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# Degradation of sodium 4-dodecylbenzenesulphonate photoinduced by Fe(III) in aqueous solution

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# Abstract

The Fe(III)-photoinduced degradation of 4-dodecylbenzenesulphonate (DBS) in aqueous solution was investigated. The mixing of DBS (1 mm) and Fe(III) (1 mm) solutions immediately led to the formation of a precipitate that contained DBS and monomeric Fe(OH)<sup>2+</sup>, the predominant Fe(III) species. Both species were also present in the supernatant. Irradiation of the supernatant solution resulted in a photoredox process that yielded Fe(II) and •OH radicals. The disappearance of DBS was shown to involve only attack by •OH radicals; the quantum yield of DBS disappearance is similar to the quantum yield of •OH radical formation. A wavelength effect was also observed; the rate of DBS disappearance was higher for shorter wavelength irradiation. Five photoproducts, all containing the benzene sulphonate group, were identified. •OH radicals preferentially abstract hydrogen from the carbon in the  $\alpha$  position of the aromatic ring. The results show that the Fe(III)-photoinduced degradation of DBS could be used as an alternative method for polluted water treatment. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photodegradation; Dodecylbenzenesulphonate; Iron(III); Solar light

# 1. Introduction

Environmental contamination by toxic or carcinogenic chemicals is a serious global problem. The surfactants that are widely employed in domestic and industrial fields constitute one of the main families of pollutants in surface and ground water (Faust, 1975); they can cause a severe ecological problem due to their very slow and inefficient biodegradation (Swisher and Pollut, 1963; Larson and Payne, 1981; Larson and Perry, 1981; Larson et al., 1983. Several days or even weeks are required for the complete biodecomposition of surfactants, which often leads to the formation of more persistent and even more toxic metabolites. Over the last few years, Hidaka et al. (1992, 1994) and Zhao et al. (1992) extensively reported on the rapid photodegradation ( $\lambda \ge 330$  nm) of several kinds of anionic, cationic and non-ionic surfactants catalysed by TiO<sub>2</sub> semiconductors in aqueous aerated suspensions; for aromatic surfactants, the aromatic ring was decomposed more rapidly than was the alkyl chain. The mechanism involved the attack of the surfactants by •OH radicals followed by further degradation to CO<sub>2</sub> (g) and SO<sub>4</sub><sup>2-</sup> ions.

Linear alkylbenzene sulphonate (LAS) is one of the most important technical surfactant in world-wide usage (Berth and Jeschke, 1989), the estimated consumption of LAS was about 1.8 million metric tons. Among the LAS-type surfactants used in household detergents, 4-dodecylbenzenesulphonate (DBS) is the most representative.

In our investigation, the photochemical behaviour of DBS in the presence of Fe(III) was studied. DBS does

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not absorb solar light, but its transformation can be photoinduced by Fe(III). With Fe(III), two main types of photoreaction can be observed depending on the nature of the pollutant: If the pollutant is a complexing agent, such as nitrilotriacetic acid (NTA) (Stolzberg and Hume, 1975; Andrianirinaharivelo et al., 1993), ethylenediaminetetraacetic acid (EDTA) (Carey and Langford, 1973; Svenson et al., 1989; Kari et al., 1995) or ethylenediaminetetra-(methylenephosphonic acid) (ED-TMP) (Matthijs et al., 1989), a complex between the pollutant and Fe(III) is formed, which absorbs light into the visible spectral region; an intramolecular photoredox process is generally observed that leads to the degradation of the pollutant. On the other hand, if Fe(III) is not complexed by the pollutant, it can absorb the solar light and undergo a photoredox process giving rise to Fe(II) and •OH radicals (Baxendale and Magee, 1955; Dainton and Tordoff, 1957). The pollutant is then attacked by •OH radicals, which is a very strong oxidising agent. We also examined the photochemical degradation of the 4ethylbenzenesulphonic acid (EBS)  $c_2H_5 \rightarrow SO_3^{\circ}$ , a model compound of DBS, in the presence of Fe(III).

#### 2. Experimental

#### 2.1. Reagents and solutions

Technical grade 4-dodecylbenzenesulphonic acid sodium salt (DBS) (Aldrich) was used without further purification. This commercial product is generally a mixture of various alkyl homologs (C10-C14) and phenyl position isomers (2-CnLAS, 3-CnLAS,...) with an average carbon chain length of approximately n = 12.4-acetyl-benzenesulphonic acid sodium salt (1) (98%), 4-hydroxybenzenesulphonic acid sodium salt dihydrate (3) (98%) and 4-sulphobenzoic acid potassium salt (5) (95%) (Aldrich) and p-EBS acid sodium salt (TCI Extra Pure) were used without further purification. Ferric perchlorate nonahydrate (Fe(ClO<sub>4</sub>)<sub>3</sub>, 9H<sub>2</sub>O) (Fluka > 97%) was stored in a dessicator.

All solutions were prepared from deionised ultrapure water ( $\rho = 18.2 \text{ M}\Omega$  cm). When necessary, the solutions were deaerated by bubbling with Ar for 30 min at room temperature. The pH was adjusted with NaOH and measured with an ORION pH meter to  $\pm 0.02$  pH units; pH = 3.0 for a solution of [Fe(III)] = 0.3 mm. The ionic strength of the solution was not controlled. Fe(III) solutions were prepared by diluting stock solutions (2 mM Fe(ClO<sub>4</sub>)<sub>3</sub>) to the appropriate concentration.

#### 2.2. Apparatus and procedures

Monochromatic irradiations at 296, 313 and 365 nm were carried out with a high-pressure Hg lamp (Osram HBO 200 W) and a grating monochromator (Bausch and Lomb). The beam was parallel, and the reactor was a cylindrical quartz cell (2 cm path length). The photon flux was measured by ferrioxalate actinometry (Calvert and Pitts, 1966).

A high-pressure Hg lamp (Philips HPW 125 W), giving an emission at 365 nm was located at a focal axis of an elliptical stainless steel cylinder used for kinetic and preparative experiments. The reactor, a water-jacketed Pyrex tube (d = 2.8 cm) was centred at the other focal axis. The reaction medium was well stirred. The unit provided illumination ( $I_0 \approx 4.0 \times 10^{15}$  photons s<sup>-1</sup> cm<sup>-2</sup>) of a large volume (40 ml) of solution.

UV-visible spectra were recorded with a CARY 3 double beam spectrophotometer. EPR spectra were obtained with a BRUKER ER-200D spectrometer at 9.30 GHz with a modulation field of 100 KHz. A Xe–Hg Hanovia lamp was used for irradiation in the EPR spectrometer cavity ( $\lambda \ge 305$  nm).

HPLC chromatograms were carried out with a WATERS 540 system equipped with a diode array UVvisible detector (WATERS 990) and a 25-cm Lichrosphere RP18 Merck column (reverse phase). The eluent, at a flow rate of 1 ml min<sup>-1</sup>, was a mixture of deionised water (with 1% H<sub>3</sub>PO<sub>4</sub>) and methanol, the composition of which depended on the product investigated; convenient compositions were 1.5:1 (v/v) for the characterisation of DBS and 9:1 (v/v) for the characterisation of the photoproducts. The kinetics of DBS disappearance was evaluated from the integrated areas of the peaks of the homologs.

The photoproducts were separated by preparative HPLC ("Fast" procedure, Gilson Co.) on a C-18 reverse phase column ( $21.4 \times 50$  mm), using successively, water  $+1\%_{o}$  of H<sub>3</sub>PO<sub>4</sub> and pure water as eluents. Negative electrospray mass spectra (ESMS) were obtained from "Service Central d'analyse", CNRS, Vernaison, France. Infrared spectra were recorded on a Nicolet 20 SX FTIR spectrometer (KBr pellets). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC 400 MHz Fourier transform spectrometer.

# 2.3. Analysis

The concentration of Fe(II) was determined by complexometry with *o*-phenanthroline, taking  $\varepsilon_{510} = 1,118 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$  for the Fe(II)-phenanthroline complex (Calvert and Pitts, 1966). HCHO formation was measured by colorimetry with chromotropic acid as described by Bricker and Vail (1950).

The method used to determine the concentration of monomeric Fe(III) was a modification of Kuenzi's procedure Kuenzi, 1982: 1 ml each of 0.05 M 8-hy-droxyquinoline-5-sulphonic acid (HQSA) and acetic acid buffer (pH = 4.6) were poured into a 10-ml volumetric flask; 8 ml of sample was added to this solution and rapidly mixed. Within 30 s of mixing, the

absorbance of the tris complex of 8-hydroxyquinoline-5-sulphonate with Fe(III) (Fe(HQS)<sub>3</sub>) was measured at  $\lambda = 572$  nm; the same solution with 8 ml of water instead of sample was used as a blank. HQSA reacts much more rapidly with monomeric Fe(III) species than with Fe(III) dimers or polymers; Fe(HQS)<sub>3</sub> absorbs in a spectral region in which these latter species or Fe(III) precipitates do not. Values of  $\varepsilon_{572}$  of Fe(HQS)<sub>3</sub> have been reported by Kuenzi (1982) (5180 M<sup>-1</sup> cm<sup>-1</sup>) and by Faust and Hoigné 1990 (4970 M<sup>-1</sup> cm<sup>-1</sup>); an average value of 5075 M<sup>-1</sup> cm<sup>-1</sup> was used here.

The DBS concentration was determined by the Methylene-Blue-Active-Substance (MBAS) method (Apha et al., 1981), which depends on the formation of a blue salt or ion pair when methylene blue, a cationic dye reacts with anionic surfactants such as LAS. The results were in agreement with those obtained by HPLC measurements.

The formation of the photoproducts was followed by HPLC with detection at 220 and 260 nm. The determination of the quantum yields of DBS disappearance and Fe(II) formation were calculated from the concentration as a function of irradiation time at conversion percentage lower than 10%.

# 3. Results

3.1. Characterisation of DBS and Fe(III) in aqueous solution

Commercial DBS is a mixture of about 30 homologs



among which the species with n = 9 and the phenyl ring bonded on carbon-2 (2-C<sub>12</sub>LAS) is the major one. The UV-Visible spectrum exhibits a maximum at 223 nm ( $\varepsilon \approx 10\ 300\ M^{-1}\ cm^{-1}$ ) and a structured band centred at 260 nm ( $\varepsilon \approx 350\ M^{-1}\ cm^{-1}$ ). Adachi and Kobayashi (1984) reported that there is no direct photodegradation of DBS upon irradiation at  $\lambda > 290$  nm. The concentrations in DBS used in this work (0.1 or 1 mM) were lower than the critical micelle concentration (CMC) reported in the literature (1.6 mM at 25°C) (Fendler and Fendler, 1975; Furton and Norelus, 1993).

In order to interpret accurately the absorption spectrum and photochemical behaviour, it is crucial to understand the hydrolytic speciation of Fe(III), which is described by the following equilibria in dilute aqueous solution (Escot, 1973). For simplicity, coordinated water molecules are not explicitly included in the chemical formula; thus, Fe(OH)<sup>2+</sup> refers to Fe(OH)(H<sub>2</sub>O)<sup>2+</sup><sub>2</sub>.

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$$
(1)

$$\mathrm{Fe}^{3+} + 2\mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{Fe}(\mathrm{OH})_2^+ + 2\mathrm{H}^+ \tag{2}$$

$$\operatorname{Fe}^{3+} + 3\operatorname{H}_2\operatorname{O} \rightleftharpoons \operatorname{Fe}(\operatorname{OH})_3(\operatorname{aq}) + 3\operatorname{H}^+$$
 (3)

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$$

$$\tag{4}$$

Under our experimental conditions  $(0.1 \leq [Fe(III)] \leq 1$ mM and  $2.5 \leq pH \leq 4.0$ , the formation of Fe<sub>2</sub>(OH)<sup>4+</sup><sub>2</sub> can be neglected; it would appear that  $Fe(OH)^{2+}$  is the predominant monomeric Fe(III)-hydroxyl complex (Knight and Sylva, 1975; Wagman et al., 1982), with  $Fe^{3+}$  representing ~10% of the total Fe(III) concentration. For the rest of the discussion, we will only consider  $Fe(OH)^{2+}$ ;  $Fe^{3+}$ , the minor monomeric species, does not absorb at  $\lambda \ge 310$  nm and does not interfere in the photochemical behaviour of the system. The concentration of Fe(OH)<sup>2+</sup> rapidly decreased after the dissolution of  $Fe(ClO_4)_3$  in water, this disappearance has been attributed to the possible formation of soluble aggregates of Fe(III) (Knight and Sylva, 1975). It appears that the concentration of Fe(OH)<sup>2+</sup>, the most photoactive species (Faust and Hoigné, 1990), strongly depends on the age of the ferric solution (before and after dilution) and on the starting concentration. We were able to determine  $[Fe(OH)^{2+}]$  with the HQSA method.

3.1.1. Evolution of the mixture of DBS and Fe(III) in aqueous solution

The addition of 1 mm Fe(III) to the 1 mM DBS resulted in flocculation; the FTIR analysis of the precipitate showed the presence of both Fe(III) and DBS. Centrifugation and elimination of the precipitate left a supernatant solution that contained  $Fe(OH)^{2+}$  and DBS with the concentrations of 0.23 and 0.40 mM, respectively. 60% of starting DBS was eliminated from the solution.

# 3.2. Photochemical behaviour

All attempts to detect any complexation between DBS and Fe(OH)<sup>2+</sup> in the supernatant failed; the UV-visible spectrum matched the sum of the three components (Fe(OH)<sup>2+</sup>, Fe<sup>3+</sup> and DBS). At  $\lambda \ge 310$  nm, where neither DBS nor Fe<sup>3+</sup> absorb, the spectrum only corresponded to that of Fe(OH)<sup>2+</sup> as established by comparison with the spectrum reported by Faust and Hoigné (1990),  $\varepsilon$  being equal to 1760 and 270 mol<sup>-1</sup> l cm<sup>-1</sup> at 313 and 365 nm respectively. The fact that the absorption at long wavelengths was only that of Fe(OH)<sup>2+</sup> ruled out any significant formation of ionpairs between DBS and Fe(OH)<sup>2+</sup>. Upon irradiation, Fe(OH)<sup>2+</sup> can act as a photoinitiator of degradation

through internal electron transfer. Its charge transfer band strongly overlaps the solar UV spectrum (290– 400 nm) and its photolysis efficiently produces •OH radicals and Fe(II) (Baxendale and Magee, 1955; Dainton and Tordoff, 1957; Faust and Hoigné 1990; Matsuura and Smith, 1970).

$$\operatorname{Fe}(\operatorname{OH})^{2+} + h\nu \xrightarrow{\lambda \ge 290 \text{ nm}} \operatorname{Fe}^{2+} + \cdot \operatorname{OH}$$
(5)

Benkelberg and Warneck (1995) measured the quantum yield of  $\cdot$ OH radicals formation ( $\phi$ ) as a function of excitation wavelength (Table 1). They attributed the increase in the quantum yield when the excitation wavelength is decreased to the kinetic energy required to achieve the ejection of  $\cdot$ OH radicals from the solvent cage.

The •OH radicals, being very strong oxidation agents, are able to attack DBS; irradiation at 365 nm effected the complete removal of DBS.

### 3.2.1. Kinetics measurements

Irradiation of the supernatant containing  $Fe(OH)^{2+}$ and DBS at 365 nm, resulted in a continuous decrease in absorbance across the spectrum, reflecting the disappearance of Fe(III) and DBS (Fig. 1); a similar result was obtained for irradiation at 296 and 313 nm.

Table 1

Quantum yields of DBS disappearance and quantum yields of OH radical formation

$\lambda$ (nm)	$\Phi_{ m dis.}~{ m DBS^a}$	$\lambda$ (nm)	$\phi \; (\cdot \mathrm{OH})^{\mathrm{b}}$
296	$0.33\pm0.03$	290	$0.288\pm0.025$
313	$0.17\pm0.01$	310	$0.195\pm0.033$
365	$0.08\pm0.02$	370	$0.074\pm0.015$



<sup>b</sup>(30).



Fig. 1. Evolution of Fe-DBS UV-visible spectrum upon irradiation at 365 nm.

The quantum yields of DBS disappearance ( $\Phi$ ) were determined in the presence of oxygen for irradiation at 296, 313 and 365 nm with triplicate runs. The results, which are summarised in Table 1, show that the quantum yields of DBS disappearance are strongly wavelength dependent and are similar to the values of the quantum yield of  $\cdot$ OH radical formation as reported by Benkelberg and Warneck (1995). This agreement leads to the conclusion that at least at the beginning of the reaction all the photolytically generated  $\cdot$ OH react with DBS.

#### 3.2.2. HPLC experiments

The decrease in DBS concentration was measured by HPLC and complexometry (MBAS) for irradiation at 365 nm; the results obtained by both methods were in good agreement (Fig. 2); the rate of DBS disappearance decreased when the initial concentration of  $Fe(OH)^{2+}$ was decreased. The appearance of peaks mixed with the injection peak was observed from the start of the irradiation; several photoproducts with very high polarity were formed. With the use of the 9:1 (v/v)  $H_2O/CH_3OH$ eluent, the formation of five main photoproducts was observed. The rate of formation and degradation of the photoproducts also increased with increasing [Fe(OH)<sup>2+</sup>]. At long irradiation times, the absorbance of DBS and of the photoproducts at 220 nm disappeared. In the presence of 1% (v/v) 2-propanol as a scavenger of ·OH radicals, the degradation of DBS was totally inhibited. This result confirmed that DBS degradation is only due to the •OH radicals produced upon irradiation of Fe(III) in aqueous solution.

### 3.2.3. Formation of Fe(II)

In all cases, Fe(II), as determined by complexometry, was formed. [Fe(II)] quickly rises, then reaches a constant value upon continued irradiations (Fig. 3); the



Fig. 2. Decrease in DBS concentration upon irradiation at 365 nm measured by HPLC ( $\blacksquare$ ) and complexometry with MBAS ( $\bigcirc$ ). [Fe(OH)<sup>2+</sup>] = 0.03 mm; [DBS] = 0.08 mm.

plateau is due to the reoxidation of Fe(II) species. The value of the [Fe(II)] at the plateau is a positive function of the initial concentration of Fe(OH)<sup>2+</sup>. Any involvement of a Fenton-type reaction in the early stages of the reaction can be ruled out; no  $H_2O_2$  was added to the system.

# 3.2.4. EPR spectroscopy upon irradiation ( $\lambda \ge 305 \text{ nm}$ )

For spin-trapping EPR experiments, 5,5-dimethyl-1pyrroline-1-oxyde (DMPO) (1 mg/ml), was added to the Fe(III) and DBS solution. Upon irradiation, a 1:2:2:1 quartet (a = 14.6 G) was obtained, a signal that is characteristic of the stable adduct with •OH radicals (Fig. 4) (Janzen et al., 1978). The observation of a



Fig. 3. Formation of Fe(II) as a function of irradiation time at 365 nm in aerated solution; at t = 0 [Fe(OH)<sup>2+</sup>] = 0.11 mM: [Fe(III)]<sub>0</sub> = 0.3 mM, [DBS]<sub>0</sub> = 0.1 mM, pH = 3.0.



1:2:2:1 quartet pattern (a = 14.6 G) was observed due to the equality of  $a_{\rm N}$  and  $a_{\rm H}$ .

Fig. 4. Spin-trapping experiments with DMPO (1 mg per 1 ml of solution) by EPR spectroscopy upon irradiation ( $\lambda \ge 305$  nm) : [Fe(III)]<sub>0</sub> = 0.3 mM, [DBS]<sub>0</sub> = 0.1 mM, pH = 3.0.

quartet instead of a triplet of doublets was due to the identical value of the coupling constants  $a_N$  and  $a_H$ . In the presence of 1% of 2-propanol, no signal was detected.

### 3.2.5. Photoproduct analyses

Irradiation of Fe(III)-DBS solutions yields five main photoproducts; (1), (3) and (5) were identified with authentic compounds commercially available. The characterisation of photoproducts (2) and (4) was realised from additional experiments with 4-EBS acid, which contains a short alkyl chain; the same five photoproducts were formed upon irradiation of EBS.

As a matter of fact, even at high concentrations (6 mM Fe(III) and 4 mM EBS), the immediate formation of a precipitation when the Fe(III) and EBS aqueous solutions were mixed in aqueous solution was never observed, rendering the separation and identification of the common photoproducts easier. The photoproducts (2) and (4) were separated by preparative HPLC without any damage, but some thermal reactions occurred when they were thoroughly dried. In general, these species were kept wet and negative electrospray mass spectrometry was performed directly on the aqueous solution; exchange in D<sub>2</sub>O was necessary prior to the recording of their NMR spectra.

The characteristics of the five photoproducts are summarised in Table 2.

The photodegradation of 4-acetylbenzenesulphonate (1), the major photoproduct, was also investigated in the presence of Fe(III). Photoproducts (3) and (4) were also obtained upon irradiation of (1) at 365 nm; (2) and (5) were not observed under these conditions.

#### 3.2.6. Oxygen effect

The quantum yield of DBS disappearance was not significantly changed in the absence of oxygen. In contrast, the absence of oxygen affected the formation of the photoproducts very strongly. The rate of formation of the five main photoproducts was divided by 10 and we observed the formation of the new photoproducts, certainly some alcohols as already observed with tributyltin in the absence of oxygen (Mailhot et al., 1999). In the same time, we observed an important increase of the rate of formation of Fe(II), multiplied by 5. These observations can be explained by the redox reaction with Fe(III) for the termination reaction of radicals.

$$R' + Fe(III) \rightarrow ROH + Fe(II)$$

#### 4. Mechanism and discussion

The primary and secondary photoproducts that were isolated all contain the sulphonate group, indicating that the carbon in the  $\alpha$  position of the aromatic ring is the principal site of attack by 'OH radicals that leads to the cleavage of the alkyl chain.

Table 2 Characteristic of the five major photopro	oducts				
	CH <sub>3</sub>	I—	НО	CH <sub>3</sub>	HO_
	- <sup>8</sup> (C	ů-(C	$\langle \bigcirc \rangle$	j j	
	∑_o <sup>s</sup>	)}_€os	SO3⊕	P-os	so-
	[1] major	[2]	[3]	[4]	[5]
HPLC <sup>a</sup> retention time	8.3 min	5.3 min	2.9 min	12.0 min	4.2 min
UV spectrum	247	251	229	221, 254,	233
$\lambda_{\max}$ (nm)	280 (sh)	280 (sh)	270 (sh)	320	280 (sh)
ESMS main peak (m/z)	199	185	173	215	201
NMR $^{1}$ H (D <sub>2</sub> O)	2.75 (s)				
	8.00(d, j = 8.4  Hz)		7.05(d, j = 8.5  Hz)		8.00(d, j = 8.5  Hz)
$\delta$ (ppm)	8.15(d, j = 8.4  Hz)		7.80(d, j = 8.5  Hz)		8.20(d, j = 8.5  Hz)
<sup>a</sup> 9:1 (v/v) H <sub>2</sub> O (+1% H <sub>3</sub> PO <sub>4</sub> )-CH <sub>3</sub> OH.					

0
Ĥ
Y
0
$H_3P$
$(+1\%_{00})$
${\rm H}_2{\rm O}$
(v/v)
_

Sehested et al. (1975) studied the different sites of attack of 'OH radicals on methylated benzene and concluded that in mildly acidic solution benzyl radicals were formed via path A.



At lower pH, the rate of the direct formation of the benzyl radical via path B increased and became competitive with the elimination of  $H_2O$  from the  $\cdot OH$  adduct to the benzene ring in path A. We cannot rule out the formation of the corresponding phenol from the  $\cdot OH$  adduct with the aromatic ring of DBS; but we never observed it in our experiments.

Considering that the pH of the Fe(III) – DBS solution is  $\sim$ 3, one would expect the tertiary radical (*R*<sup>\*</sup>), which should have a greater stability then the benzyl radical, to be formed by both paths A and B.



From the above results and observations the following mechanism can be put forward.



Reaction of R' with O<sub>2</sub> yields RO<sub>2</sub>, peroxy radicals that can undergo a head-to-head termination reaction to form intermediate tetroxides R–O–O–O–O–R (Sonntag and Schuchmann, 1991); their decomposition to give molecular oxygen and two alkoxy radicals is a wellknown reaction. The  $\beta$ -scission of the resulting alkoxy radicals is the typical decomposition pathway reported in Carlson and Wiles (1969).

- The scission of the C−R' bond (route A) directly leads to the formation of 4-acetylbenzenesulphonate [1] as a major photoproduct with the homologs 2-C<sub>n</sub>LAS. Hydroxy-4-acetylbenzenesulphonate [4] results from the subsequent attack of [1] by •OH radicals.
- In route B, the scission of the C-phenyl bond gives rise to the phenyl radical, and through reaction with O<sub>2</sub> or Fe(III) leads to the formation of 4-hydroxy-benzenesulphonate [3].
- The formation of 4-formylbenzenesulphonate [2] can be explained by considering the presence of isomers with the phenyl group attached to the first carbon  $(1-C_nLAS)$  in commercial DBS. In this case, [2] could be obtained via the  $\beta$ -scission of the C–C bond of the corresponding RO• alkoxy radical. This type of radical can also isomerise to a carbon centred radical which reacts with oxygen and after elimination of HO•2 give rise to a long chain keto compound. Photoproduct [5] would be obtained by further oxidation of [2].



Photoproducts [3] and [4] are also produced by the Fe(III)-photoinduced degradation of [1]. It is worth noting that this mechanism is not only valid for the different homologs present in commercial DBS but also for EBS, as evidenced by the similarity of the photoproducts.

In the absence of oxygen, the attack of  $\cdot$ OH radicals on DBS leads to ROH and Fe(II) by a redox process between  $R \cdot$  and Fe(III).

#### 5. Conclusion

This work shows that the degradation of DBS in aqueous solution when photoinduced by Fe(III) is a very efficient process, which could be used for the destruction

of surfactants in polluted waters. The precipitation observed when DBS and Fe(III) are mixed is also an interesting example of the physical elimination of DBS from water that could also be fruitfully employed in water treatment. After removal of the precipitate, Fe(OH)<sup>2+</sup> is the predominant species of Fe(III) present in the solution. The photolysis of Fe(OH)<sup>2+</sup> produces •OH radicals; the degradation of DBS is due to attack by ·OH radicals followed by secondary reactions that involve O<sub>2</sub>. The primary step of the decomposition of the surfactant involves H-abstraction at the carbon atom in the  $\alpha$  position of the aromatic ring, giving rise to different benzenesulphonate derivatives. For long irradiation times, the total disappearance of DBS and of the photoproducts is observed. Our experimental conditions, which are very well controlled in terms of pH, concentration and water quality, permit a clear assessment of the photochemical mechanism of DBS degradation.

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