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Competitive oxidative cleavage and epoxidation of 4,4′-diaminostilbene-2,2′-disulfonic acid by Fe(III) aqua complexes

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4,4′-Diaminostilbene-2,2′-disulfonic acid (DSD) has been investigated as a model compound of fluorescent whitening agents. The reaction of DSD with Fe(III) aqua complexes has been studied in the dark at room temperature: a fast degradation of DSD was observed under our experimental conditions. HPLC analysis was used to follow the kinetics of the redox reaction. The process involves epoxidation, leading to DSD epoxide (**1**), and the oxidative cleavage of the double bond, leading to 5-amino-2-formyl-benzenesulfonic acid (**2**) together with the reduction of Fe(III) into Fe(II). The dependence of the redox process on $[Fe(H_2O)_5(OH)]^{2+}$ concentration indicates that the dominant reaction pathway is a reaction between DSD and the Fe(III) monomeric species, $[Fe(H_2O)_5(OH)]^{2+}$. The complete degradation of DSD is observed with an excess of oxidant; the ratio $[Fe(H_2O)_5(OH)]^{2+}$:[DSD] has to be higher than 2. A mechanism giving rise to the two degradation products is proposed.

Introduction

4,4′-Diaminostilbene-2,2′-disulfonic acid (DSD) is an important intermediate in the synthesis of a great number of fluorescent whitening agents. As a result, it can be discharged in non negligible amounts into the aquatic environment. Stilbene derivatives have been investigated during the last few decades,[1–3] because they are difficult to remove through the usual biological wastewater treatments and because of their inefficient photodegradation,[4] that is, poor degradability either by microorganisms or by sunlight in surface waters. The development of new techniques to eliminate such compounds from water becomes, therefore, important. In addition, DSD is a convenient model molecule of stilbenic fluorescent whitening agents for such studies.

Among the photodegradation processes, Fenton's method, which leads to reactive OH radicals, strong oxidising agents, has been widely used to eliminate these types of compounds.[5] Moreover, Sörensen and Frimmel showed that DSD in water can be eliminated significantly in the UV/H_2O_2 process.[6] More recently, Yu *et al.* and Zhu *et al.* improved the degradability of DSD by a pre-treatment combining ferrous hydrogen peroxide oxidation and ozonation or coagulation-flocculation processes.[7,8]

In our laboratory, a method based on the Fe(III) aqua complexes appeared to be very efficient in the photoinduced degradation of different pollutants: 4-chlorophenol,[9] 4-octylphenol[10] and 2,6-dimethylphenol,[11] for example. The reaction involves hydroxyl radicals ($^{\bullet}OH$) formed during the photolysis of Fe(III) aqua complexes.[12,13] In all the investigated systems, the monomeric species $[Fe(H_2O)_5(OH)]^{2+}$, so-called $Fe(OH)^{2+}$, appears to be the most photoactive species.

This method has been applied to eliminate this compound. The work on the fate of DSD was separated into two different parts: (*i*) the direct photolysis of DSD, this compound absorbing up to 380 nm and therefore undergoing a photoreaction under solar light,[14] and (*ii*) the Fe(III) photoinduced degradation.[15] However, it appears that there is also an immediate dark degradation of DSD in the presence of Fe(III) at room temperature. With the aim of elucidating the reaction and the Fe(III) species involved in the process, we studied the behaviour of different DSD and Fe(III) mixtures. This paper deals with a complete investigation on the Fe(III) induced degradation of DSD.

Experimental

Reagents

4,4′-Diaminostilbene-2,2′-disulfonic acid (*trans*-DSD) was an Acros product (95%) used without further purification. Sodium perchlorate was a Prolabo product (99%) and perchloric acid was a Merck product. Ferric perchlorate nonahydrate $[Fe(ClO_4)_3{\cdot}9H_2O$; 97%] was a Fluka product kept in a dessicator. The Fe(III) solutions were prepared by diluting a stock solution [2.0×10^{-3} mol L^{-1} in $Fe(ClO_4)_3{\cdot}9H_2O$] to the appropriate Fe(III) concentration. All the solutions were prepared with ultrapure aerated water (Millipore αQ, resistivity = 18.2 MΩ cm). The pH was adjusted with $HClO_4$ and pH measurements were carried out with an Orion pH meter to 0.01 unit. The ionic strength was not controlled. Deoxygenated solutions were obtained by bubbling with argon for 20 min at room temperature.

A chemical method,[16] shortly described here, was used to separate the products obtained from the reaction of DSD with Fe(III) (3.4×10^{-5} and 3.0×10^{-4} mol L^{-1}, respectively). Firstly, the solution was concentrated by vacuum evaporation of most of the solvent. Afterwards, an aqueous solution of NaOH was added dropwise until the pH was around 9.5. The solution was filtered to eliminate the iron hydroxide precipitate. Separation was then achieved by elution through a silica gel column (silica gel 60) using AcOEt–EtOH–H_2O (φ = 70:18:12) as eluent. The purification of the products was achieved by passing through an Amberlite column (H^+/Na^+). The final products were dried by lyophilisation.

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Apparatus and procedures

HPLC experiments were carried out using a Waters chromatograph equipped with a Waters 990 photodiode array detector giving the full UV-visible spectrum at any time (sampling time = 80 ms). The chromatographic separation was performed with a reverse-phase Waters Spherisorb ODS2 C_{18} column of 25 cm length (particle diameter 5 μm). The eluent was water with either $HClO_4$ or $NaClO_4$ (1.0×10^{-2} mol L^{-1}) and the flow rate was 1 mL min^{-1}. The acidification (pH = 3.4) of the eluent or the presence of Na^+ cations permitted good separation conditions.

UV-visible spectra were recorded on a Cary 3 double beam spectrophotometer. Negative ion electrospray mass spectral analyses (ES-MS) were obtained from the "Centre Régional de Mesures Physiques" (Clermont-Ferrand, France), on a Hewlett Packard 5989B spectrophotometer with a Hewlett Packard 59987B ioniser. NMR spectra were recorded with a Bruker Avance DSX 300 spectrometer and IR spectra on a Nicolet 20SXC FT-IR spectrometer on KBr pellets.

Analysis

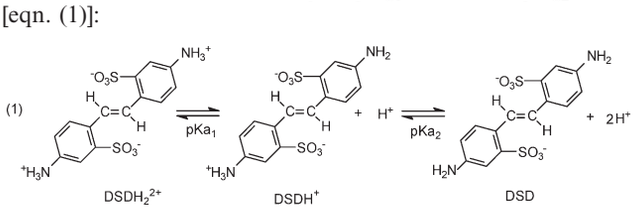
The Fe(II) concentration was determined by complexometry with *ortho*-phenanthroline, taking $\varepsilon_{510} = 1.118 \times 10^4$ L mol^{-1} cm^{-1} for the Fe(II)–phenanthroline complex.[17] The monomeric concentration of Fe(III) species, *i.e.* $[Fe(OH)]^{2+}$ (which refers to $[Fe(H_2O)_5(OH)]^{2+}$), was determined by using the modified[18] Kuenzi procedure with 8-hydroxyquinoline-5-sulfonic acid (HQSA).[19]

The kinetics of DSD disappearance and of the formation of oxidation products were determined by high performance liquid chromatography experiments ($\lambda_{detection} = 255$ nm).

Results

Characterisation of the DSD–Fe(III) mixture

The maximum solubility of DSD in water was determined to be 4.0×10^{-5} mol L^{-1} at room temperature and this solution was thermally stable (for a few days at room temperature in the dark). As a function of pH, DSD exists in three different forms: DSD, monoprotonated DSD ($DSDH^+$) and diprotonated DSD ($DSDH_2^{2+}$). The two dissociation constants have been determined by monitoring the absorbances at 265, 300 and 337 nm as a function of pH: $pK_{a1} = 3.7$ and $pK_{a2} = 4.5$ [eqn. (1)]:



(1)

Under our experimental conditions ([Fe(III)] between 3.4×10^{-5} and 3.0×10^{-4} mol L^{-1} and [DSD] = 3.4×10^{-5} mol L^{-1}), the pH of the solution was in the range 4.2–3.4. But all the experiments were performed at pH = 3.4, the pH being adjusted to this value with $HClO_4$. This implies that the solutions contain the mono- and the diprotonated forms of DSD, and that $Fe(OH)^{2+}$ is the predominant monomeric Fe(III) hydroxy complex.[13] However, the concentration of monomeric species rapidly decreased after the dissolution of ferric perchlorate in water. The disappearance was attributed to the possible formation of soluble aggregates.[20] The percentage of $Fe(OH)^{2+}$ strongly depends on the starting concentration and on the age of the ferric solution.[13] In all the previous work with[9–11] or without light,[21] the starting percentage of $Fe(OH)^{2+}$ in the Fe(III) solution was revealed to be a major parameter governing the rate of the reaction.

Using the 8-hydroxyquinoline-5-sulfonic acid (HQSA) method,[18] the percentage of $Fe(OH)^{2+}$ in the solution was determined according to the following eqn. (2):

$$\%Fe(OH)^{2+} = 100 \times [Fe(OH)^{2+}]/[Fe(III)_{tot}] \qquad (2)$$

where $[Fe(III)_{tot}]$ is the concentration of Fe(III) added to the solution. The different percentages of monomeric species $Fe(OH)^{2+}$ were obtained by the use of Fe(III) solutions of different ages.

We monitored the UV-visible spectrum of a freshly prepared mixture of DSD (3.4×10^{-5} mol L^{-1}) and Fe(III) (3.0×10^{-4} mol L^{-1}; ≈100% monomeric species) as a function of time. The resulting UV-visible spectrum was not the sum of the spectra of the two components [Fig. 1(a)]. The difference spectrum between the mixture and a Fe(III) solution showed that two new absorption bands ($\lambda_{max} = 247$ and 336 nm) appeared from the beginning of the reaction [Fig. 1(b)]. No significant evolution of the spectrum was then observed.

This thermal reaction was investigated in detail by HPLC analysis; on the chromatogram of a mixture, two new products appeared along with the complete disappearance of DSD. This implies a fast reaction between Fe(III) and DSD: a transformation of the compounds and/or a ground state complexation.

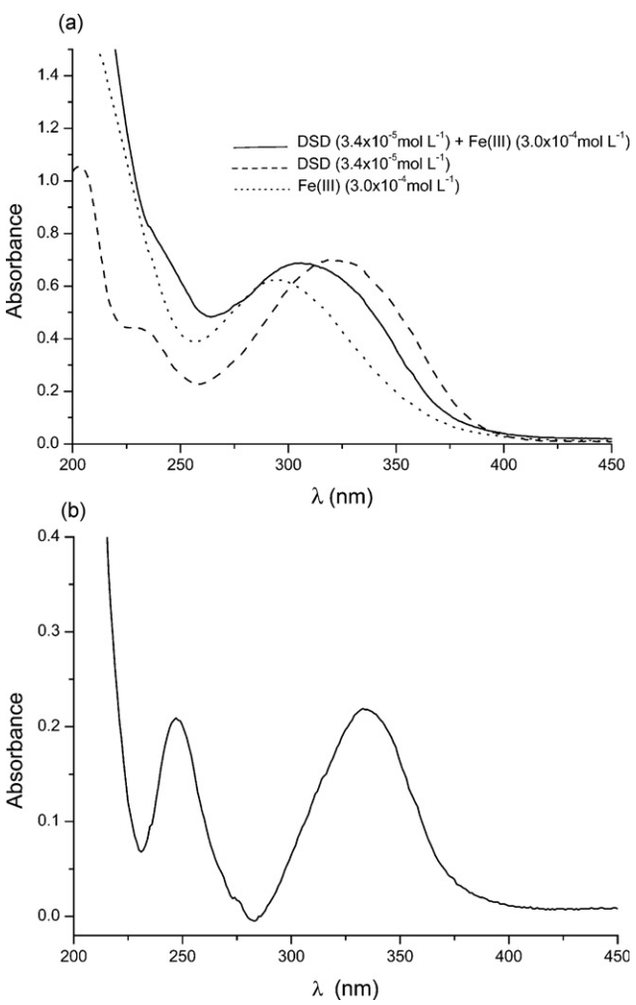


Fig. 1 (a) UV-visible absorption spectra of the indicated solutions in water, at room temperature, 1 min after preparation. (b) Difference absorption spectrum of a mixture of DSD (3.4×10^{-5} mol L^{-1}) and Fe(III) (3.0×10^{-4} mol L^{-1}) and a Fe(III) solution at the same concentration, in water, at room temperature and 1 min after preparation.

Influence of Fe(III) concentration

The thermal reaction (degradation of DSD) is related to the presence of Fe(III) since it was previously established that DSD is stable in acidic medium. In order to estimate the influence of Fe(III) on the process, its concentration was varied and taken as 3.4×10^{-5}, 6.8×10^{-5}, 1.2×10^{-4} and 3.0×10^{-4} mol L^{-1}; in all cases, the percentage of $Fe(OH)^{2+}$ species was not far from 100% and the concentration of DSD was 3.4×10^{-5} mol L^{-1}.

To confirm the involvement of $Fe(OH)^{2+}$ ($[Fe(III)] = 3.0 \times 10^{-4}$ mol L^{-1}) in the reaction, the effect of the percentage of $Fe(OH)^{2+}$ species was also investigated in the presence of DSD (3.4×10^{-5} mol L^{-1}). The percentage values (100%, 47% and 7%) were determined by using the HQSA method, just before adding DSD. The results are summarised in Table 1.

In the presence of $Fe(OH)^{2+}$, the concentration of DSD continuously decreased until its total disappearance or until a constant value was reached during the process. The disappearance showed two distinct domains [Fig. 2(A)]: for short periods of time, the degradation of DSD was very fast and then it slowed down and levelled off. The results related to DSD disappearance as a function of $[Fe(OH)^{2+}]$ are gathered in Fig. 3. It clearly appears that there is a linear relationship between initial $[Fe(OH)^{2+}]$ and [DSD] degraded until the concentration in $Fe(OH)^{2+}$ is sufficient to completely degrade DSD. The total disappearance of DSD occurs for a concentration of $Fe(OH)^{2+}$ higher by a factor of approximately 2. The results, which are summarised in Table 2, show that the initial rate constant of the degradation was also affected by the concentration of $Fe(OH)^{2+}$: the higher the concentration, the faster the degradation. We also established the kinetic parameters considering that at shorter times, only the reaction between DSD and $Fe(OH)^{2+}$ occurs. The initial rate can be expressed as followed:

$$v_0 = k[Fe(OH)^{2+}]_0^{\alpha}[DSD]_0^{\beta} \qquad (3)$$

where v_0 is the initial rate, k is the rate constant, $[Fe(OH)^{2+}]_0$ and $[DSD]_0$ are the initial concentrations in both products and α and β are the kinetic orders of the reaction in $Fe(OH)^{2+}$ and DSD, respectively.

With respect to eqn. (3), we determined the values of α and β by respectively plotting log v_0 as a function of log $[Fe(OH)^{2+}]_0$ and log $[DSD]_0$, taking the other parameters to be constant; the slope measured for each curve corresponds to α and β. The expression for the initial rate is thus:

$$v_0 = 15[Fe(OH)^{2+}]_0^{1.55}\ [DSD]_0^{1.16} \qquad (4)$$

This rate coefficient is an average calculated from the different results obtained under all the experimental conditions [$k = 15 \pm 2$ (mol L^{-1})$^{-1.8}$ s^{-1}]. This value is high when compared to that obtained in the 2,6-dimethylphenol and Fe(III) system [$k = 0.75 \pm 0.12$ (mol L^{-1})$^{-0.53}$ s^{-1}][9] and is in agreement with the very fast process observed.

Table 1 Effect of the $Fe(OH)^{2+}$ monomeric species on the concentrations of Fe(II) and the corresponding DSD disappearance at the plateau in a mixture of Fe(III) and DSD (3.4×10^{-5} mol L^{-1}), at room temperature and in aerobic conditions

$[Fe(III)]$/ mol L^{-1}	% $Fe(OH)^{2+}$	$[Fe(OH)^{2+}]$/ mol L^{-1}	$[Fe(II)]_{plateau}$/ mol L^{-1}	$[DSD]_{disap}$/ mol L^{-1}
3.4×10^{-5}	≈100	3.4×10^{-5}	3.1×10^{-5}	1.4×10^{-5}
6.8×10^{-5}	≈100	6.8×10^{-5}	6.3×10^{-5}	3.3×10^{-5}
1.2×10^{-4}	≈100	1.2×10^{-4}	9.0×10^{-5}	3.4×10^{-5}
3.0×10^{-4}	≈100	3.0×10^{-4}	9.5×10^{-5}	3.4×10^{-5}
3.0×10^{-4}	47	1.4×10^{-4}	9.5×10^{-5}	3.4×10^{-5}
3.0×10^{-4}	7	2.1×10^{-5}	1.5×10^{-5}	0.8×10^{-5}

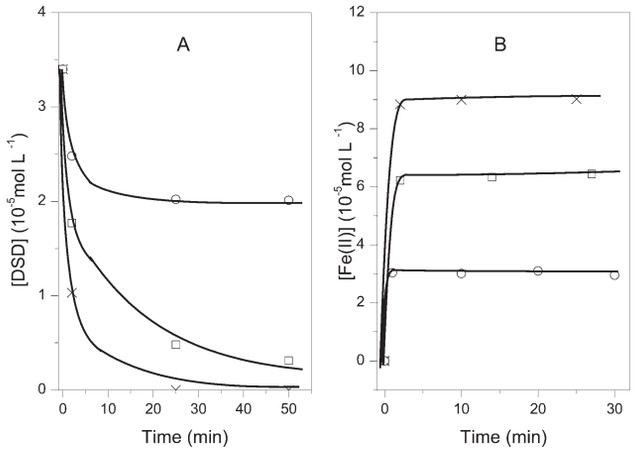


Fig. 2 Kinetics of (A) DSD disappearance and (B) Fe(II) formation in a mixture of DSD (3.4×10^{-5} mol L^{-1}) and Fe(III) at different concentrations, at room temperature: (○) 3.4×10^{-5}, (□) 6.8×10^{-5} and (×) 1.2×10^{-4} mol L^{-1} with 100% of $Fe(OH)^{2+}$.

During these experiments, the formation of Fe(II) was observed and followed by complexometry. Likewise for DSD disappearance, the Fe(II) concentration immediately rose and reached a plateau value [Fig. 2(B)]. An important point is that the plateau value of the Fe(II) concentration increased with increasing Fe(III) concentration until the DSD had completely reacted. This occurred at a concentration in $Fe(OH)^{2+}$ higher than 1.2×10^{-4} mol L^{-1}, resulting in a Fe(II) concentration around 9.5×10^{-5} mol L^{-1} (Table 1). Until DSD is completely degraded, the upper value of [Fe(II)] corresponds, within experimental error, to the starting value of the $[Fe(OH)^{2+}]$. This implies that these reactive species are mainly responsible for the process. Once DSD has totally disappeared there is no longer Fe(II) formation, even in the presence of a large excess in $Fe(OH)^{2+}$.

Consequently, these results confirm a redox reaction between DSD and $Fe(OH)^{2+}$ in the dark at room temperature.

Product identification

Only two peaks appeared on the HPLC chromatogram of a DSD and Fe(III) mixture. Their UV-visible spectra are given in Fig. 4. The same peaks were observed whatever the percentage of monomeric species. Compounds **1** and **2** were isolated as described in the experimental section from a solution of DSD and Fe(III).

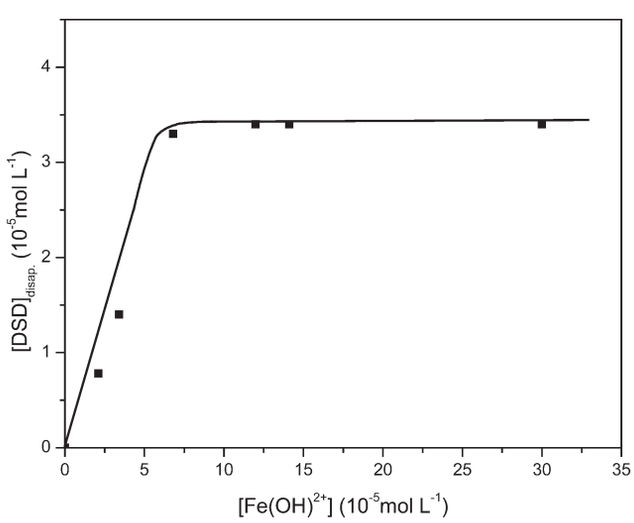
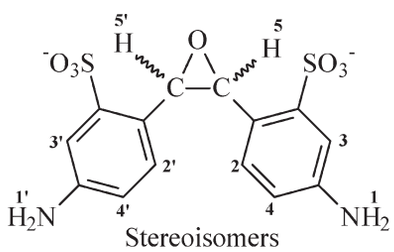


Fig. 3 DSD disappearance as a function of $Fe(OH)^{2+}$ concentration, $[DSD]_0 = 3.4 \times 10^{-5}$ mol L^{-1}.

Table 2 Influence of $Fe(OH)^{2+}$ concentration on the initial rate of DSD disappearance in a mixture of DSD (3.4×10^{-5} mol L^{-1}) and Fe(III), at room temperature and in aerobic conditions

$[Fe(OH)^{2+}]$/mol L^{-1}	Initial rate of $DSD_{disap.}$/mol L^{-1} s^{-1}
3.4×10^{-5}	0.8×10^{-7}
6.8×10^{-5}	1.4×10^{-7}
1.2×10^{-4}	2.0×10^{-7}
1.3×10^{-4}	2.4×10^{-7}
3.0×10^{-4}	$> 6.0 \times 10^{-7}$

Product **1** was unstable in solution especially after separation and concentration; as a consequence it was difficult to determine its structure by classical analytical techniques (NMR, MS). This compound has only been analysed by ES-MS technique after separation. The analysis gave three major peaks at $m/z = 385$, 213 and 192 with respective relative abundances of 30, 36 and 100. The predominant ion at $m/z = 192$ could correspond to the molecular compound, the DSD epoxide, doubly charged, and the presence of the peak at $m/z = 385$ could be attributed to the $[M+H]^-$ ion coming from the epoxide; the main fragment ($m/z = 213$) obtained seems to correspond to the heaviest fragment resulting from a heterolytic C–C scission between one aromatic ring and the epoxide. These results are in agreement with the chemical structure of both DSD epoxides.

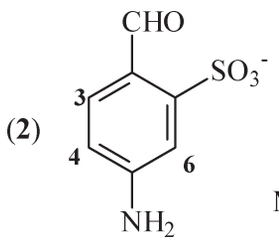


MW = 384 g mol^{-1}

(1)

Indeed, all the attempts to separate and to observe the two isomers (*trans* and *cis* forms) failed. Only one peak was observed by HPLC analysis in different conditions. Moreover, the specific theoretical chemical shifts of the isomers of **1** in ^{1}H-NMR analysis, calculated by ACD® software, show no differences between the two isomers. The calculated values of δ_H are 3.87 (s; H_5, $H_{5'}$), 6.04 (d; $J = 8.3$ Hz; H_2, $H_{2'}$), 6.37 (s; NH_2; H_1, $H_{1'}$), 7.07 (d; $J = 1.95$ Hz; H_3, $H_{3'}$), 7.66 (dd; $J = 8.3$ and 1.95 Hz; H_4, $H_{4'}$); this result is in good correlation with the experimental values obtained for product **1** in D_2O. Nevertheless, the signal at 3.87 ppm was not clearly observed because of a possible effect of the sulfonate groups, which increased the relaxation time of the hydrogen of the epoxide group.[16]

The separation gave another stable product, **2**, with the ^{1}H-NMR spectrum in $CD_3(SO)CD_3$ having peaks at: δ_H (400 MHz,) 7.35 (dd; $J = 8.5$ and 2.4 Hz; H_6), 7.65 (d; $J = 2.4$ Hz; H_4), 8.25 (d; $J = 8.5$ Hz; H_3) and 10.70 (s; CHO) and with an IR spectrum having a new vibration band, with respect to DSD, at around 1700 cm^{-1}, which corresponds to a typical C=O vibration band in an aldehyde. The analysis by ES-MS gave a major peak at $m/z = 200$, which could correspond to the molecular compound $[M]^-$ of the aldehyde derivative. All these results are in agreement with the identification of product **2** as 5-amino-2-formyl-benzenesulfonic acid.



(2)

MW = 200 g mol^{-1}

Moreover, the pure compounds **1** and **2** obtained by chromatographic separation were back injected for HPLC analysis: their retention times and their UV spectra were completely similar to those observed in the mixture.

For shorter reaction times, the kinetics of the product formation are represented in Fig. 5. The concentrations were determined from the calibration curves of **1** and **2** obtained after the separation of the two products. The products **1** and **2** were formed very quickly without any induction period. We noted that the formation of the products was strongly affected by the initial $Fe(OH)^{2+}$ concentration: the ratio [**2**]:[**1**] increases with the concentration of $Fe(OH)^{2+}$ (Table 3). In the presence of a very large excess of Fe(III) (around 10^{-2} mol L^{-1}), only formation of the aldehyde **2** was observed.

Epoxide **1** formed by the very fast oxidative reaction, appeared not to be totally stable in the mixture ([DSD] = 3.4×10^{-5} mol L^{-1} and $[Fe(OH)^{2+}] = 3.0 \times 10^{-4}$ mol L^{-1}): a slow transformation is observed giving rise to **2**; after two days, 10% of **1** had disappeared.

Effect of oxygen

The effect of oxygen was investigated on two mixtures of DSD (3.4×10^{-5} mol L^{-1}) and Fe(III) (1.5×10^{-4} and 6.0×10^{-5} mol

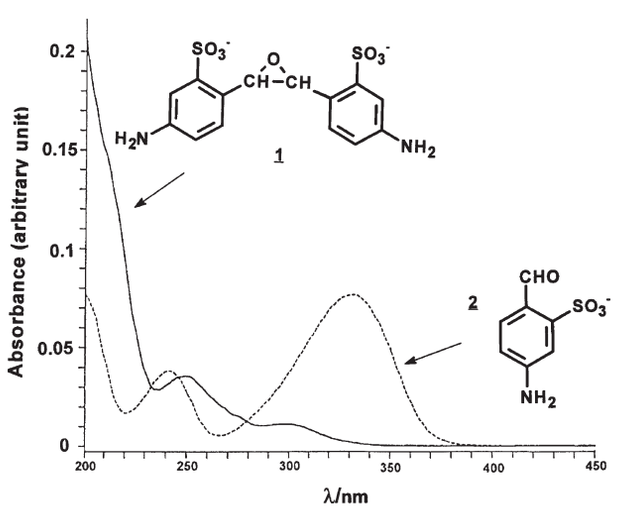


Fig. 4 UV-visible absorption spectra of (—) **1** and (---) **2** in water at room temperature.

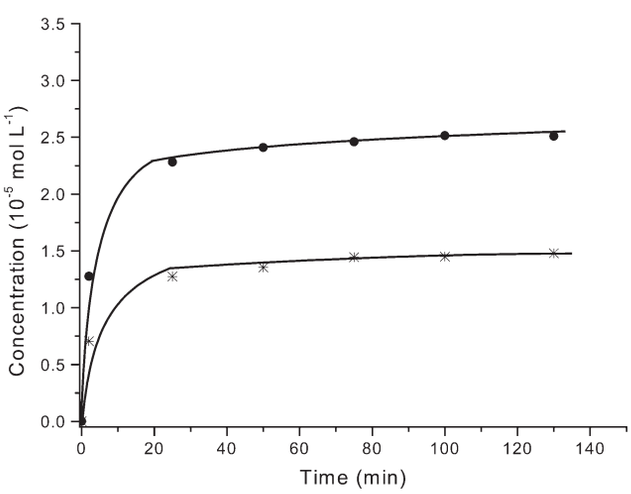


Fig. 5 Kinetics of (●) **1** and (*) **2** formation in a mixture of DSD (3.4×10^{-5} mol L^{-1}) and $Fe(OH)^{2+}$ (6.8×10^{-5} mol L^{-1}) as a function of time, at room temperature.

Table 3 Concentrations of DSD, **1** and **2** at the plateau as a function of the concentration of $Fe(OH)^{2+}$, $[DSD]_0 = 3.4 \times 10^{-5}$ mol L^{-1}, at room temperature and in aerobic conditions

$[Fe(OH)^{2+}]$/ mol L^{-1}	$[DSD]_{plat.}$/ mol L^{-1}	$[\mathbf{1}]_{plat.}$/ mol L^{-1}	$[\mathbf{2}]_{plat.}$/ mol L^{-1}	[**2**]:[**1**]
3.4×10^{-5}	1.95×10^{-5}	1.2×10^{-5}	0.5×10^{-5}	0.42
6.8×10^{-5}	0.15×10^{-5}	2.5×10^{-5}	1.4×10^{-5}	0.56
1.2×10^{-4}	0	2.6×10^{-5}	1.6×10^{-5}	0.62
3.0×10^{-4}	0	2.5×10^{-5}	1.8×10^{-5}	0.72
1.2×10^{-3}	0	2.4×10^{-5}	2.0×10^{-5}	0.83

L^{-1}). The percentage of monomeric species was roughly 90% in the first case and 66% in the second case. In both cases, the initial rate of DSD disappearance and its percentage degradation at the plateau are not affected by the presence of oxygen (Table 4). Therefore, O_2 appears not to have a significant role in the primary steps of the oxidative reaction.

cis-DSD

The behaviour described above is that of *trans*-DSD. Because of the efficient *trans* ⇋ *cis* photoisomerisation, we investigated the behaviour of the *cis* isomer. The experiments were carried out on solutions with 93% of *cis*-DSD prepared from a pure *trans*-DSD solution irradiated for a short period of time (9 min) at 365 nm. Similar results were obtained with a *cis*-DSD–Fe(III) mixture (3.4×10^{-5} and 3.0×10^{-4} mol L^{-1}, respectively): 9.5×10^{-5} mol L^{-1} of Fe(II) was formed together with products **1** and **2**, in similar concentrations. Also in this case, the total degradation of DSD was observed. Accordingly, the reactions are not dependent on the isomer used.

Discussion

We studied the reactions of DSD in the presence of Fe(III) in aqueous solution. The disappearance of DSD takes place with the formation of two products: **1** is supposed to be DSD epoxide and **2** is 5-amino-2-formyl-benzenesulfonic acid. The hypothesis of DSD epoxide formation is based on ES-MS analysis of **1** in aqueous solution, NMR, and on the literature.

Only a few papers relating to such a reaction were found in the literature. A similar reaction was described between DSD and permanganate ion but only 5-amino-2-formyl-benzenesulfonic acid is formed during this oxidative reaction, perhaps because of some excess in the oxidative material; the authors gave no details about the mechanism involved.[22] Morvillo and Bressan, in the case of ruthenium complexes, proposed a catalytic cycle for the oxidation of stilbenes leading to the epoxide and/or to the aldehyde derivative.[23] They showed that one of the two competitive reactions can be favoured by changing the concentration conditions or the ligands around ruthenium(II). Moreover, Chatterjee *et al.* described that the catalysed oxidation of stilbene by Mg(III) or Ru(III) complexes led to the formation of benzaldehyde and stilbene epoxides.[24,25] In our case, according to the product identification, the redox reaction between DSD and $Fe(OH)^{2+}$ could also involve similar processes.

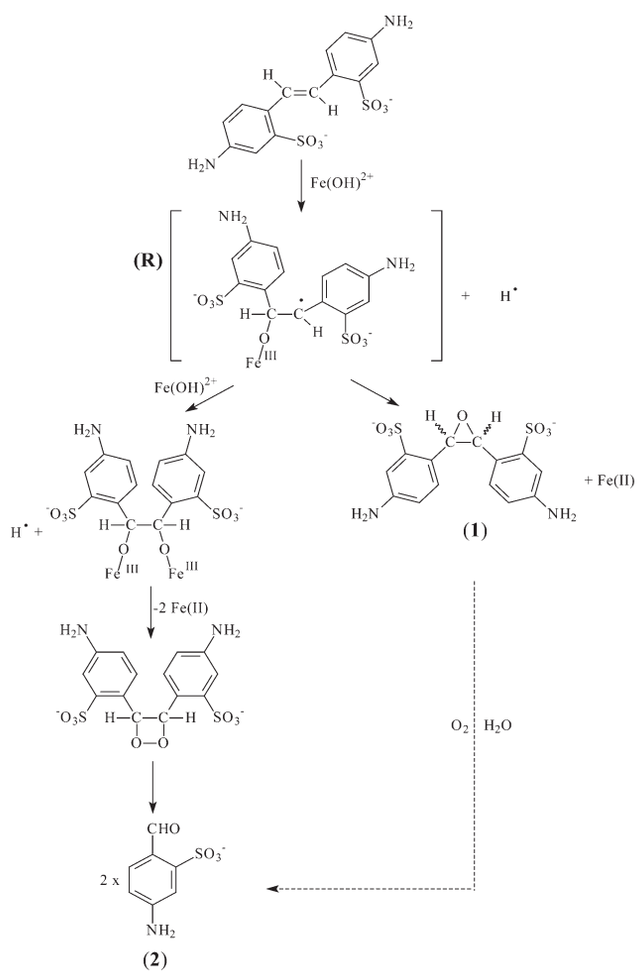
Table 4 Initial rate and percentage of DSD disappeared at the plateau in a mixture of DSD (3.4×10^{-5} mol L^{-1}) and Fe(III), aerobic and anaerobic conditions, at room temperature

$[Fe(III)]$/ mol L^{-1}	Condition	% Monomeric species	% DSD disappeared	Initial rate of $DSD_{disap.}$/ mol L^{-1} s^{-1}
1.5×10^{-4}	Anaerobic	93	100	2.7×10^{-7}
1.5×10^{-4}	Aerobic	87	100	2.4×10^{-7}
6.0×10^{-5}	Anaerobic	68	62	1.1×10^{-7}
6.0×10^{-5}	Aerobic	64	60	1.0×10^{-7}

The analysis by UV-visible spectrophotometry showed that the difference spectrum [between the absorbance of a Fe(III)–DSD mixture and the absorbance of Fe(III) alone], obtained after one minute, is about the sum of the two spectra of the transformation products, reflecting how fast the degradation process is. At high concentrations of $Fe(OH)^{2+}$, the yield of epoxide formation was negligible.

The lack of oxygen effect on the rate of DSD disappearance and on the nature of the products argues against the involvement of oxygen in this process; the fact that the reaction takes place without oxygen is surprising. However, we can propose that the oxygen atoms come from the metallic complex in the form $Fe(OH)^{2+}$, as Morvillo and Bressan did for ruthenium complexes,[23] or from water: the stilbene derivative interacts with the metal species, giving rise to an intermediate radical (**R**) with one Fe(III) linked to the ethylenic carbon through the oxygen atom. Then, from this radical, two pathways are possible: (*i*) formation of the epoxide derivative along with Fe(II) and (*ii*) reaction with an another Fe(III), leading to a compound containing two metal species linked to DSD; a dioxo bridge can be then formed between the two adjacent carbon atoms. This product can then fragment to two aldehyde derivatives (Scheme 1). The hydrogen radicals H• formed during this process, which have a very low reactivity, should not significantly interfere in the mechanism.

The formation of **1** or **2** would depend on the availability of $Fe(OH)^{2+}$, which agrees with the experimental data: the ratio [**2**]:[**1**] increases with the concentration in $Fe(OH)^{2+}$ (Table 3). At very high concentrations, aldehyde **2** is the only product



Scheme 1

formed. In contrast, at very low concentrations $Fe(OH)^{2+}$ does not permit the complete degradation of DSD, even though the formation of both products is observed. Accordingly, we are observing two competitive reactions with $Fe(OH)^{2+}$, the degradation of DSD and the further oxidation of the intermediate radical **R**.

Conclusion

The very fast and efficient thermal (in the dark at room temperature) reaction observed between 4,4′-diaminostilbene-2,2′-disulfonic acid and Fe(III) species is a redox process. It occurs by the supposed epoxidation and the oxidative cleavage of DSD leading to two products, DSD epoxide (**1**) and 5-amino-2-formyl-benzenesulfonic acid (**2**), together with the formation of Fe(II). This process essentially depends on the concentration in monomeric species $Fe(OH)^{2+}$, which appears to be the major oxidative agent in the reaction. Two concomitant reactions are present, both involving $Fe(OH)^{2+}$, the epoxidation and the oxidative cleavage of DSD. The concentration of $Fe(OH)^{2+}$ governs the extent of DSD degradation and the proportion between the two products (**1** and **2**). All the results related to a this model molecule of fluorescent whitening agents raise the question of the generalisation of such reactions to derivatives of similar structure. Furthermore, this redox reaction could be used as an easy and efficient way to synthesise 5-amino-2-formyl-benzenesulfonic acid, a non commercially available product, and perhaps be extended to the synthesis of other similar compounds.

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