

# DEGRADATION OF A STILBENE-TYPE FLUORESCENT WHITENING AGENT WITH HYPOCHLORITE: IDENTIFICATION OF THE DEGRADATION PRODUCTS BY CAPILLARY ELECTROPHORESIS

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**Abstract**—The *E*,*E*-(4,4'-bis[2-sulfostyryl]biphenyl) (DSBP) is a fluorescent whitening agent widely used by the textile and detergent industries to whiten fabrics. Hypochlorite used to bleach fabrics oxidizes DSBP slowly at room temperature and in a higher rate at 60°C. The ions of metals such as Fe, Cu, and Mn accelerate the process considerably. At ambient temperature, the oxidation results from cleavage of the stilbene bonds and involves the formation of various intermediates that evolve to end products. The intermediates form within minutes to hours and the end products within months. At 60°C or in presence of the previously mentioned transition metals, intermediates form within minutes and the end products within days. The end products of the oxidation are 4-sulfobenzaldehyde and 4,4'-bisaldehyde biphenyl; in the presence of excess of hypochlorite, however, the process yields their corresponding oxidized derivatives 4-sulfobenzoic acid and 4,4'- biphenyldicarboxylic acid. Despite the chlorinating ability of hypochlorite, the major degradation products formed contain no chlorine.

Keywords—Bleach Hypochlorite Detergent Fluorescent whitening agent Chlorinated organics

# INTRODUCTION

The fluorescent whitening agents (FWAs), also called optical brighteners, used in detergents are water-soluble organic compounds with a high affinity for cellulosic material. Fluorescent whitening agents act by absorbing ultraviolet (UV) light and emitting visible light in the blue region [1]. This offsets natural yellowing in materials such as fabric, paper, and soap and provides superior whites. However, the ability to absorb short-wavelength light also makes them liable to undergo photochemical transformations [2,3].

Fluorescent whitening agents contained in detergents at an average concentration around 0.15% by weight serve to replace textile FWAs, which are photodegraded during wearing or removed during washing. Depending on the particular type of FWA, detergent composition, and washing temperature used, a variable proportion of the optical brightener in the detergent from 20 to 95% is not adsorbed by fabrics and is thus discharged with the wash liquor yielding sewage treatment plants. The FWAs are partly retained by wastewater purifying systems; a fraction, however, reaches natural waters and poses potential environmental risks [4].

The DSBP is a stilbene-type FWA commonly used in household detergents. In fact, the estimated worldwide production of DSBP in 1992 was 3,000 tones. The product is commercially available in its E, E form, as the other isomers exhibit little or no fluorescence. The DSBP, like other stilbene-type optical brighteners, degrades to a variable extent on exposure to light or hypochlorite.

The photodegradation of DSBP has been studied since the early 1970s and is still under evaluation [5,6]. The kinetics [7] and mechanism of photodegradation of DSBP in natural

waters [8], in suspension [9], and on metal oxides [10] have been reported.

The photolysis of DSBP yields mainly aldehydes, which are formed by cleavage of the stilbene groups, and alcohols, which result from the addition of water to the stilbene double bond [6]. In all these studies the presumption has been made that DSBP is discharged to the aquatic environment without any conversion.

Hypochlorite for domestic use (bleach) is a dilute solution (about 5% by weight) widely used as disinfectant and stain remover. Hypochlorite is known to chlorinate organic products; recent studies have revealed that about 3% of sodium hypochlorite in household products is converted into chlorinated organics [11,12].

In a previous study [13], DSBP was found to be oxidized slowly by hypochlorite (compared to other stilbene-type FWAs); also, the process was found to be accelerated by transition metals such as Fe, Cu, and Mn, which are usually present in the tap water used for washing. The reaction, however, can be avoided by using a suitable chelating agent. This oxidation reaction is very likely to occur, as the successive use of detergent and bleach is a very common practice in washing white fabrics. The process starts during washing and may continue in the wastewater. The chlorinating ability of hypochlorite and the toxicity of chlorinated organics have raised the need to identify precisely the degradation products and elucidate the underlying mechanism in order to avoid environmental risks. The degradation process is also a major issue for the detergent industry because it leads to a loss of whiteness and also adsorption of FWA degradation products by fabrics through yellowing [14].

The aim of this work was to identify for the first time the degradation products of DSBP and to elucidate the mechanism of its reaction with hypochlorite in the presence and absence of metals with a view to clarifying the underlying chemistry.

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The negative charge of the molecule facilitated the separation of the degradation products by capillary zone electrophoresis (CZE).

### **EXPERIMENTAL**

#### Reagents

The optical brightener E, E(4, 4'-bis[2-sulfostyryl]biphenyl)(E,E-DSBP) and its E,Z and Z,Z isomers-2-sulfobenzaldehyde (aldehyde 1), 4,4'-bisaldehyde biphenyl (aldehyde 2), 2-

sulfobenzoic acid (acid 1), 4,4'-biphenyldicarboxylic acid (acid 2), and 3-benzaldehyde-2'-sulfonic acid stilbene-were supplied by Ciba Specialty Chemicals (Basel, Switzerland) and used as received. The purity of all was greater than 95% with the exception of the E,E-DSBP isomer, which was only 82% pure and accompanied by the inorganic salts used to precipitate it.

Ammonium iron (II) sulfate, sodium tetraborate, and sodium carbonate (all proanalysis reagents from Merck, Darmstadt, Germany) were also used. Milli-Q® water from a Millipore Water Purification system (Millipore, Molsheim, France) was used throughout.

#### Apparatus

Electrophoretic separations were conducted on a 3D capillary electrophoresis instrument from Hewlett-Packard (Waldbronn, Germany) equipped with a diode array detector, an autoinjector, and a capillary thermostat. Samples were injected in the hydrodynamic mode, using a pressure of 50 mbar on the injection vial for 5 s. Direct polarity (with the cathode next to the detector) was used throughout, and electropherograms were recorded at wavelengths where the analytes exhibited strong absorption (198, 270, 279, 292, and 348 nm). The electrophoretic separation was carried out in a 56-cm-long (effective length) by 50-µm-i.d. fused silica capillary thermostated at 25°C. A 20-mM sodium tetraborate solution adjusted to pH 9.3 with 0.1 M NaOH was used as background electrolyte, and a voltage of 30 kV was applied between both capillary ends. All pH measurements were made with a micropH 2001 pH-meter from Crison (Alella, Spain).

Fluorescence measurements were made on a Perkin-Elmer LS50 fluorimeter (Norwalk, CT, USA), using a continuousflow system consisting of a peristaltic pump, a Hellma flowcell of 1 cm light path, and a 30% beam attenuator at the detector gate. The sample, maintained under continuous stirring in the dark, was propelled to the measuring cell, where its fluorescence was excited at 348 nm and its emission measured at 430 nm. The beam attenuator was used in order to avoid excessive dilution of DSBP because the brightener possesses very strong fluorescence.

### Procedure

Solutions containing 112 mg/L DSBP and different amounts of hypochlorite in the presence and absence of iron (II) were kept at room temperature or 60°C as required, away from light in order to avoid photodegradation. Several aliquots of these solutions were withdrawn at different times after preparation and injected into the electrophoretic capillary system, which was previously conditioned by passing the background electrolyte for 10 min and equilibrated by applying a potential of 30 kV for 10 min. After each separation, the capillary was reconditioned by passing 1 M NaOH for 5 min and then 0.1 M NaOH for a further 10 min. Degradation products were identified by comparing the spectra and migration times of the peaks with those for pure standards.

Solutions containing 10 mg/L DSBP and 1 mg/L concentration of the transition metals (buffered with sodium carbonate at pH 9) were used in the fluorescence experiments. They were allowed to circulate in the absence of hypochlorite for 1,000 s, the time during which the initial fluorescence was measured, then the hypochlorite was added and the fluorescence decay with time recorded.

## **RESULTS AND DISCUSSION**

Preliminary experiments were carried out, monitoring the UV spectra for DSBP solutions exposed to hypochlorite buffered at pH 9 (washing baths are normally alkaline). The UV spectrum for the DSBP solution exhibited an absorption maximum at 348 nm, and the addition of hypochlorite gave rise to a band at 290 nm (the UV maximum for hypochlorite). This spectrum evolved to complete disappearance of DSBP band and the appearance of a new band peaking at 280 nm. These changes expose the instability of DSBP against hypochlorite and suggest the formation of new species.

The initial tests were conducted to identify the DSBP oxidation products by hypochlorite involved preparing a 50-mg/ L solution containing DSBP and NaClO (mole ratio 1:6.5, pH 9) that was stored at room temperature. Aliquots of this solution were injected into the capillary electrophoresis system on different days over a three-month period (results not shown). These tests revealed the oxidation of DSBP to involve the formation of various intermediates that evolve very slowly. However, the derivatives aldehyde 1 and aldehyde 2 were successfully identified from among the other degradation intermediates. In order to expedite the process, the sample was subjected to accelerated aging by storage at 60°C in a stove. This increased temperature resulted in significantly simpler electropherograms than those obtained at room temperature and also in a faster evolution of the intermediates.

Two degradation tests at 60°C in the absence of light and metals were then performed: one at a 1:8 DSBP/hypochlorite mole ratio (112 mg/L DSBP, 119 mg/L NaClO) and the other at a 1:24 ratio (112 mg/L DSBP, 357 mg/L NaClO).

The electropherogram obtained for the initial 1:8 DSBP/ hypochlorite solution approximately 30 min after preparation exhibited two small peaks (peaks 1 and 2) and three overlapped peaks (Fig. 1) that were assigned to the initial brightener species (E,E-DSBP) in addition to two intermediate species with maximum absorption at 270 and 320 nm, respectively. Subsequently, the species with maximum absorption at 320 nm, which was designated intermediate I, evolved to the one with maximum absorption at 270 nm (intermediate II). Subsequent electropherograms (Fig. 2) showed that intermediate II also evolved and that it yielded the derivatives aldehyde 1 and aldehyde 2, which were then partially oxidized to their corresponding acid derivatives (acid 1 and acid 2). No change in these species was apparent from electropherograms recorded at longer times.

A degradation test conducted in the presence of a large excess of hypochlorite revealed the formation of intermediate II to be much faster. A freshly made solution yielded a main peak corresponding to intermediate II and weak signals corresponding to residual amounts of E,E-DSBP and intermediate I. Subsequent electropherograms revealed that the degradation end products were the acid derivatives, which were accompanied by residual amounts of the aldehyde derivatives. How-



Fig. 1. Electropherogram at 198 nm obtained for a solution containing 112 mg/L 4,4'-bis(sulfostyryl)biphenyl (DSBP) and 120 mg/L hypochlorite (mole ratio 1:8, pH 9) approximately 15 min after preparation. The ultraviolet (UV)-Vis spectra of DSBP (348 nm), intermediate II (270 nm), and intermediate I (320 nm) is also shown. See text for explanation of peaks 1 and 2.

ever, a third minor species with maximum absorption at 236 nm and a migration time of 13 min was detected after one week that could not be identified. This species was observed only when the acid derivatives were present in solution.

These results show that the degradation rate depends on the hypochlorite concentration. The process involves three steps: the formation of intermediates I and II, the oxidation to the aldehyde derivatives, and the subsequent oxidation to the corresponding acid derivatives. Based on this experimental evidence that the degradation of DSBP leads to the acid derivatives, the following chemical equation is proposed to account for the overall process of DSBP oxidation by hypochlorite:

$$DSBP + 8 \text{ NaClO} \rightarrow 2 \text{ acid } 1 + \text{acid } 2 + 8 \text{ NaCl} \quad (1)$$

Note that the major products of degradation from the 1:8 DSBP/hypochlorite mixture are not those one would be expect from Equation 1. This is a result of the partial decomposition of hypochlorite under the operating conditions used (pH 8.5 and 60°C), where it was present in a proportion lower than the initial stoichiometric ratio; as a result, a mixture of degradation products in a higher oxidation state (acid derivatives) and a lower one (aldehyde derivatives) was obtained.

Figures 3a and b illustrate the previously described changes in the different species; they show the corrected area of the



Fig. 2. Electropherogram at 198 nm obtained after one week at  $60^{\circ}$ C for a solution with mole ratio 4,4'–bis(sulfostyryl)biphenyl (DSBP)/NaClO 1:8. The question mark (?) is used to indicate the unknown species. Other conditions as in Figure 1.



Fig. 3. (a) Evolution of the oxidation products at 60°C at a mole ratio 4,4'-bis(sulfostyryl)biphenyl (DSBP)/NaClO is 1:8. (**■**) aldehyde 1, (**●**) aldehyde 2, (**▼**) acid 1, (**▲**) acid 2, (—) intermediate I. (**b**). Evolution of the oxidation products at 60°C at a mole ratio 4,4'-bis(sulfostyryl)biphenyl (DSBP)/NaClO is 1:24. (**■**) aldehyde 1, (**●**) aldehyde 2, (**▼**) acid 1, (**▲**) acid 2, (—) intermediate I, (**♦**) unknown species.

electrophoretic peak-which is proportional to the concentration-for each identified species as a function of the time from preparation of the DSBP/hypochlorite solution. This corrected area was calculated by dividing integrated peak area by migration time in order to correct artificial changes in the peak area caused by different residence times of each analyte in the detection region. Changes in E,E-DSBP were not plotted because the oxidation of DSBP to intermediate II was virtually complete within 30 min and even faster in the presence of a excess of hypochlorite. The subsequent formation of aldehydes and acids is very unlikely to occur in wastewater because the reaction is very slow at ambient temperature and the concentration and hydraulic residence time of hypochlorite in wastewater very low [15]. These conclusions were drawn from results under laboratory conditions using solutions that contained only the chemicals of interest; the environmental degradation pathway may thus be different, as microbial attack and the presence of catalytic surfaces would interfere with hypochlorite oxidation. In any case, these aldehyde derivatives have been found in sunlit natural waters by effect of the photodegradation of DSBP [6].

We also studied the degradation process in the presence of



Fig. 4. Fluorescence decay curves at room temperature for the oxidation of 10 mg/L of 4,4'-bis(sulfostyryl)biphenyl (DSBP) with 100 mg/L hypochlorite in presence of transition metals. The concentration of the metal was 1 mg/L and the solution buffered at pH 9.

low concentrations of transition metals. Fluorimetric monitoring of the degradation of DSBP (Fig. 4) by hypochlorite at room temperature in the presence of metals (Fe, Cu, and Mn) revealed the degradation rate for the brightener to be a function of the nature and concentration of the metal [13]. These experiments exposed a catalytic effect of the metals on the degradation of DSBP by hypochlorite and that the effect is stronger with Fe(II) than with Mn(II) and similar—much weaker—with Cu(II) and Fe(III). Note that fluorescence decay is observed only when hypochlorite is added to a solution containing DSBP and the metal, so it cannot be ascribed to a metal-quenching effect but rather to degradation of the FWA. These metals are usually present in the tap water used by household laundries, so their effect on the process was studied.

By using capillary electrophoresis to monitor changes in a 1:8 DSBP/hypochlorite mixture containing 5 mg Fe<sup>2+</sup>/L, the previously mentioned catalytic effect was found to reflect in the rapid formation of intermediate II (probably preceded by intermediate I), which is responsible for the nearly instantaneous fluorescence decay observed when a solution of DSBP and Fe(II) was supplied with hypochlorite. Subsequent electropherograms revealed that the room-temperature oxidation of this intermediate species is slower (only residual amounts of the aldehyde derivatives were detected after one week) than in the degradation processes conducted at 60°C in the absence of metal. Therefore, the metal catalyzes the formation of intermediates I and II but plays no catalytic role in their subsequent oxidation. When the Fe(II)-containing solution was stored in a stove at 60°C, the process led to the same end products as in the absence of metal.

# Mechanism for the degradation of the brightener by hypochlorite

The previously described CZE experiments confirmed that the proposed aldehyde and acid derivatives are the end products of the oxidation of DSBP by hypochlorite. The oxidation takes place via a process involving the formation of two intermediate species (intermediates I and II). Based on the UV and fluorescence spectroscopic results and also on the CZE migration times, we propose a tentative structure for these species. Thus, we believe that intermediates I and II are formed by epoxidation of the stilbene double bonds (via chlorohydrin and subsequent internal cyclization), the resulting epoxide un-





Fig. 5. Plot of fluorescence decays after each addition of hypochlorite. The solution contains 12.5 mg/L 4,4'-bis(sulfostyryl)biphenyl (DSBP) and 5 mg/L Fe<sup>2+</sup> and was maintained at room temperature and buffered at pH 9.

dergoing opening to a vicinal diol in the alkaline medium. These reactions between hypochlorite and double bonds are well known and documented [16]. In fact, peaks 1 and 2 in Figure 2 can be assigned to residual epoxide derivative. These very small peaks might correspond to the two diasteromers potentially formed in the epoxidation of the double bonds, depending on whether the electrophilic attack of Cl takes place on the same or opposite sides of the double bonds. The absorption maximum (similar to that for intermediate II) is consistent with the DSBP structure where the stilbene bonds are epoxidized.

This ability of double bonds to yield vicinal diols is widely known and confirmed by the need for two hypochlorite molecules to form the corresponding intermediate (Fig. 5). This mole ratio was checked in the following experiment carried out at room temperature: a 12.5-mg/L solution of DSBP buffered at pH 9 with sodium carbonate and containing 5 mg Fe<sup>2+/</sup> ml (to accelerate the formation of the intermediate) was supplied, at present intervals, with 50 µl of a hypochlorite solution (0.77 g/L) corresponding to one-half of the DSBP molar content. Under these conditions, CZE confirmed that intermediate II was the species immediately formed (the formation of intermediate I was so fast that it could not be detected). The fluorescence decayed abruptly after each addition and was very weak beyond the fourth (at a DSBP/hypochlorite ratio of 2: 1); this indicates that virtually the whole brightener had reacted by that time and confirms the reaction of the two double bonds and the need for two hypochlorite molecules to form intermediate II, which is nonfluorescent.

The proposed structure for intermediate II is also consistent with the migration time for this species, which possesses the same negative charge as DSBP and a very similar size, so it must have a very similar electrophoretic migration time, as is indeed the case. Its absorption maximum (270 nm) is consistent with the proposed structure taking into account the loss of conjugation in these species: DSBP (348 nm), aldehyde 2 (300 nm), acid 1 (280 nm), and intermediate II (270 nm). This loss of conjugation explains why this intermediate is nonfluorescent. Moreover, if one accepts this structure for intermediate II, then intermediate I may be the result of the reaction of only one of the stilbene bonds to yield a diol. The UV maximum (320 nm) for intermediate I is consistent with the chemical

#### Metal catalytic effect observed





Fig. 6. Scheme proposed for the oxidation of 4,4'-bis(sulfostyryl)biphenyl (DSBP) with hypochlorite.

structure obtained when only one of the double bonds has reacted.

The end products of the oxidation of DSBP (aldehyde 2 and aldehyde 1) can be readily ascribed to oxidative cleavage of intermediate II. These aldehydes are subsequently oxidized to their corresponding acid derivatives by residual hypochlorite in solution. The proposed evolution of the species, summarized in Figure 6, is supported by the fact that eight molecules of hypochlorite are required to thoroughly oxidize DSBP to the acid derivatives, consistent with the stoichiometry of Equation 1.

#### CONCLUSIONS

The DSBP is oxidized by hypochlorite, and the products formed result from cleavage of the stilbene double bonds. The oxidation reaction is slow and involves the formation of various intermediates at ambient temperature. A higher temperature (60°C) or the presence of low concentrations of transition metals accelerates the reaction, which takes place via two intermediate species (intermediates I and II) that are rapidly formed. These intermediates evolve to end products: 4-sulfobenzaldehyde and 4,4'-bisaldehyde biphenyl or, in the presence of a large excess of hypochlorite, their corresponding acids (4-sulfobenzoic and 4,4'-biphenyldicarboxylic acids). Consequently, despite the chlorinating ability of hypochlorite, the major degradation products contain no chlorine.

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