KINETIC STUDY OF ACID BLUE 1 DISCOLORATION WITH PERSULFATE

Zeinab Ali Ayoub, Ogarite Ali Yazbeck, Mouhiaddine Mohamed El Jamal

Inorganic and Organometallic Coordination Chemistry Laboratory LCIO
Faculty of Sciences (I), Lebanese University
Rafic Hariri Campus El Hadath, Lebanon
E-mail: mjamal@ul.edu.lb

ABSTRACT

The discoloration of the food colorant Acid Blue 1 (AB1) by persulfate is mainly investigated by UV-VIS spectroscopy. The rate of discoloration is proportional to increase of persulfate and Fe (II) concentration, as well as temperature, whereas it decreases slightly with increase of food colorant and chloride ion concentration. The blue color disappearance is first order with respect to the food colorant and persulfate. The thermodynamic parameters of discoloration of AB1 (E_a, ∆H#, ∆S#, ∆G#) in presence and absence of Fe(II) are calculated. Discoloration of AB1 can be accomplished in both acidic and basic medium, with formation of one or more intermediate(s) depending on the [dye]/[persulfate] ratio and the reaction mixture pH. However, even a 100-fold excess of persulfate does not result in AB1 mineralization. The mechanism(s) of AB1 discoloration based on UV-VIS spectra and comparison to other triphenylmethane dyes degradation patterns are advanced.

Keywords: Acid Blue 1, persulfate, discoloration, advanced oxidation, kinetic.

INTRODUCTION

Bread, margarine, juice, candies are just some of the food products which can lead to numerous problems for human health, including cancer and weakens in the immune system, because these foods are hiding a number of harmful organic (colorants) and inorganic (bromates, sulphite, and persulfate) compounds. Nowadays, preservatives, which are actually designed to keep food edible for a longer time, are in a high concentration not only in various exotic foods, but in foods we consume daily, too. A number of studies have focused on the use of additives and their influence on humans and on the environment [1 - 3].

Acid Blue 1 (AB1), also called Sulfan Blue 5 or E131 VF, is a synthetic triphenylmethane dye (Fig. 1). It is structurally very similar to the food colorant Patent Blue V (E131 V, or PBV), Brilliant Blue FCF (E133), Malachite Green (MG), and Crystal Violet (CV) to mention a few (Fig. 1). All these dyes have one or more alkylamine which can stabilize the triphenylmethyl cation by electron donation through resonance becoming an imine. Bromothymol Blue (BTB) belongs also to the same dye group but it has fairly different functional groups, two bromines on the aryl rings and an oxide anion instead of an amine stabilizing the triphenylmethyl cation (Fig. 1).

Food dyes are one of the most widely used and dangerous additives. Triphenylmethane dyes find large applications in food industry (beverages, jelly sweets, candies, ice-cream, etc.). For example, there is a great concern about the thyroid peroxidase-catalyzed oxidation of the triphenylmethane dyes because the reactions might form various N-dealkylated primary and secondary aromatic amines, whose structures are similar to those of aromatic amine carcinogens [4]. The European Union placed regulations on labeling food dyes to inform consumers of the health risks.

Many dyes are environmentally persistent and have strong absorption bands in the visible light region; and
when released into water bodies generally reduce light transmission thereby affecting aquatic biota. An environmental regulation applied in most countries requires discoloring industrial wastewater prior to its discharge. The problem to choose a suitable treatment in this respect is old and not yet solved. Furthermore, it is important to note that color removal is not attributed to the complete mineralization of the organic dye as it may simply involve transformation of the chromophore groups into non-chromophore ones. A number of techniques of dyed wastewater purification based on biodegradation [5-7], and photocatalytic degradation [9-11] are investigated. Other purification strategies include electrochemical treatment [12-16], adsorption [17], and advanced oxidation [18-21]. The latter processes, which involve in situ chemical oxidation (ISCO) generating powerful oxidants, have emerged as an important and cheaper class of technologies for removal of a wide range of organic contaminants in wastewater, and for remediation of organic contaminants in polluted soil and groundwater [22, 23]. These oxidation methods use oxidants like K$_2$S$_2$O$_8$ [24-27], KBrO$_3$ [28], KIO$_4$ [29], Fenton’s reagent [30, 31], H$_2$O$_2$ [34] and ozone, which is a strong non-selective oxidizer [35, 36]. Potassium persulfate, K$_2$S$_2$O$_8$ (KPS, E923) is one of the strongest oxidants used in an aqueous solution and has a higher reduction potential (E° of S$_2$O$_8^{2-}$/SO$_4^{2-}$ = 2.01 V) than that of H$_2$O$_2$ (E° of H$_2$O$_2$/H$_2$O = 1.76 V) [37]. It offers some advantages over other oxidants as a solid chemical at ambient temperature with ease of storage and transport, high stability, high aqueous solubility and a low cost [25]. It has great capability for degrading numerous organic contaminants through powerful free radical oxidants as SO$_4^{•-}$ and OH$^•$ which are generated in the persulfate system [38]. To enhance further the oxidation strength KPS may be activated in order to produce sulfate radicals (SO$_4^{•-}$) of a higher standard reduction potential (E° = 2.6 V) capable of acting as a much stronger oxidant towards organic contaminants [39]. Persulfate activation can be accomplished by heat [40, 41], UV irradiation [42] and reactions with transition metals (Eq. (2)) [43, 44]. These activation mechanisms are well described.

$$S_2O_8^{2-} + (heat, UV, OH^-) \rightarrow 2SO_4^{•-} \quad (1)$$

$$S_2O_8^{2-} + 2M^{n+} \rightarrow 2SO_4^{•-} + 2M^{(n+1)+} \quad (2)$$

$$2S_2O_8^{2-} + 2H_2O + OH^- \rightarrow 3SO_4^{•-} + SO_4^{2-} + O_2^{•-} + 4H^+ \quad (3)$$

Strong alkaline pH has also been used [22, 45] to activate KPS (Eq. (3)). The sulfate radicals obtained are very reactive in aqueous solution, as they can initiate a cascade of reactions [45] leading to the formation of other oxidants.

![Structurally similar triphenylmethylene dyes with either an amine or oxide group stabilizing the triphenylmethyl cation by resonance.](image-url)
(H₂O₂) and other radicals like hydroxyl radical (E° = 2.7 V) and hydrogen peroxide, as shown in Eqs. (4 - 6):

\[
\begin{align*}
SO_{4}^{2-} + H_2O & \rightarrow HO^+ + HSO_4^- \\
SO_{4}^{2-} + OH^- & \rightarrow HO^+ + SO_3^{2-} \\
2HO^+ & \rightarrow HOOH
\end{align*}
\]

The addition of persulfate to colored foods causes alteration of the food color as well as undesirable reactions with time. The purpose of this work is to investigate the parameters that influence Acid Blue 1 discoloration by K₂S₂O₈. The parameters studied refer to the concentration of the food colorant and the oxidant, the solution pH, the presence of Fe (II), the matrix effect, and the temperature. The UV-VIS absorption spectra obtained and the pathway of AB1 discoloration will be compared with those of some other triphenylmethane dyes (Fig. 1).

**EXPERIMENTAL**

**Materials and analytical procedures**

The food colorant Acid Blue 1 (AB1) was used as purchased from Sigma Aldrich (C₁₂H₁₅N₂O₃SNa, purity of 50 %, molecular mass of 565.67 g). Na₂SO₄ and NaCl were the main inorganic salts in the food colorant as confirmed by an ionic chromatography analysis. The other chemical reagents used were of analytical grade. Dilute solutions of AB1 were prepared from an initial solution (40 mg/L) aiming to draw a calibration curve. Solutions of 1 M KCl were prepared to study the effect of the ionic force on the discoloration rate constant. A solution of 10⁻² M Fe (II) in 10⁻² M H₂SO₄ was prepared to study iron catalytic effect on AB1 discoloration rate.

The kinetic study of AB1 discoloration by KPS was carried out on a double beam spectrophotometer, Specord 200 (Analytical Jena). The relation found between the absorbance at 640 nm and the mass concentration of AB1 was \(A_{640} = 0.07x\) [AB1] (mg/L) with \(R^2 = 0.999\).

HPLC analysis was performed using a RP-C18 stationary phase and a mobile phase composed of 50 % methanol and 50 % H₂O (or 25 mM aqueous (NH₄)₂SO₄, the flow rate was 1 ml/min, while the injection volume was 20.0 µL [9].

**Method of discoloration**

The kinetic study aiming to determine the reaction order with respect to AB1 was carried out in the presence of a large excess of persulfate: \(x\) ml of 40 mg/L (7x10⁻⁵ M) of the AB1 (4 ≤ \(x\) ≤ 7) was added to a mixture of 5 ml of 0.1 M persulfate and (7- \(x\)) ml of H₂O (the total volume of the solution was 12 ml). The reaction order with respect to persulfate was determined in the presence of different excess amounts of KPS: \(x\) ml of 0.1 M persulfate (3 ≤ \(x\) ≤ 6) were added to 5 ml of AB1 40 mg/L and (7- \(x\)) ml of H₂O (the total volume of the solution was 12 ml). The UV-VIS spectrum of the solution was recorded at a predetermined time defined by the absorbance at 640 nm – it had to be less than 0.1. The rate of the discoloration reaction first step (referring to change of color from blue to yellow) was expressed by:

\[
\text{Rate} = k \times [S_2O_8^{2-}]^m [\text{AB1}]^n = k_{obs} \times [\text{AB1}]^n
\]

where \(k\) was the rate constant, \(m\) and \(n\) were the pseudo orders of the reaction with respect to AB1 and KPS, respectively. The absorbance (A) at 640 nm was proportional to the concentration of AB1. Thus, the slope of the function \(A_{640}\) vs. time defined \(k_{obs}\).

The effect of pH on the discoloration rate (the change of color from blue to yellow) was studied by replacing water with dilute solutions of H₂SO₄ (10⁻⁴ M to 1 M) or NaOH (10⁻³ M to 0.1 M). The effects of Cl⁻, and Fe(II) on the rate constant were followed using solutions containing different concentrations of the ions mentioned.

Some experiments were repeated under softer conditions aiming a comparison. The initial standard solution used was either 10⁻² M or 10⁻³ M in respect to persulfate.

**RESULTS AND DISCUSSION**

**The UV-VIS absorption spectra**

The UV-VIS spectrum of AB1 shows three absorption bands with maxima at 312 nm, 412 nm and 640 nm (Fig. 2a). There is a relatively rapid depletion with time of the characteristic absorption band responsible for the blue color (around 640 nm, \(\pi\rightarrow\pi\) transition of C=N) (Fig. 2a) in case of a high concentration of KPS, hard oxidation conditions (equal volumes of 20 mg/L of AB1 and 0.1 M of KPS, pH ~ 3.5). Meanwhile, the second band at 412 nm shows an initial slow decrease accompanied by appearance of shoulders in the range 334 nm - 404 nm and 422 nm - 490 nm slightly increasing with time (Fig. 2a). The evolution of AB1 UV-VIS spectrum differs from the absorbance decrease and bathochromic shift...
(from 435 nm to 475 nm) observed with the oxidative degradation of MG by KPS (Fig. 2b). It is also not similar to the variation of UV-VIS spectrum observed with CV and KPS, which shows a new absorbance peak at 470 nm disappearing with time [44].

These results differ from those referring to the reaction of the commercial E131 V with KPS [46] which brings about decrease of all absorbance peaks without any shift in their wavelength. We may only conclude that despite the very light variation in the functional groups of the aromatic rings of these triphenylmethyl dyes, the evolution of the spectra varies greatly with each dye due to the different mechanism of their degradation/discholoration.

The same reaction proceeding at a lower concentration of KPS, i.e. under soft oxidation conditions (equal volumes of 40 mg/L of AB1 and 0.01 M of KPS), is slow enough to accumulate intermediates and hence to monitor the formation of differently colored species. It is clear that the second band responsible for the yellow color broadens and the absorbance at 412 nm actually increases right after mixing with KPS (Fig. 2c); it starts eventually to decrease very slowly with time. The same results are obtained when the concentration of KPS is decreased further to 10^{-3} M. The disappearance of the yellow intermediate is proportional to the concentration of KPS. The rate of absorbance decrease at 640 nm is faster than that at 412 nm, irrespective of KPS concentration. The absorbance at 312 nm, which refers to the aromatic content, becomes weaker with time. The spectrum of AB1/KPS (0.1M) in a basic medium (pH ~9) shows also a decrease of A_{640} with time (fading of the blue color), but it is accompanied by a bathochromic shift of the max.

Fig. 2. (a) UV-VIS spectra of AB1 solution during the discoloration by KPS (hard oxidation conditions), 10 mL of 20 mg L^{-1} AB1 +10 mL of 0.1 M KPS, pH 3.5 at 296K, duration 12 min; (b) UV-VIS spectra of MG and 0.1 M KPS; (c) UV-VIS spectra of AB1 solution during the discoloration by KPS (soft oxidation conditions), dashed blue line: just after mixing of 10 mL of 40 mg L^{-1} AB1 with 10 mL of 0.01 M KPS; red dashed line: mixture after 1 h; (d) UV-VIS spectra in basic medium, 5 mL NaOH, 5 mL AB1 40 mg L^{-1} + 5 mL KPS 0.1 M, duration 17 min.
wavelength from 640 nm to 654 nm, and an increase in the 424 nm - 538 nm range (Fig. 2d).

One can appreciate the color changes occurring in AB1/KPS solution irrespectively of the dye or KPS concentration. The solution turns initially green just after the addition of KPS (Fig. 3a) due to: (i) decrease of the mixture pH, and (ii) a reaction with KPS. Then the solution turns yellow (10 min with 0.1M KPS), and finally it turns slowly transparent (~ two days at 298 K). The yellow color of AB1/KPS mixture does not simply correspond to the acidic form of AB1, via diethylamine protonation or protonation of the sulfonate groups of the aromatic ring. This is verified by the shape of the band at 412 nm (Fig. 2b) and the fact that the addition of NaOH changes the yellow color back to blue. The latter reaction gives a spectrum different from that of the AB1 solution (with maxima at 375 nm and 654 nm) indicating a different compound presence. Thus it can be concluded that the yellow intermediate has acid-base properties like AB1, but it is not simply protonated AB1. The blue solution, which re-appears, becomes transparent with time; besides, NaOH addition to this transparent solution (the fourth cell in Fig. 3a) does not turn it blue.

In general, most of the triphenylmethane dyes, as those in Fig. 1, show (in presence of 0.01 M KPS), either one or several isobestic points in their UV-VIS spectra (see Table 1) and an absorbance increase in some ranges of the spectrum during the initial period of the reaction of the dye with KPS [44]. This indicates that the first step in the attack of KPS leads to the formation of one or more intermediates with only a small change in the structure of the dye. The spectrum of AB1/0.01M KPS (Fig. 2c) shows several isobestic points at 288 nm, 336 nm, 404 nm, 422 nm and 486 nm (Table 1), i.e. it very similar to that of Bromothymol Blue/KPS.

MG does not turn yellow with time when compared to 0.01 M of KPS, but several isobestic points are outlined (Table 1). However, no isobestic points are observed in 0.1 M KPS/MG but a bathochromic effect (shift from 438 to 472 nm) is outlined (Fig. 2c) accompanied by the appearance of a yellow color intermediate. On the other hand, CV in presence of 0.01M KPS does not show any isobestic point or a yellow color intermediate. But a shift in the max wavelength ranging from 594 nm to 582 nm is observed. Our previous study referring to CV/

Table 1. The Spectroscopic data about the behavior of some triphenylmethane dyes with 0.01 M KPS. Phenolphthaleine (PHP).

<table>
<thead>
<tr>
<th>Dye</th>
<th>λ_{max} (nm)</th>
<th>Isobestic points (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB1</td>
<td>640</td>
<td>288  336  404  422  486</td>
</tr>
<tr>
<td>BTB</td>
<td>620</td>
<td>292  328  378  426  472</td>
</tr>
<tr>
<td>PHP</td>
<td>554</td>
<td>314  368  402  428   ---</td>
</tr>
<tr>
<td>MG</td>
<td>618</td>
<td>334  386  452  505   ---</td>
</tr>
<tr>
<td>CV</td>
<td>570</td>
<td>---  ---  ---  ---   ---</td>
</tr>
<tr>
<td>E131*</td>
<td>616</td>
<td>---  ---  ---  ---   ---</td>
</tr>
</tbody>
</table>

*: Commercial E131 (Naser Elddine et al., 2015)
KPS (0.05M standard solution) does not show isobestic points after 800 s of discoloration, but points to the appearance of a new absorbance band in the yellow color region (470 nm) [44]. It seems that the appearance of the yellow color is determined by the concentration of KPS which affects the pH of the solution. It is so because the yellow compound has acid-base properties and its visible appearance depends on the dye/intermediate pKa(s).

These spectral changes reveal that the discoloration of AB1 and other triphenylmethane dyes can be accomplished with KPS (under soft and hard oxidation conditions) in acidic and basic media with formation of different intermediates depending on the dye/KPS concentration ratio and solution pH. This result is in agreement with Gennaro et al. [18] who show that the intermediates formed during the oxidative degradation of the food dye Brilliant Blue depend on the dye/KPS ratio. The evolution of the spectra varies greatly with each dye despite the slight difference in their structure. There is no obvious trend relating the concentration of KPS to the spectral changes (nor to the mechanism of discoloration), but discoloration is occurring in a step-wise fashion irrespective of KPS concentration with intermediate(s) not varying much from of the original dye structure. Besides, there is no consent in respect to discoloration mechanism steps.

**TLC and HPLC analyses**

The mixture (AB1+ KPS) becomes yellow after 15 min, and shows the presence of two spots on the TLC. They correspond to two compounds, both turning blue on silica gel. The first one corresponds to AB1 ($R_f=0.12$), while the second one refers to a compound with $R_f=0.68$. The first spot disappears with time, but the second remains. The spot corresponding to AB1 disappears completely after 1 h. Then another spot appears at a higher level ($R_f=0.72$) after 2 h. The spot at $R_f=0.68$ disappears completely after 10 h but that of $R_f=0.72$ remains. Since water is the mobile phase, AB1 is the least polar compound when compared to the other intermediates. The reaction seems to go through two steps, with the first intermediate being less polar than the second.

### Table 2. Variation of TOC values of AB1 solutions before and after treatment with KPS.

<table>
<thead>
<tr>
<th>Vol. of KPS</th>
<th>Vol. of AB1</th>
<th>Initial TOC mg/L</th>
<th>Final TOC* mg/L</th>
<th>% decrease of TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml 0.1 M KPS</td>
<td>10 ml of 20 mg/L</td>
<td>8.86</td>
<td>5.76</td>
<td>35</td>
</tr>
<tr>
<td>10 ml 0.1 M KPS</td>
<td>10 ml of 40 mg/L</td>
<td>18.78</td>
<td>15.19</td>
<td>19</td>
</tr>
<tr>
<td>10 ml 0.1 M KPS</td>
<td>10 ml of 60 mg/L</td>
<td>27.5</td>
<td>24.5</td>
<td>11</td>
</tr>
</tbody>
</table>

* Value of TOC after 1 week of mixing of AB1 solution with KPS solution

Fig. 4. (a) Effect of the initial concentration AB1 on the rate constant. x ml of 40 mg L$^{-1}$ of AB1 (3 ≤ x ≤ 6), 5 ml of 0.1 M KPS (total vol. 12 ml) pH ~ 3.5, at 293 K; (b) Pseudo order with respect to persulfate (KPS) x ml of 0.1 M KPS (3 ≤ x ≤ 6), 5 ml of 40 mg L$^{-1}$ AB1 (total vol. 12 ml), at 293 K.
one after 2 h. The attempt to isolate the intermediate and the product and identify them by NMR and IR failed.

HPLC is carried out aiming to identify the discoloration/degradation intermediates. The standard solution of AB1 is detected only with a mobile phase containing 50 % H2O (or a solution of ammonium acetate) and 50 % methanol. The calibration curve of AB1 (5 < [AB1] (mg/L) < 20) shows 130.45 [AB1] (R²: 0.985), and 31.67 [AB1] (R²: 0.985) at 640 nm and 350 nm, respectively. The conditions of the experiment do not allow the detection of any reaction intermediate even in other quantity or in presence of a mobile phase gradient as mentioned by Chen et al. [9].

### TOC analysis

TC value of 0.1 M KPS and 0.01 M KPS are zero. TC and TOC of several solutions of AB1 are similar (no inorganic carbon is present in these solutions). The calibration curve of TOC as a function of AB1 concentration gives the linear relation TOC (mg/L) = 0.95x[AB1](mg/L) with R² = 0.998. The variation of TOC values prior to and after treatment with KPS is given in Table 2. The TOC % value decreases with increase of AB1 concentration in the mixture. Since the maximum TOC decrease refers to 35 %, it appears that KPS provides a partial degradation of AB1, but not its total mineralization [18].

### Reaction order with respect to AB1

The concentration of KPS in the mixture is in large excess with respect to the food colorant AB1. The variation of Aν(λν) as a function of time gives an exponential curve. It is concluded that the reaction is a pseudo-first order as R² value is greater than 0.99 (Fig. 3b). Order zero and two are rejected, since R² value is less than 0.9 in both cases. Similar results are reported [8, 11, 46] for malachite green and the commercial food colorant E131.

### Effect of pH

The food colorant AB1 is yellow in an acidic medium (λmax = 412 nm) and blue in a basic medium (λmax = 640 nm). The overlay of the spectra recorded at several pH values shows several isobestic points (280 nm, 334 nm, and 506 nm). The molar coefficient at 640 nm is higher than that at 412 nm (Fig. 2a). The pKa of the amino group is determined experimentally (pKa = 2.2) according to the relation:

\[
pH = pK_a + \log \frac{A_{\text{pH}} - A_{\text{acide}}}{A_{\text{base}} - A_{\text{pH}}}
\]

Indeed, the rate of AB1 discoloration/degradation by KPS is effective over a broad range of pH. Under acidic condition the formation of sulfate free radicals can be catalyzed by protons as shown [47] by the equations below:

\[ S_2\text{O}_8^{2-} + H^+ \rightarrow HS_2\text{O}_8^- \quad (7) \]

\[ HS_2\text{O}_8^- \rightarrow SO_4^{2-} + SO_2^{2-} + H^+ \quad (8) \]

Thus, the optimal pH to form SO₂⁻ refers to the case when most of S₂O₈²⁻ is in HS₂O₈⁻ form. The acidic form of persulfate (H₅S₂O₈) can also yield Caro’s acid (H₇S₂O₉), which hydrolyzes further to H₂O₂ [22].

So, the oxidizing agent from KPS (SO₄⁻⁺, OH⁻, H₂O₂) and the chemical structure of the dye (the amine group of AB1 may be protonated) will both vary with pH. The solution of 0.1 M KPS is not neutral. Its pH is less than 4. The pH value of the mixture containing 5 ml of 40 mg/L of AB1 + 5 ml of 0.1 M KPS is ca 3.5. In acidic medium (pH < 1), the discoloration rate is very slow. In the range of pH 1 < pH < 3.5, the increase of pH increases the food colorant discoloration rate to reach a
maximum at pH 3. It decreases with further pH increase (Fig. 5). The food colorant discoloration is observed in a very basic medium even in absence of KPS, likely due to OH nucleophilic attack of the triphenylmethyl cation, forming a carbinol derivative. Nonetheless, the presence of KPS speeds up this discoloration. The mechanism of AB1 discoloration is different from that at pH > 5. There is a decrease in the whole visible spectrum without any increase in the absorbance in the region between 400 nm and 500 nm. The highest rate is obtained near pH of 3.

**Mechanism of discoloration**

ZnO-mediated processes of AB1 photocatalytic degradation pattern has been studied [9] in detail and the intermediates identified by HPLC-PDA-ESI-MS and GC-MS techniques. Reverse-Phase HPLC-MS has been applied to identify [18] the degradation intermediates of Brilliant Blue by KPS. LC-ESI-MS has been used to identify [24] the degradation pattern of Malachite Green with KPS. These studies, which attempt to propose a mechanism for photocatalytic or oxidative degradation of a particular triphenylmethane dye, seem to provide a stereotype support for (i) the formation of one or more intermediates including N-dealkylated primary and secondary aromatic amines; (ii) the formation of a complete deamination product; (iii) a loss of an aryl ring; (iv) hydroxylation of the aryl ring(s) and sulfonylated benzene ring; (v) hydroxyl substitution of the sulfonate groups and sulfate adducts. Some authors propose that the faded dye is the Michler’s ketone formed by the hydrolysis reaction of C=NH₂⁺ group to C=O along with a loss of an aromatic group [24]. Other authors suggest a loss of resonance conjugation between the aromatic rings [18].

Sulphate and hydroxyl radicals generated by ISOC of K₂S₂O₈ could generate such a variety of even more reactive intermediates in course of their reaction with dyes that the identification of all intermediates by mass spectrometry is not always possible. We believe that unless the dye degradation intermediates are stable enough to be separated, purified and identified (by NMR and MS), it will be difficult to undoubtedly prove a definitive mechanism of the process. Nonetheless, by combining UV-VIS, TOC and TLC results, as well as the effect of pH on the reaction of AB1/KPS, and comparing them to those referring to other triphenylmethane dyes, a mechanism which fits the data and is reasonable for free radical reactions may be proposed. At this point we have no doubt that oxidative degradation by KPS does not lead to total mineralization of neither AB1 nor any of the triphenylmethane dyes which we have previously studied [44, 46]. This is indicated by the low decrease of TOC values, which means that despite the complete discoloration of AB1, E131V, MG, CV with KPS, much of the organic species remains intact.

The mechanism of discoloration/degradation of AB1 is pH dependent. Besides, the decrease in UV-VIS absorbance is accompanied by isobestic points appearance. This means that the discoloration occurs stepwise, but

Scheme 1. Proposed mechanism of discoloration of AB1 by KPS: hydroxylation (by addition or substitution) of one or more aromatic ring(s), followed by carbinol derivative formation.
not necessarily simultaneously, and with a little change of AB1 structure. It is well recognized that the decrease in absorbance does not necessarily mean elimination of auxochromes (deamination) or breakdown of the whole chromophore (degradation of the aryl ring). Discoloration may be due to formation of a leuco form of the dye (oxidation of the amines, de-alkylation of the amines, hydroxylation of the ring) followed by hydroxide attack on the central triphenylmethyl carbon (cation or radical) \[18, 46\]. In case of AB1, there is evidence of formation of such leuco intermediates, and eventual break-up of the resonance conjugation between the aromatic rings through a hydroxide attack leading to an uncolored product.

N-de-ethylation of the amine prior to cleavage of AB1 conjugated chromophore structure has been proposed \[9\] whenever hypsochromic shifts are observed in the characteristic absorption band in the UV-VIS spectra. In case of MG and CV, total deamination of formation of a triphenyl-carbocation is proposed as the yellow intermediate (\(\lambda \sim 445\) nm). Absorbance shifts are not observed in this study referring to oxidative degradation of AB1 or E131V with KPS at lower pH. This means that the results obtained support neither N-dealkylation nor deamination. Gosetti et al. have also no evidence of N-de-ethylation of Brilliant Blue FCF.

In our previous study \[46\] using commercial E131 V and KPS we have suggested the formation of a triphenylmethyl radical derivative (pale yellow) by OH\(^+\) oxidation of the quaternary aromatic diethylamines to amine-N-oxide or oxidation by hydrogen peroxide eventually forming a yellow trityl cation derivative. The present study referring to AB1/KPS in a basic medium provides no support for N-de-ethylation since bathochromic shifts are accompanied by absorbance decrease at \(\lambda_{640}\). Hence, it seems probable that the degradation studied proceeds, as in our previous proposal \[46\], via amines oxidation. However, the mechanism differs in an acidic medium (pH \(< \text{pK}_{a} = 2.2\)). Since oxidation of the leuco forms of AB1 (ammonium groups instead of free amine groups) is not be possible, and there is no spectral support for N-de-ethylation (no shifts), we suggest aromatic ring(s) hydroxylation as shown in Scheme 1. Such a mechanism is comparable to that proposed by Gosetti et al. \[18\]. According to the TLC results the hydroxylation of one/or more of the aromatic rings (Scheme 1) gives an intermediate more polar than AB1. Such an intermediate will have acid-base properties (\(\text{pK}_{a}\) of aromatic hydroxyl \(\sim 9.5-10\)) which differ from those of the original AB1. This also fits the results obtained. Substitution of a sulfonate may also take place (Scheme1) instead of hydroxyl addition. This is supported by the fact that gas bubbles, likely to be SO\(_2\), are observed during the discoloration. Also, any of these hydroxylated intermediate(s) is likely to accumulate in the solution since the OH group is a donor stabilizing the triphenylmethyl cation (supported by the increase in absorbance at 412 nm and its slower disappearance with time). We have previously proposed that the complete discoloration of E131 V occurs through formation of a carbinol derivative by either the addition of OH\(^-\) to the central triphenylmethyl radical, or by nucleophilic attack of OH\(^-\) (or H\(_2\)O) on the central triphenylmethyl cation. We stick to this suggestion in case of AB1 as the reaction pointed above is faster in a basic medium and slower in an acidic one. Furthermore, the formation of a carbinol derivative will break up the conjugation between the aromatic rings leading to complete discoloration of the dye. These concepts are in agreement with the discoloration mechanism proposed by Gosetti et al. \[18\] for oxidative degradation of Brilliant Blue by KPS.

**Effect of chloride and Fe (II) presence**

The reduced effectiveness of ISCO of activated persulfate is due to reactions between the produced radicals and non-target chemical species present in food, soil and aquatic material. These reactions are often referred to as scavenging reactions. Chloride ions and carbonates have the potential to impact the pathway, the kinetics,
and the efficiency of the oxidation reactions both as radical scavengers, and metal complexing agents. Chloride ions can rapidly react \cite{48, 49} with sulfate radicals, as shown in the reactions below:

\[ \text{SO}_4^{2-} + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{Cl}^- \]

\[ \text{OH}^- + \text{Cl}^- \rightarrow \text{ClO}^- + \text{H}_2\text{O} \]

Thus they can slow down or inhibit the oxidation of the organic targets. Indeed, the addition of KCl to AB1/KPS decreases the rate constant, but the effect is lower than expected, probably due to the fact that the purchased compound contains 50% of the inorganic salts (sulfate and chloride).

The chemical oxidation of organic pollutants by persulfate can be accelerated by metal ion activation through enhancing sulfate radical generation, as shown in reaction (2). Cu (II) and Fe (II) are shown to enhance oxidation efficiency of organic dyes. There is neither discoloration, nor change in the UV-VIS spectrum after the addition of Fe(II) to the AB1 solution. Thus, no reaction takes place between Fe (II) and AB1. The addition of Fe(II) to the mixture (AB1+ KPS) increases the discoloration rate. The discoloration of 5 ml of 40 mg/L AB1 + 5 ml 0.1 M KPS in the presence of 1 ml of 0.1 M Fe(II) added (Total volume: 15 ml).

Table 3. The thermodynamic activation parameters associated with the discoloration of AB1 (same conditions as in Fig. 6).

<table>
<thead>
<tr>
<th>Condition</th>
<th>(E_a) (kJ/mol)</th>
<th>(\Delta H^#) (kJ/mol)</th>
<th>(\Delta S^#) (kJ/mol.K)</th>
<th>(\Delta G_{298}^#) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Fe(II)</td>
<td>31.85</td>
<td>45.1</td>
<td>-0.195</td>
<td>103.2</td>
</tr>
<tr>
<td>With Fe(II)</td>
<td>47.5</td>
<td>29.7</td>
<td>-0.140</td>
<td>71.42</td>
</tr>
</tbody>
</table>

Fig. 6. (a) Variation of the absorbance \(A_{640}\) as a function of time at different concentration of Fe(II), 5 ml 40 mg L\(^{-1}\) of AB1 + 5 ml of KPS 0.05 M + x ml of acidic solution of Fe(II) \(10^{-3}\) M (0 ≤ x ≤ 5) (increasing x from top to down, ♦ 0 ml Fe(II)), at 293 K (Total volume: 15 ml); (b) Variation of the discoloration rate constant of AB1 by KPS as a function of the volume of \(10^{-3}\) M Fe(II) added (Total volume: 15 ml).

Fig. 7. Arrhenius plot of \(\ln k_{obs}\) as a function of \(10^3/T(K)\) (□ with Fe(II), ■ without Fe(II))

5 ml of AB1, 40 mg L\(^{-1}\) + 5 ml of KPS 0.05 M + 5 ml of Fe(II) \(10^{-3}\) M

5 ml of AB1, 40 mg L\(^{-1}\) + 5 ml of KPS 0.05 M + 5 ml H\(_2\)O.
M Fe (II) is very fast. That is why lower concentrations of Fe (II) and KPS have to be used (Fig. 6a). The rate constant increases with increase of Fe(II) concentration to reach a plateau (with 10⁻³ M KPS, Fig. 6b). The reaction order in respect to AB1 remains one. The absence of any isobestic points and the absorbance decrease in the whole visible spectrum determine the main difference observed in presence of Fe (II).

**Effect of temperature**

Temperature increase increases the degradation rate of the food colorant AB1 in presence of KPS. Fe(II) increases the discoloration rate constant but also increases the activation energy (Fig. 7). So Fe(II) does not play the role of an active catalyst. It is rather a passive catalyst since Fe(II) increases only the number of SO₄⁡ᵣ⁻, which is the principal reactant. The activation parameters associated with the discoloration are calculated as follows: plot of ln kₐ(obs) vs. 1/T gives the value of the activation energy (Eₐ) according to the Arrhenius equation:

\[
\ln k_{obs} = -\frac{E_a}{R} \times \frac{1}{T} + \text{cte} \quad \text{with } R : 8.31 \text{J} / \text{K.mol}
\]

The values of ΔH*, ΔS* and ΔG* values are determined on the ground of the two equations:

\[
\ln\left(\frac{k_{obs}}{T}\right) = (\ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^*}{R}) - \frac{\Delta H^*}{R \times T},
\]

\[
\Delta G^* = \Delta H^* - T \Delta S^* \quad \text{(ln (k_B/h) = 23.76)}
\]

The values of the activation energy and the others kinetics parameters obtained in the temperature range studied (16°C - 36°C) are listed in Table 3.

**CONCLUSIONS**

The discoloration of the food colorant AB1 by persulfate is effective, but its total mineralization is not achieved. The first step of the process (the color change from blue to yellow) is pseudo-first order with respect to AB1 and to persulfate. The speed of discoloration increases with increase of the temperature and KPS concentration. A drastic increase is observed after addition of Fe (II). The discoloration is slower with increase of AB1 concentration. The rate constant increases with pH increase to reach a maximum at pH ~ 3.

The presence of persulfate as an additive in colored food leads progressively to its discoloration. The colored intermediates formed during UV/KPS oxidation processes could not be decisively identified in this study, but mechanisms of AB1 discoloration are advanced. A thorough investigation on intermediates formation mechanism is required. The conditions for further degradation of the skeletal structure of triphenylmethane dye (phenyl degradation) or complete mineralization by in situ chemical oxidation (ISCO) using KPS are still not identified. Toxicity studies of the degraded intermediates have to be undertaken in choosing strategies for dyed food and waste-water remediation as the discolored product may be more toxic and harmful to us and to the environment than the dye itself.

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