresponding sulfonylchloride in alkaline medium.[67] 1-Hydroxy-4-methoxybenzene-2-sulfonic acid as well as 3-hydroxytoluene-4- and 5-hydroxytoluene-2-sulfonic acid were synthesised by sulfonation with concentrated H_2SO_4.[68–70] The compounds were identified by ^1H and ^{13}C NMR spectroscopy.[71,72]

3 EPR results and specific discussion

3.1 *para*-Toluenesulfonic acid (TSA)

Three different radical species were observed with TSA, each of which predominated in a particular pH range [Fig. 1]. The distribution of relative signal intensities is shown in Fig. 2, and the EPR parameters are tabulated together with those of all the other systems in Table 2. The signal intensities of the benzyl radicals (**1** in Table 2) seem to adopt a maximum at about pH 0.1, diminish at intermediate pH and recover almost exponentially at pH ≥ 12.

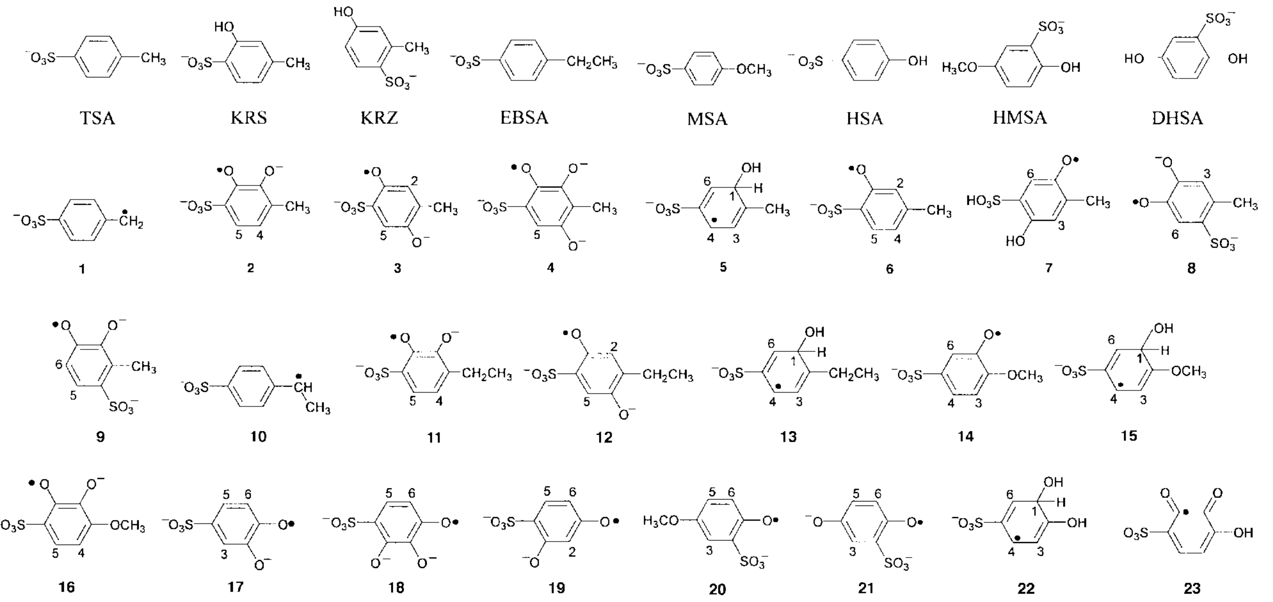
Between pH 1.5 and 11.0, HO• addition to the aromatic ring in *ortho* position to the methyl group forming the cyclohexadienyl adduct **5**[42,60] predominated [Fig. 1(b)]. Compared with previous studies[41,42] an additional splitting of 0.62 G was resolved. Similar splittings have been attributed to the hydroxy coupling in hydroxycyclohexadienyl radicals derived from other aromatic compounds.[64]

A third type of radical species with slightly elevated *g*-value and small hyperfine splittings was detected in the pH range 10.0–13.9 [Fig. 1(c)] with a signal intensity reaching a maximum at about pH 11.5. These species remained undetected in the previous EPR studies.[41,42] The EPR parameters show that the signals originate from three different phenoxyl radicals **2**–**4** with almost identical *g*-values. The signals of **4** are much weaker and detectable only at low flow rates of about 10 ml h^{-1}. The small quartet splittings for **2** and **3** point to phenoxyl radicals with a CH_3 group in the *meta* position. In the *ortho* and *para* positions they are expected to be 7.5 and 12.7 G.[64,71] Comparison of the number of doublets observed with the number of H atoms in the aromatic ring reveals that one coupling is missing for the radicals **2** and **3**, and two for radical **4**.

The lack of H couplings within aromatic rings suggests secondary reactions like further hydroxylation or dimerisation of the monophenoxyl radicals. Coupling of phenoxyl radicals forming either phenoxyl-, phenol- or biphenyl-like radicals has previously been described.[19,74–76] The formation of biphenyls however can be excluded in our systems, because of the absence of additional splittings from the hydrogen atoms in the attached ring.[64] We therefore focus on phenoxyphenol-like or higher hydroxylated systems. The formation of dimers in second order reactions is expected to depend pronouncedly on the concentration of the substrate, but reducing the TSA concentration by a factor of ten left the signals unchanged. An increase of the flow rate (up to 150 ml h^{-1}) did not appreciably change the distribution of the signals, except for the phenoxyl radical **4** which was only present under conditions of low flow. The formation of dioxysemiquinone-like radicals is the more probable reason for the lack of H couplings in **2** and **3**, since the hyperfine splittings agree fairly well with literature increments for CH_3 substituted *ortho*- or *para*-semiquinone-like radicals[64,71] (see section 3.2.).

An additional contribution to the formation of higher substituted products may be due to the increased absorption coefficient of H_2O_2 solutions in alkaline conditions (pH 0.2: $\varepsilon_{230} = 54$ l mol^{-1} cm^{-1} for H_2O_2, pH 12.6: $\varepsilon_{230} = 332$ l mol^{-1} cm^{-1} for HOO^-) with a concomitant higher radical yield. This is however not quantitatively reflected by the relative benzyl radical intensities, which at pH 13.8 are only about 1.5 times higher than at pH 0.2 (Fig. 2). However, benzyl radicals at pH > pK_a (HO•) = 11.9 are formed *via* direct H abstraction by $O^{\bullet -}$ radicals, and the rate constant for this process is only one sixth of the corresponding value for HO• addition at lower pH (Table 3).

Table 2 EPR parameters for intermediates in the reaction of HO• radicals with sulfonated aromatics. Hyperfine splittings were derived from computer simulations using WINSIM[73] and assigned by comparison with literature values of similar radical systems[41,42,60,64]



Substrate	Conditions	Hyperfine splittings/G	g	Proposed structure
TSA	pH < 1 pH > 12 (≥10 ml h^{-1})	2 H(CH$_2$): 16.03 (15.89)[41] 2 H(*o*): 5.10 (5.07)[41] 2 H(*m*): 1.77 (1.76)[41]	2.0027 (2.00265)[41]	**1**
	pH 10–13 (≥10 ml h^{-1})	1 H(4): 2.71 3 H(CH$_3$): 1.11 1 H(5): 4.50	2.0048	**2**
	pH 10–13 (≥10 ml h^{-1})	1 H(2): 3.15 3 H(CH$_3$): 1.20 1 H(5): 2.09	2.0049	**3**
	pH 10–13 (10 ml h^{-1})	3 H(CH$_3$): 2.59 1 H(5): 4.16	2.0049	**4**
	pH 2–10 (≥10 ml h^{-1})	1 H(1): 32.30 (32.5)[42] 1 H(OH): 0.62 3 H(CH$_3$): 9.60 (9.5)[42] 1 H(3): 2.78 (2.75)[42] 1 H(4): 12.90 (13.0)[42] 1 H(6): 8.50 (8.5)[42]	2.0027 (2.0025)[41]	**5**
KRS	pH 5 (≥10 ml h^{-1})	1 H(2): 6.62 3 H(CH$_3$): 1.94 1 H(4): 10.41 1 H(5): 1.52	2.0050	**6**
	pH > 13 (≥10 ml h^{-1})	1 H(4): 2.64 3 H(CH$_3$): 1.13 1 H(5): 4.57	2.0049	**2**
	pH > 13 (≥10 ml h^{-1})	1 H(2): 3.14 3 H(CH$_3$): 1.20 1 H(5): 2.05	2.0048	**3**
	7 < pH < 13.5 (≥10 ml h^{-1})	3 H(CH$_3$): 2.61 1 H(5): 4.18	2.0049	**4**
	pH 0.25 (10 ml h^{-1})	3 H(CH$_3$): 3.63 1 H(3): 0.51 1H(OH): 1.41 1H(6): 3.48	2.0046	**7**
KRZ	pH ≥ 7 (≥10 ml h^{-1})	1 H(3): 0.28 3 H(CH$_3$): 3.78 1 H(6): 1.58	2.0050	**8**
	pH ≥ 7 (≥10 ml h^{-1})	3 H(CH$_3$): 1.94 1 H(5): 3.76 1 H(6): 0.31	2.0049	**9**
EBSA	pH < 1 (≥10 ml h^{-1})	3 H(CH$_3$): 17.52 1 H(CH): 15.92 2 H(*o*): 4.91 2 H(*m*): 1.61	2.0029	**10**

Table 2 (*Continued*)

Substrate	Conditions	Hyperfine splittings/G	*g*	Proposed structure
	pH 10–12 ($\geqslant$10 ml h^{-1})	1 H(4): 2.65 2 H(CH_2): 1.14 1 H(5): 4.59	2.0048	**11**
	pH 10–12 ($\geqslant$10 ml h^{-1})	1 H(2): 3.16 2 H(CH_2): 1.20 1 H(5): 2.04	2.0047	**12**
	pH 6 ($\geqslant$70 ml h^{-1})	Assignment difficult, possibly formation of additional isomer		**13**
MSA	0$<$pH$<$6 ($\geqslant$10 ml h^{-1})	3 H(OCH_3): 1.82 1 H(3): 1.83 1 H(4): 8.04 1 H(6): 4.57	2.0048	**14**
	pH 3–6 ($\geqslant$50 ml h^{-1})	1 H(1): 26.16 1 H(OH): 0.47 3 H(OCH_3): 0.98 1 H(3): 2.37 1 H(4): 12.53 1 H(6): 8.59	2.0025	**15**
	pH 10–12 ($\geqslant$10 ml h^{-1})	3 H(OCH_3): 0.77 1 H(4): 1.13 1 H(5): 4.88	2.0050	**16**
	pH 10–13.5 (100 ml h^{-1})	1 H(3): 0.96 1 H(5): 3.09 1 H(6): 1.35	2.0050	**17**
	pH 10–13.5 (10 ml h^{-1})	1 H(5): 3.55 1 H(6): 1.87	2.0048	**18**
	pH 10–12 (70 ml h^{-1})	1 H(2): 0.36 1 H(5): 4.18 1 H(6): 8.99	2.0050	**19**
HMSA	pH 0–6 ($>$70 ml h^{-1})	1H(3): 0.28 1 H(OCH_3): 2.18 1 H(5): 0.69 1 H(6): 5.35	2.0050	**20**
	pH$\geqslant$5 (10–150 ml h^{-1})	1 H(3): 1.54 1 H(5): 2.64 1 H(6): 3.03	2.0050	**21**
DHSA	pH$\geqslant$5 (10–70 ml h^{-1})	1 H(3): 1.5 1 H(5): 2.65 1 H(6): 3.04	2.0050	**21**
HSA	pH 6 (130 ml h^{-1})	1H(1): 28.25 1H(OH): 0.55 1H(OH): 0.55 1H(3): 2.30 1H(4): 12.36 1H(6): 8.33	2.0031	**22**
	pH$>$10 (130 ml h^{-1})	1 H(3): 0.97 1 H(5): 3.10 1 H(6): 1.35	2.0050	**17**
	pH$>$10 (10 ml h^{-1})	1 H(5): 3.62 1 H(6): 1.92	2.0048	**18**
	pH$>$13 (10–150 ml h^{-1})	1 H(3): 1.58 1 H(5): 2.62 1 H(6): 3.08	2.0051	**21**?
	pH$<$1 (150 ml h^{-1})	1 H: 13.0 1 H: 8.8 1 H: 2.2	1.9924	**23**?

In fact several products of H_2O_2 decomposition (HO•, HO_2•, O_2•$^-$, O_2), some of them generated by mutual reactions of the primary species HO•/O•$^-$, participate in the formation of the phenoxyl radicals (see section 4.3). Nevertheless, as seen in Fig. 2, the total radical yield is not a strong function of pH, except below pH 2 where it drops off by a factor of two.

In addition to the signals originating from organic radicals a singlet with $g = 2.0033$ was observed in most of the spectra [see, for example, Fig. 1(a)], even in the absence of H_2O_2. It was identified in the reaction with the 5,5-dimethyl-1-pyrroline-*N* oxide (DMPO) spin trap as the SO_3•$^-$ radical,[36] originating from photolysis of TSA.[37,38] At elevated pH values it is no

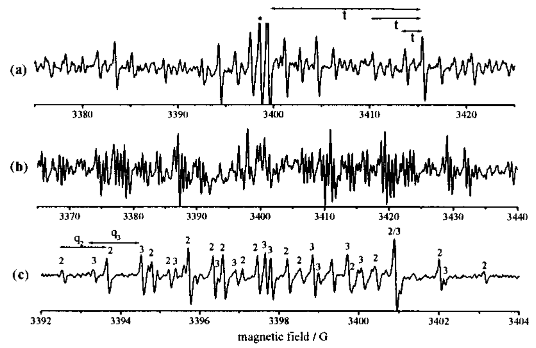


Fig. 1 The dependence of pH upon the EPR spectra obtained during TSA degradation by HO• radicals (q = quartet, t = triplet) (a) benzyl radical **1** and $SO_3•^-$ (*) at pH 0.4 (25 ml h^{-1}), (b) hydroxycyclohexadienyl radical **5** at pH 4.8 (90 ml h^{-1}) (c) phenoxyl radicals **2** and **3** at pH 11.5 (20 ml h^{-1}).

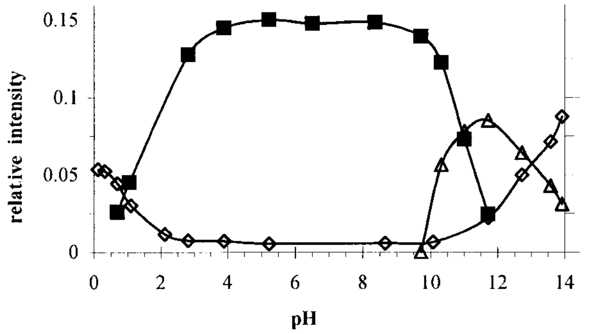


Fig. 2 The dependence of pH upon the normalised relative intensities of EPR signals obtained on TSA degradation by HO• at a flow rate of 125 ml h^{-1}: (◇) benzyl radical **1**, (■) hydroxycyclohexadienyl radical **5**, (△) phenoxyl radical (sum of radicals **2** and **3**).

Table 3 Rate constants for reactions of HO• radicals[10,20,41]

Reaction	Rate constant, $k/10^9$ dm^3 mol^{-1} s^{-1}
a: pH > 11.7: $HO• + HO_2^- \rightarrow H_2O + O_2•^-$	7.5
b: pH < 11.7: $HO• + H_2O_2 \rightarrow H_2O + HO_2•$	0.027
c: $HO• + O_2•^- \rightarrow HO^- + {}^1O_2$	8
d: $HO• + 4\text{-}CH_3C_6H_4SO_3^- \rightarrow 4\text{-}CH_3(OH)C_6H_4SO_3•^-$	6.1
e: $O•^- + 4\text{-}CH_3C_6H_4SO_3^-$ $\rightarrow 4\text{-}C•H_2C_6H_4SO_3^- + HO^-$	0.99
f: $HO• + HO• \rightarrow H_2O_2$	5.5
g: $O•^- + HO_2^- \rightarrow HO^- + O_2•^-$	0.4
h: $O_2•^- + O•^- + H_2O \rightarrow 2\ HO^- + {}^1O_2$	0.6

longer observed in accord with the increased absorption coefficient of H_2O_2 relative to TSA. The corresponding phenyl radical was not observed, its lifetime is too short so that the stationary concentration remains below the detection limit of *ca.* 10^{-9} mol l^{-1} of paramagnetic centres.[77] The formation of cresols by SO_3-substitution [33,35] was not detected, as coupling constants for the benzyl and hydroxy-cyclohexadienyl radicals agree well with those for the SO_3-substituted compounds,[41,42] whereas HO substitution should lead to slightly different values.[60,64]

In another experiment the molar ratio between H_2O_2 and TSA was varied between 0.03 and 33.2 with a fixed TSA concentration of 70 mmol l^{-1} at three characteristic pH values. At low H_2O_2 concentrations the intensities increase linearly, showing that HO• is the precursor of all of them (Fig. 3). For the benzyl radicals (pH 0.6) the relative signal intensities show a distinct maximum for about equimolar concentrations of H_2O_2 and TSA, whereas for the cyclohexadienyl radical (pH 4.8) a saturation behaviour is suggested when the molar ratio approaches 10. This reflects the high optical density where no light is available to cleave the additional H_2O_2 (pH 5 and also pH 0.6: TSA: $\varepsilon_{230} = 4865$ l mol^{-1} cm^{-1}, H_2O_2: $\varepsilon_{230} = 54$ l mol^{-1} cm^{-1}). Obviously, most of the light is absorbed by TSA, which then transfers the energy efficiently to H_2O_2. Alternatively, one would have to postulate photoionisation of TSA and subsequent reaction of the radical cation with H_2O_2. In the absence of H_2O_2 only the $SO_3•^-$ radical is observed. The occurrence of a maximum at equimolar concentrations in the case of the benzyl radical on the other hand may have to be attributed to further reactions with H_2O_2, leading to a drop in the steady state signal intensity (based on the bond strengths, abstraction of H from H_2O_2 by benzyl is thermoneutral, while it is endothermic by 65 kJ mol^{-1} for cyclohexadienyl radicals). For the phenoxyl radicals (pH 12.6) no measurements were possible above 0.14 mol l^{-1} H_2O_2 due to extensive gas evolution at these pH values (presumably singlet oxygen, see section 4).

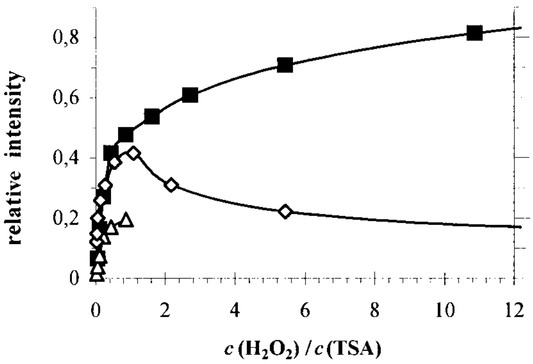


Fig. 3 The dependence of the molar ratio between H_2O_2 and TSA (at a fixed TSA concentration of 70 mmol l^{-1}) upon the normalised relative intensities ($1/2 \times \Delta H_{pp} \times$ signal height) of EPR signals for TSA degradation by HO• radicals at a flow rate of 100 ml h^{-1} (◇) benzyl radical **1** at pH 0.6, (■) hydroxycyclohexadienyl radical **5** at pH 4.8, (△) phenoxyl radical at pH 12.6 (initial pH value).

3.2 3-Hydroxytoluene-4-sulfonic acid (KRS) and 5-hydroxytoluene-2-sulfonic acid (KRZ)

KRS is a *p*-toluenesulfonic acid which already bears a hydroxy group *meta* to the CH_3 group. In reactions with H_2O_2 at pH 13.5, where HO• is no longer available for addition due to the predominance of $O•^-$ [pH > pK_a(HO•)] we obtained the phenoxyl radical EPR spectra for **2** and **3** which were also observed with TSA. This is clear evidence that additional oxy substitution can occur by mechanisms other than direct HO• addition to the ring. At elevated pH values this occurs possibly *via* the reaction of $O•^-$ with HO_2^- (see Discussion).

At pH 7–12 a species predominates which shows the same hyperfine splittings as the phenoxyl radical **4** from TSA, that was observed only at reduced flow rates. These signals probably originate from the corresponding 1,2,4-trioxy radical. When the pH is further decreased to about 5 a rather weak and poorly resolved spectrum with an additional splitting is obtained. It represents the phenoxyl radical **6**, obtained by H abstraction from KRS. At pH < 1 a weak spectrum was observed which we assign to the protonated *para*-semiquinone radical **7**.

From KRZ, a byproduct in the synthesis of KRS, a superposition of only two phenoxyl radicals was obtained in a wide range of pH > 7. They are attributed to the two *ortho*-semiquinone radicals **8** and **9**. Weak and poorly resolved spectra were obtained with both compounds at lower pH values. This is probably due to HO• addition to several positions of the aromatic ring, resulting in different cyclohexadienyl radicals and several successive products in relatively small yields.

3.3 *para*-Ethylbenzenesulfonic acid (EBSA)

With EBSA, radicals analogous to those observed with TSA were obtained in about the same pH ranges. At pH 0.3, the

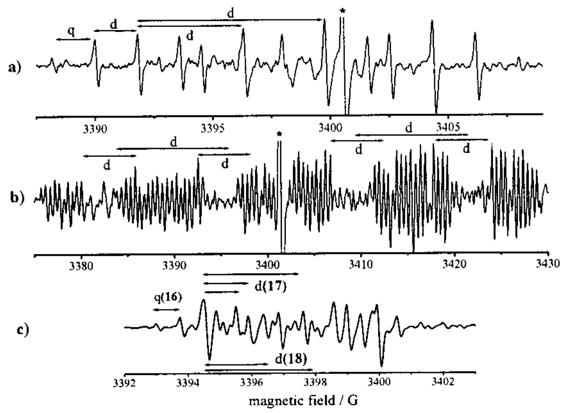


Fig. 4 The dependence of pH upon the EPR spectra obtained during MSA degradation by HO• radicals, $SO_3{}^{\bullet -}$ (*) (d = doublet, q = quartet), (a) phenoxyl radical **14** at pH 0.4 (110 ml h^{-1}), (b) hydroxycyclohexadienyl radical **15** at pH 4.8 (110 ml h^{-1}), (c) phenoxyl radicals at pH 11.5 (110 ml h^{-1}).

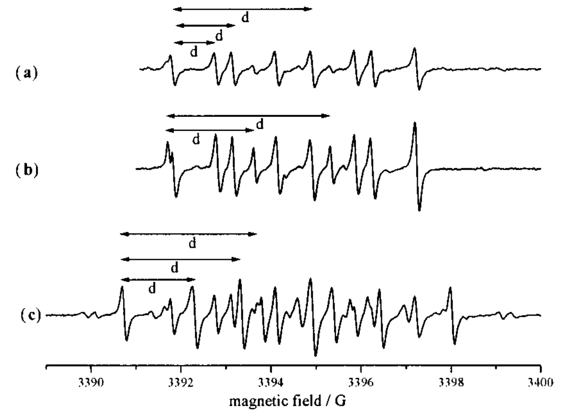


Fig. 5 The dependence of pH and flow rate upon the EPR spectra obtained during HSA degradation by HO• radicals (a) **17** at pH 11.5 (130 ml h^{-1}), (b) **18** at pH 11.5 (10 ml h^{-1}), (c) **21** at pH 13.5 (130 ml h^{-1}).

methyl substituted benzyl radical **10** was observed. At pH 11.2, again a superposition of two phenoxyl radicals was attributed to the CH_2CH_3 substituted *ortho-* or *para*-semiquinone radicals **11** and **12**. A rather complex EPR spectrum at pH 5.3 probably belongs to the hydroxycyclohexadienyl radical **13**. Owing to too many overlapping signals we were unable to further assign it. Similar problems were reported for the isopropyl substituted aromatic sulfonic acid.[41] The same holds for pH values above 13, where besides the signals from the phenoxyl radicals, a variety of additional EPR lines were detected, possibly based on a superposition of radicals due to H abstraction from the CH_3 and CH_2 groups or oxy adducts, respectively.

3.4 *para*-methoxybenzenesulfonic acid (MSA)

MSA shows a behaviour totally different from that of the other compounds at pH < 1. A phenoxyl radical **14** is obtained with a somewhat misleading quintet splitting because one of the H splittings on the aromatic ring has exactly the same value as the OCH_3 substituent. This is typical for *o*-OCH_3 substituted phenoxyl radicals,[64,71] and the splitings of 1.85 G are correct for the *ortho* species, whereas 0.6 and 2.0 G were reported for the *meta* and *para*-OCH_3 groups, respectively. The radical is still observed at reduced intensity at pH 5.3, but when the flow rate is increased to 100 ml h^{-1} it disappears, and the *o*-hydroxycyclohexadienyl radical **15** [Fig. 4(b)] is observed. In contrast to the reactions of *p*-methoxybenzoic acid with $O^{\bullet -}$ [51] and the reactions using photolysed di-*tert*-butyl peroxide as radical initiator[78] no H• abstractions from the methoxy group were observed in our investigation.

At pH 10–12 a superposition of several phenoxyl radicals was obtained. With a rather small signal, radical **16** was detected, which again lacks one H splitting compared with the phenoxyl radical **14** at lower pH values [Fig. 4(c)]. It is probably again due to additional hydroxylation. The splittings agree quite well with those of the corresponding OCH_3 substituted *ortho*-semiquinone.[64] In addition, intense spectra belonging to a variety of phenoxyl radicals **17–19** appear above about pH 10 [Fig. 4(c)] which do not show splittings due to the OCH_3 group anymore. Identical coupling constants resulted from HSA, indicating that the OCH_3 ether bridge is not stable at elevated pH values (see section 3.6 and discussion).[79–83]

3.5 1-Hydroxy-4-methoxybenzenesulfonic acid (HMSA) and 2,5-dihydroxybenzenesulfonic acid (DHSA)

Fission of the OCH_3 ether bridge is also observed with HMSA, where in the pH range 0–6 at flow rates $\geqslant 70$ ml the product **20** of direct H abstraction from the OH group still predominates, whereas at higher pH values the radical **21** without the OCH_3 substituent was obtained. DHSA lead to a radical with coupling constants identical to **21**. With these compounds, H (and CH_3!) loss from the oxygen substituent, can already be achieved by UV-illumination of the solutions in the absence of H_2O_2. This is in contrast to MSA, where fission of the OCH_3 ether bridge occurred only when H_2O_2 was present during photolysis. With HMSA and DHSA no hydroxycyclohexadienyl radicals and no higher hydroxylation products of the aromatic ring were found.

3.6 *para*-Hydroxybenzenesulfonic acid (HSA)

At pH 6 HSA showed signals of an *o*-hydroxycyclohexadienyl radical **22**. They appear only at elevated flow rates (130 ml h^{-1}) and are accompanied by the above mentioned phenoxyl radicals **17** and **18** from MSA, which predominate at low flow rates (section 3.4). At about pH 10 and flow rates of 130 ml h^{-1} the phenoxyl radical with splittings due to three different H atoms dominates [Fig. 5(a)], whereas at reduced flow the spectrum of another species with one splitting less becomes more clearly visible [Fig. 5(b)]. We attribute the first signals to the ortho oxy species **17**, which was also observed with MSA and which by longer exposure to HO• (lower flow rate) is further hydroxylated to the corresponding trioxy radical, which is again the same as **18** from MSA. A similar product distribution has been reported for *p*-hydroxybenzoic acid, where also *ortho* addition occurred.[82] Omura and Matsuura assigned the species with the three oxy groups to the 2,3,4 and the symmetric 3,4,5 isomers. The two different coupling constants in our case point to the asymmetric product, which we attribute to the 1,2,3 isomer **18**. These signals are also observed in smaller amount at pH values above 13, but here a third phenoxyl radical predominates, also consisting of splittings due to three H atoms [Fig. 5(c)]. This species has almost the same coupling constants as the radical **21** obtained by H abstraction from the dihydroxy compound DHSA and by OCH_3 substitution in HMSA, and the question is, how a phenoxyl radical species resulting from HSA can have the same hyperfine splittings. One explanation is that in all of the three molecules the SO_3 group has been replaced by an O group, but the resulting benzene with three oxy groups is reported to have different coupling constants (1H: 0.6 G, 1 H: 4.98 G, 1H: 1.34 G).[64] Another explanation is that the initially formed *ortho*-semiquinone radical rearranged into the more stable *para*-isomer, so that finally phenoxyl radicals identical to the ones from DHSA and HMSA result.

In contrast to an earlier investigation of HSA by Dixon and Murphy,[42] the phenoxyl radical resulting from direct H abstraction from the OH group (2 H: 7.25 G, 2 H: 2.1 G) was not detected. Dixon and Murphy used Ti^{3+}–H_2O_2 as the source of HO• radicals, and the question is, whether this system offers a sufficiently large number of free HO• radicals for addition, or whether a fraction of them remains complex-bound to Ti^{3+} and therefore prefers to react by H abstraction.[47,49]

At acidic pH values all hydroxylated compounds lead to rather poorly resolved EPR spectra with low line intensities. Besides the singlet attributed to $SO_3{•}^-$ they contain triplet splittings belonging to not further attributable oxy radicals ($g = 2.005$; 2.8 and 4.8 G) and some unassigned lines in the coupling range 0.6–1 G (see Discussion). Here again, HSA and DHSA lead to almost identical spectra. Sometimes the hydroxylated compounds known from the higher pH values are still detectable (HMSA), but with much lower resolution. With HSA at pronouncedly increased flow rates (up to 150 ml^{-1}) an additional species with a lower g-value of 1.9924 appears, possibly originating from an acyl type σ radical **23** due to rupture of the aromatic ring. The details of its structure are uncertain, the hyperfine splittings are somewhat large for the structure suggested in Table 2.

4 Discussion

4.1 Reasons for pH dependence

The pronounced pH dependence shown by the HO• radical in reactions with substituted aromatic hydrocarbons has been attributed to its deprotonation ($pK_a = 11.9$)[10] in alkaline conditions. The resulting $O{•}^-$ radical possesses only negligible tendency to add to the aromatic ring,[10,20] so that at pH values exceeding the pK_a of HO•, H• abstraction from the substituents leading to benzyl or phenoxyl radicals is expected to be the predominating process.

4.2 Formation of benzyl radicals

The appearance of benzyl radicals in acidic conditions was explained by an acid catalysed loss of water from hydroxycyclohexadienyl radicals, as given in Fig. 6 and previously suggested by others.[37,42,50] The higher extent of protonation of the hydroxycyclohexadienyl intermediates at decreasing pH leads to the almost linear increase of the intensity in the pH range 1.5–0.5 (Fig. 2) and to a saturation behaviour at pH <0.3, presuming that the formation of hydroxycyclohexadienyl adducts is independent of pH. A competing water elimination from the unprotonated adducts which has been suggested to also lead to benzyl radicals[49] was not observed here, the formation of benzyl radicals was almost negligible at higher pH values (see Fig. 2). H_2O elimination at acidic pH values can only arise from compounds with alkyl or hydroxy substituents with α-H atoms, like toluenes or phenols,[23,29,33,43,63,84] but it is not possible from β-H atoms or from the OCH_3 group in MSA.

Radical cations have also been reported as intermediates in the formation of benzyl radicals, when aromatics substituted by electron donating methyl, methoxy or amino groups are involved.[19,85–87] Even though not yet observed with TSA, possibly due to the electron withdrawing property of the SO_3H group,[41] they have to be considered as short-lived intermediates in our case as well.

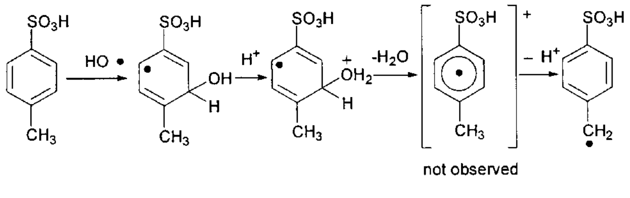


Fig. 6 Formation of benzyl radicals by acid catalysis from hydroxycyclohexadienyl radicals.[42,50]

4.3 Formation of polyoxy aromatics

Further hydroxylation by HO• is the most direct way to polyoxy aromatics,[63,84] and it is probably responsible for the formation of higher hydroxylated products at neutral and acidic pH values according to Fig. 7 (I). This mechanism requires the presence of O_2 in solution, it could thus be very relevant under actual fuel cell conditions. In the present work however, the solutions were O_2-free.

Owing to its electrophilic nature, the HO• radical shows preference for ring positions *ortho* or *para* to an activating substituent. According to Hammett's law,[88,89] the rate constant for HO• addition to an aromatic ring is about doubled when there is an OH substituent in *para* (*ortho*) position to the site of attack, whereas electron withdrawing substituents (SO_3^-) considerably reduce it. A number of representative rate constants are given in Table 4. The highest values approach the diffusion limit. The data show further that addition of HO• radicals to compounds which already bear hydroxy substituents is favoured.[82] A further increase occurs for the deprotonated forms of the phenols (pK_a 7–10).[89,90] This is probably the reason why with p-hydroxysulfonic acid (HSA) only higher substituted phenoxyl radicals are observed at alkaline pH values.

Oxygen has a strong tendency to add directly to cyclohexadienyl-like adducts, forming peroxy radical intermediates, which can lead to higher hydroxylated products as shown in Fig. 7, **I**[19,63,91] and finally to bond breaking reactions (Fig. 7, **II**).[23,29,33,43,92]

The phenoxyl radicals derived from TSA are, however, still observed at pH 13.9 where the formation of hydroxycyclohexadienyl adducts seems no longer possible due to the predominance of the $O{•}^-$ radicals (see Fig. 9), they can therefore be excluded as intermediates and other mechanisms which lead to additional oxygen substituents on the aromatic rings have

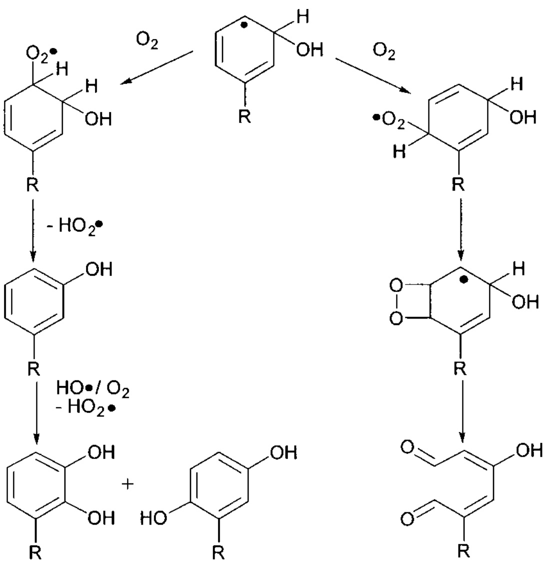


Fig. 7 Mechanism for consecutive reactions of hydroxycyclohexadienyl radicals with oxygen leading to different phenolic compounds and to bond breaking.[29,33,34,43,93]

Table 4 Rate constants for the *para* addition of OH• radicals to substituted benzenes[88]

Substituent	Rate constant, $k_{OH+Substrate}/10^9$ dm^3 mol^{-1} s^{-1}
H	3.3
SO_3^-	1.76
CH_3	3.0
OCH_3	3.6
OH	5.1

to be considered. The fact that the same polyoxy radicals were observed with unhydroxylated and with partly hydroxylated reactants (TSA, KRS) is a clear indication, that these species arise from successive reactions.

It is remarkable that the formation of phenoxyl radicals from TSA as shown in Fig. 2 occurs just in the pH range close to the pK_a of the HO• radicals ($pK_a=11.9$) and of H_2O_2 ($pK_a=11.7$). H• abstraction from the deprotonated form HO_2^- is about 300 times faster than from H_2O_2 (see Table 3, reactions a and b).[20] The resulting $O_2^{\bullet -}$ undergoes oxidation by HO• or $O^{\bullet -}$ (see Table 3, reactions c and h), so that oxygen is formed *in situ* in the reacting solutions.[10] This is supported by the evolution of gas observed in this pH range at elevated H_2O_2 concentrations. Gas still evolves when H_2O_2 is photolysed without the addition of a substrate molecule, showing that it does not originate from mineralisation of the organic substrate to SO_2 or CO_2 as mentioned elsewhere.[33,35,37,38,93]

Oxygen formed by this reaction is reported to be of singlet character.[22,93] This is obviously true, since $^3O_2$ would lead to extensive spin exchange and thus to the loss of hyperfine structure in the EPR spectra, in contrast to our observation [Fig. 1(c)].

Because the rate constants of the reactions contributing to the formation of oxygen and $O_2^{\bullet -}$ (see Table 3, reactions a and c) are of the same order of magnitude as the competing direct HO• addition and H• abstraction reactions (see Table 3, reactions d and e) the resulting concentration of $^1O_2$ reaches quite high values. $^1O_2$ is known to have a pronounced tendency to undergo direct [2+2] and [2+4] cycloadditions to organic double bonds.[94,95] Hydroxycyclohexadienyl radicals are not needed as precursors since $^1O_2$ can add directly to the aromatic ring, introducing oxygen substituents as shown in Fig. 8 (**I**). Investigations of lignin model compounds showed rapid breakdown of the molecules under alkaline conditions, which was attributed to singlet oxygen.[22] The ability of $^1O_2$ to add directly to aromatic rings may be the reason for the formation of phenoxyl radicals at pH values where hydroxycyclohexadienyl intermediates are no longer formed (*e.g.* TSA, KRS). The $O_2^{\bullet -}$ radical formed according to reactions a and g (Table 3) in contrast to its protonated form ($HO_2^{\bullet}$, $pK_a=4.8$) also shows tendencies to add directly to aromatic rings and hence must be considered as an intermediate to phenoxyl radical formation as shown in Fig. 8 (**II**).[30]

When the formation of $O_2^{\bullet -}$ comes about mainly by the reactions a and g (Table 3), its formation should strongly depend on the pH value. The same holds for the formation of $^1O_2$ according to reactions c and h (Table 3). The relative rates of formation for $O_2^{\bullet -}$ and $^1O_2$, given by the products of the rate constants and the pH dependent relative concentrations of the reactants show maxima for $O_2^{\bullet -}$ at pH 11.9 and for $^1O_2$ at 11.6 (Fig. 9). These species thus predominate in the same pH range where the phenoxyl radicals occur in Fig. 2. The curve for $O_2^{\bullet -}$ even reproduces the asymmetric shape of the phenoxyl radical intensity distribution. The asymmetry is due to the growing importance of reaction g since the concentrations of both reactants increase with pH, whereas reaction a is responsible for the maximum since the opposite pH dependence of the two reactant concentrations gives a significant contribution only at an intermediate pH of about 11.7. This correlation suggests that reactions between TSA (or the other compounds at pH > pK_a of HO•) and $O_2^{\bullet -}$ or $^1O_2$ are the most probable ways to the phenoxyl radicals observed in this pH range.

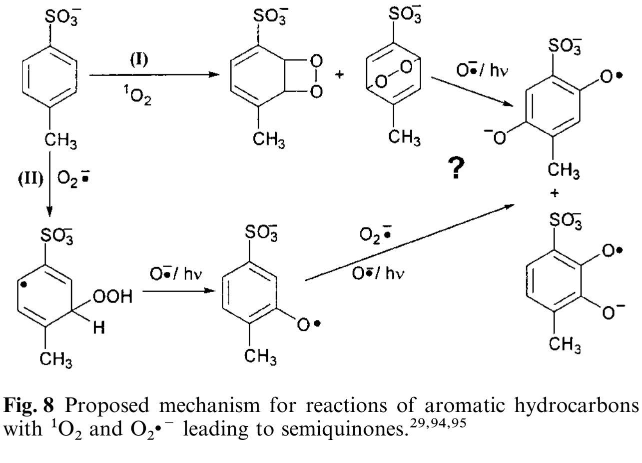


Fig. 8 Proposed mechanism for reactions of aromatic hydrocarbons with $^1O_2$ and $O_2^{\bullet -}$ leading to semiquinones.[29,94,95]

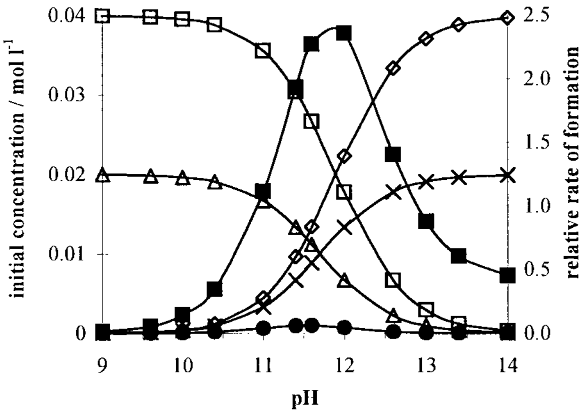


Fig. 9 Simulation of the relative rates of formation of the superoxide radical anion (■) $O_2^{\bullet -}$ and singlet oxygen (●) $^1O_2$ according to the rate constants (Table 3) dependence upon pH (assumed concentrations after photolysis: HO•: 40 mmol l^{-1}, H_2O_2: 20 mmol l^{-1}). (◇) $c(O^{\bullet -})$, (□) $c(HO^{\bullet})$, (△) $c(H_2O_2)$, (×) $c(HO_2^-)$. Open symbols relate to the scale on the left, filled symbols to the scale on the right.

4.4 OCH_3 ether bridge fission

Formal *ipso* substitutions of the OCH_3 groups in different substituted methoxy compounds by HO• radicals as observed with MSA are well known.[79,81,82,83] As a mechanism leading to the phenoxy radicals, acid catalysed[79,80] or spontaneous [79,81,82] elimination of methanol from the *ipso* hydroxycyclohexadienyl adducts was identified. With activating hydroxy substituents in the *ortho* or *para* positions to OCH_3 the yield of methanol was 4–5 times larger than for the *meta* substituted isomers.[81] The same mechanism was proposed for phenoxy phenols like thyronines, where the rupture of the diphenyl ether link occurred at higher HO• concentrations.[82] In the present work with MSA, *ipso* substitution occurred only at pH values above 10. This is in accord with the expected deactivation of MSA by the SO_3 group, so that *ipso* substitution is obviously not possible until activating oxy substituents are present in the molecule. The fact that CH_3 photoelimination from HMSA occurs even in the absence of H_2O_2 is probably due to the stability of the resulting *para*-semiquinone radical, the formation of which is favoured. With DHSA the *para*-semiquinone radical is also formed by photolysis. This is reported to occur by a homolytic cleavage of the O–H bond under basic conditions, or by an electron ejection from the phenolate ions.[76,90]

4.5 Semiquinone spectra at low pH values

In contrast to the well resolved benzyl radical spectra obtained with TSA or EBSA, or of the phenoxyl radical from MSA at acidic pH values, HSA and DHSA lead to poorly resolved EPR spectra. The two compounds give the same EPR spectra, which can only be explained when $SO_3^{\bullet -}$ elimination or substitution has taken place to a high extent, so that the identical dihydroxylated aromatics result. Loss of resolution in acidic pH ranges was ascribed to the partial protonation of the oxy groups and to a growing tendency to exchange protons between them.[96] Only at pronouncedly higher acid concentrations (1.8 mol l^{-1} H_2SO_4) is resolution reported to increase again when both of the oxy groups are protonated. We found a spectrum with a lower g value at $\mathrm{pH} < 1$, which possibly belongs to a σ radical, originating from bond breaking of the aromatic ring in HSA. The fact that this oxidation product is only seen at high flow rates may be explained by the shorter lifetime of this species compared with the radicals which still contain aromatic rings.

5 Relevance for fuel cell membranes

The present work investigates model compounds of building blocks of ion exchange membranes under conditions which are not in every respect those in fuel cells. The photolysing light absorbed by the sulfonic acid leads to the $\mathrm{SO_3}^{\bullet -}$ radical as a direct photochemical side product, which is still observed although not normally prominent in presence of $\mathrm{H_2O_2}$. However, the hyperfine splittings for the benzyl and cyclohexadienyl radicals from TSA agree very well with the literature values for the $\mathrm{SO_3}$ substituted radicals,[41,42] indicating that no $\mathrm{SO_3}$ exchange by HO• occurred.

It is a general belief that $\mathrm{HO_2}$• and HO• are responsible for the degradation process.[3,5,9] This is based on the observation of $\mathrm{H_2O_2}$ as a product of the cell reaction and on the well known degeneration processes of polymers in general,[23,29,33,43,92] thus it is a plausible assumption for which there are no proofs yet. The present study focuses on the case that HO• is the damaging species below pH 11.7. $\mathrm{HO_2}$• is formed as well *via* the reaction of HO• with $\mathrm{H_2O_2}$ (see Table 3, reaction b), but under the conditions of this work the conversion is at the 1% level, and the dominating reaction of HO• is that with the aromatic ring. No oxidation due to $\mathrm{H_2O_2}$ was observed in the absence of photolysing light.

With an ion exchange capacity of the order of 1 mequiv. g^{-1} the pH of a water swollen membrane is of the order of zero, but considerable local gradients across the membrane and near the catalyst particles are expected when the cell is operated.

It is clear from the present study that the dominating reaction is the addition of HO• to the aromatic rings, preferentially in the *ortho* position to alkyl- and RO-substituents (since in sulfonated PS, PSU, PEK and ETFE or FEP-g-PSA the *para* position is substituted and thus blocked). It demonstrates the combined *ortho* activation by these substituents and the *meta* directing effect of the $\mathrm{SO_3}^-$ group in electrophilic addition reactions.

A crucial point is the acid catalysed water elimination from hydroxycyclohexadienyl adducts according to Fig. 6. This process requires the presence of labile benzylic α-H atoms, thus it is not relevant for PSU or PEK type membranes but important in the case of ETFE or FEP-g-PSA. In an endothermic process this can lead to chain scission ('reverse polymerisation') and thus to loss of PSA groups. Assink *et al.*[39] found much higher stability for the sulfonated *tert*-butylbenzenesulfonic acid with no benzylic α-H atom than for the sulfonated isopropylbenzene with one α-H atom left. They also reported that styrene grafted membranes are much more susceptible to weight loss than the membranes grafted with α-methylstyrene, when they are exposed to oxidising solutions. The lack of α-H atoms certainly contributes to the much better long term behaviour of the RAYMION® or the BAM3G membrane, with F in the benzylic position as compared to PERMION 4010®, with the labile benzylic H.[2,3] When water was eliminated from cyclohexadienyl radicals in poly(styrenesulfonate), radical cation intermediates could be identified by UV–VIS and by EPR under acidic conditions.[40] They could also act as centres of degradation reactions in all of the newly developed polymers.

Another crucial point is the loss of $\mathrm{OCH_3}$ from the methoxy substituted compound MSA, probably initiated by *ipso* attack of HO•. This mechanism is of relevance for the polymers with phenoxybenzene ether bridges like PSU or PEK, possibly leading to bond breaking within the C–O–C connections (see Fig. 10). Fortunately, the resulting phenoxyl radical was not observed at $\mathrm{pH} < 5$ so that strand breaks of PSU and of PEK may be avoided as long as the local pH is sufficiently low. Fig. 10 surveys positions of highest sensitivity to HO• radical attack.

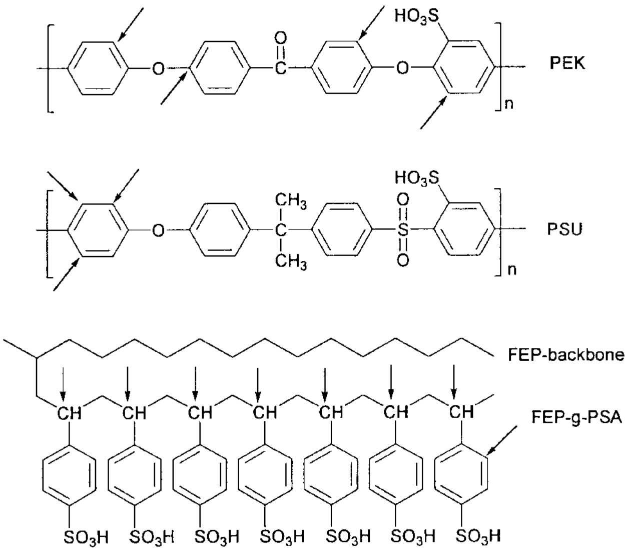


Fig. 10 Possible sites for HO• radical attack on various polymers used for proton conducting membranes in fuel cells.

It is essential for the EPR technique to work that the samples are deoxygenated. $^3\mathrm{O}_2$ reacts with free radicals by spin exchange, but in particular it adds and thus forms peroxy radicals which, owing to their broad lines are less characteristic and more difficult to see. Under fuel cell operating conditions there is plenty of $^3\mathrm{O}_2$ present, at least near the cathode, but $^1\mathrm{O}_2$ is not expected to form. We expect that $^3\mathrm{O}_2$ reacts with cyclohexadienyl radicals forming peroxy radicals, which finally lead to bond breaking within the aromatic rings (see Fig. 7).[29] In the presence of both HO• radicals and oxygen, complete degradation of the aromatic rings can be achieved within a few hours.[23,29] In view of this, the saturated and perfluorinated NAFION® which is much more inert has an inherent advantage over the new membranes based on aromatic hydrocarbons.

Since oxygen is obviously important for the degradation of a membrane, one strategy is to prevent its diffusion into the membrane (and across it to the other side, since for still mysterious reasons the degradation seems to be more severe at the anode side). This may be achieved by optimised cross linking of the membrane, or by surface coverage with a suitable barrier layer. Another strategy should attempt to suppress the formation of these radicals or make them stick better to the catalyst, but at this point it is unclear under which running conditions they are formed in fuel cells since an *in situ* detection technique is not yet available.

As a short term step to improve the stability of the aromatic hydrocarbon based polymers we suggest to consider a blocking of the aromatic ring by suitable substitution, so that HO• addition is more limited, moreover, alkyl substituents with α-H atoms, enabling the formation of benzyl radicals, should be avoided as much as possible, if this can be done economically and without badly influencing the other properties of the membrane too much. $\mathrm{SO_3}^-$ substituents are introduced to give rise to proton conductivity, but as an additional benefit they reduce the activity of the aromatic ring towards hydroxyl radical addition.

Acknowledgments

We are grateful for encouragement by and useful discussions with Prof. G. Eigenberger and Drs. J. Kerres, G. Scherer and H.-P. Brack, and we thank Dr. P. Fischer for NMR reactant analysis.

References

1 O. Savadogo and P. R. Roberge, in *Proceedings of the second international symposium on new materials for fuel cell and modern battery systems*, ed. O. Savadogo and P. R. Roberge, *Montréal*, 1997.
2 G. G. Scherer, *Ber. Bunsenges. Phys. Chem.*, 1990, **94**, 1008.
3 H. Wang and G. A. Capuano, *J. Electrochem. Soc.*, 1998, **145**, 780.
4 A. E. Steck and C. Stone, in *Proceedings of the second international symposium on new materials for fuel cell and modern battery systems*, ed. O. Savadogo and P. R. Roberge, Montréal, Québec, Canada, 1997, 792.
5 F. N. Büchi, B. Gupta, O. Haas and G. G. Scherer, *Electrochim. Acta*, 1995, **40**, 345.
6 J. Kerres, G. Eigenberger and W. Schnurnberger, *Euromembrane '95, proceedings*, 1995, vol. I, p. 284.
7 J. Kerres, W. Cui and S. Reichle, *J. Polym. Science, Chem. Ed.*, 1996, **34**, 2421.
8 S. G. Ehrenberg, J. M. Serpico, B. M. Sheikh-Ali, T. N. Tangredi, E. Zador and G. E. Wnek, in *Proceedings of the second international symposium on new materials for fuel cell and modern battery systems*, ed. O. Savadogo and P.R. Roberge, *Montréal*, 1997, p. 828.
9 R. Hodgdon, J. R. Boyack and A. B. LaConti, Advance Development and Laboratory Technical Report, No. 65DE5, General Electric Co., West Lynn, MA, 1966.
10 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513.
11 R. Sapach and T. Viraraghavan, *J. Environ. Sci. Health*, 1997, **A32**, 2355.
12 R. W. Matthews, *Pure Appl. Chem.*, 1992, **64**, 1285.
13 F. J. Beltrán, G. Ovejero and B. Acedo, *Water Res.*, 1993, **27**, 1013.
14 R. Apak and M. Hugül, *Chem. Tech. Biotechnol.*, 1996, **67**, 221.
15 I. N. Martyanow, E. N. Savinov and V. N. Parmon, *J. Photochem. Photobiol. A: Chem.*, 1997, **107**, 227.
16 R. Bauer and H. Fallmann, *Res. Chem. Intermed.*, 1997, **23**, 341.
17 F. J. Beltrán, M. González and J. F. González, *Water Res.*, 1997, **31**, 2405.
18 M. Nahen, D. Bahnemann, R. Dillert and G. Fels, *J. Photochem. Photobiol. A: Chem.*, 1997, **110**, 191.
19 J. Gierer, E. Yang and T. Reitberger, *Holzforschung*, 1992, **46**, 495.
20 J. Gierer and K. Jansbo, *J. Wood Chem. Technol.*, 1993, **13**, 561.
21 D. Lachenal, N. B. Nguyen Thi, C. Chirat and L. Soria, *Pap. Timber*, 1997, **79**, 252.
22 R. Ruggiero, A. E. H. Machado, A. Castellan and S. Grelier, *J. Photochem. Photobiol. A: Chem.*, 1997, **110**, 91.
23 N. A. Weir, *Eur. Polym. J.*, 1978, **14**, 9.
24 H. Nishide, M. D. Cho, T. Kaku and Y. Okamoto, *Macromolecules*, 1993, **26**, 2377.
25 L. A. Lindén, J. F. Rabek, H. Kaczmarek, A. Kaminska and M. Scoponi, *Coord. Chem. Rev.*, 1993, **125**, 195.
26 H. Niino and A. Yabe, *J. Photopolym. Sci. Technol.*, 1994, **7**, 369.
27 P. Ulanski, E. Bothe, K. Hildenbrand, J. M. Rosiak and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 1996, 13.
28 H. Kaczmarek, *Polym. Bull.*, 1995, **34**, 211.
29 H. Kaczmarek, L. A. Lindén and J. F. Rabek, *Polym. Degrad. Stab.*, 1995, **47**, 175.
30 C. von Sonntag and H.-P. Schuchmann, *Angew. Chem.*, 1991, **103**, 1255.
31 H. Hidaka, H. Kubota, M. Grätzel and N. Serpone, *Nouv. J. Chim.*, 1985, **9**, 67.
32 J. Bandara, C. Pulgarin, P. Peringer and J. Kiwi, *J. Photochem. Photobiol. A: Chem.*, 1997, **111**, 253.
33 B. Sangchakr, T. Hisanaga and K. Tanaka, *J. Photochem. Photobiol. A: Chem.*, 1995, **85**, 187.
34 V. Brezová, A. Stasko, S. Biskupic, A. Blazkova and B. Havlinová, *J. Phys. Chem.*, 1994, **98**, 8977.
35 V. Brezová, M. Jankovicová, M. Soldán, A. Blazkóva, M. Reháková, I. Surina, M. Ceppan and B. Havlinová, *J. Photochem. Photobiol. A: Chem.*, 1994, **83**, 69.
36 V. Brezová, A. Stasko and S. Biskupic, *J. Photochem. Photobiol. A: Chem.*, 1993, **71**, 229.
37 M. Nakamura and Y. Ogata, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2396.
38 Y. Ogata, K. Takagi and S. Yamada, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2205.
39 R. A. Assink, C. Arnold, Jr. and R. P. Hollandsworth, *J. Membr. Sci.*, 1991, **56**, 143.
40 D. Behar and J. Rabani, *J. Phys. Chem.*, 1988, **92**, 5288.
41 D. Behar, *J. Phys. Chem.*, 1991, **95**, 4342.
42 W. T. Dixon and D. Murphy, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1630.
43 S. Luňák and P. Sedlak, *J. Photochem. Photobiol. A: Chem.*, 1992, **68**, 1.
44 N. Jacob, I. Balakrishnan and M. P. Reddy, *J. Phys. Chem.*, 1977, **81**, 17.
45 E. Lipczynska-Kochany, *Chem. Oxid.*, 1994, **3**, 12.
46 E. J. Wolfrum and D. F. Ollis, *Aqu. Surf. Photochem.*, 1994, **2**, 451.
47 S. Croft, B. C. Gilbert, J. R. L. Smith and A. C. Whitwood, *Free Rad. Res. Commun.*, 1992, **17**, 21.
48 C. Walling, *Acc. Chem. Res.*, 1975, **8**, 125.
49 T. Shiga, *J. Phys. Chem.*, 1965, **69**, 3805.
50 K. Sehested, H. Corfitzen, H. C. Christensen and E. J. Hart, *J. Phys. Chem.*, 1975, **79**, 310.
51 P. Neta, M. Z. Hoffman and M. Simic, *J. Phys. Chem.*, 1972, **76**, 847.
52 K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 1186.
53 K. Makino, M. M. Mossoba and P. Riesz, *J. Phys. Chem.*, 1983, **87**, 1369.
54 A. Mills and S. Le Hunte, *J. Photochem. Photobiol. A: Chem.*, 1997, **108**, 1.
55 M. A. Fox and M. T. Dulay, *Chem. Rev.*, 1993, **93**, 341.
56 J. L. Ferry and M. A. Fox, *J. Phys. Chem. A*, 1998, **102**, 3705.
57 T. Shiga, T. Kishimoto and E. Tomita, *J. Phys. Chem.*, 1973, **77**, 330.
58 C. R. E. Jefcoate and R. O. C. Norman, *J. Chem. Soc. B*, 1968, 48.
59 W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4857.
60 P. Neta and R. H. Schuler, *J. Phys. Chem.*, 1973, **77**, 1368.
61 R. A. Jackson and M. Sharifi, *J. Chem. Soc., Perkin Trans. 2*, 1996, 775.
62 B. C. Gilbert, P. Hanson, W. J. Isham and A. C. Whitwood, *J. Chem. Soc., Perkin Trans. 2*, 1988, 2077.
63 P. Neta and W. Fessenden, *J. Phys. Chem.*, 1974, **78**, 523.
64 *Landolt–Börnstein, New Ser. II*, ed. K.-H. Hellwege and O. Madelung, Springer Verlag, Berlin, **9b** 66ff., 472ff., 550ff. (1977), **17e** 34ff (1988), **9d**$_2$ 113 (1980).
65 M. Kasha, *J. Opt. Soc. Am.*, 1948, **38**, 929.
66 A. Borthakur and V. S. B. Rao, *Org. Mass. Spectrom.*, 1984, **19**, 48.
67 M. R. Forbes and H. Maskill, *J. Chem. Soc., Chem. Commun.*, 1991, **13**, 854.
68 J. B. Pridham and M. J. Saltmarsh, *Biochem. J.*, 1963, **87**, 218.
69 W. Baker and C. Evans, *J. Chem. Soc.*, 1938, 372.
70 D. F. Evans and N. Iki, *J. Chem. Soc., Dalton Trans.*, 1990, 3773.
71 G. Strandlund and P. O. Lagerström, *Acta Chem. Scand., Ser. B*, 1979, **33**, 261.
72 H. Cerfontain, N. J. Coenjaarts and A. Koeberg-Telder, *Recl. Trav. Chim. Pays-Bas*, 1989, **108**, 7.
73 NIEHS, National Inst. of Environmental Health Science, USA.
74 K. Nakagawa, S. Tero-Kubota, Y. Ikegami and N. Tsuchihashi, *J. Photochem. Photobiol. A: Chem.*, 1994, **60**, 199.
75 M. Ye and H. Schuler, *J. Phys. Chem.*, 1989, **93**, 1898.
76 H.-I. Joschek and S. I. Miller, *J. Am. Chem. Soc.*, 1973, **88**, 3273.
77 J. A. Weil, J. R. Bolton and J. E. Wertz, *Electron Paramagnetic Resonance*, John Wiley & Sons, New York, 1994.
78 A. Hudson and K. D. J. Root, *J. Chem. Soc. B*, 1970, 656.
79 A. Valavanidis and B. C. Gilbert, *Chim. Chron., New Ser.*, 1995, **24**, 217.
80 C. von Sonntag and H.-P. Schuchmann, in *The chemistry of ethers, crown ethers, hydroxyl groups and their sulphur analogues, Part 2*, ed. S. Patai, John Wiley & Sons, Chichester, 1980, p. 956.
81 S. Steenken and P. O'Neill, *J. Phys. Chem.*, 1977, **81**, 505.
82 K. Omura and T. Matsuura, *Tetrahedron*, 1975, **24**, 3475.
83 T. Matsuura, T. Nagamachi and A. Nishinaga, *J. Org. Chem.*, 1977, **36**, 2016.
84 K. Lang, J. Brodilová and S. Lunák, *Collect. Czech. Chem. Commun.*, 1996, **61**, 1729.
85 K. Sehested and J. Holcman, *J. Phys. Chem.*, 1978, **82**, 651.
86 P. O'Neill, S. Steenken and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1975, **79**, 2773.
87 D. Behar and B. Behar, *J. Phys. Chem.*, 1991, **95**, 7552.
88 M. Anbar, D. Meyerstein and P. Neta, *J. Phys. Chem.*, 1966, **70**, 2660.
89 S. Steenken, *J. Chem. Soc., Faraday Trans.*, 1987, **83**, 113.
90 H. D. Becker, in *The chemistry of the hydroxyl group*, ed. S. Patai; Interscience Publishers, London, 1971, p. 894.
91 C. R. E. Jefcoate, J. R. Lindsay Smith and R. O. C. Norman, *J. Chem. Soc. B*, 1969, 1013.
92 K. Okamoto, Y. Yamamoto, H. Tanaka and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2015.
93 A. E. da Hora Machado, R. Ruggiero and M. G. Neumann, *J. Photochem. Photobiol. A: Chem.*, 1994, **81**, 107.
94 I. Saito, S. Kato and T. Matsuura, *Tetrahedron Lett.*, 1970, **3**, 239.
95 D. R. Kearns, *Chem. Rev.*, 1971, **71**, 395.
96 I. C. P. Smith and A. Carrington, *Mol. Phys.*, 1974, **12**, 439.

Paper 8/07129B