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and

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*15th International Conference on
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APPLICATION OF QUANTUM CHEMICAL CALCULATION IN DEFINING PEAKS IN UV-VIS SPECTRA OF OXIDATIVE TARTRAZINE DEGRADATION

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ABSTRACT

Degradation of tartrazine in presence of cobalt activated Oxone[®] (potassium peroxymonosulfate) was investigated. Aluminium pillared clay acted as a support for catalytically active Co²⁺. Oxone[®] was a precursor of SO₄^{•-} radical anions. Along with decolorization of tartrazine solution, the degradation of tartrazine and formation of oxidation products was monitored using UV-Vis spectroscopy. Quantum chemical calculations were performed in order to predict UV-Vis spectra. Different models were tested, and the results of calculation have shown that the combination of TPSS-D3 method and aug-cc-pVDZ basis set is quite satisfactory level of theory. The experimentally obtained peaks that arose during degradation were identified using this method.

INTRODUCTION

Catalytic oxidative degradation in the presence of sulfate radical anions (SO₄^{•-}), has received much attention recently [1]. Oxone[®] (KHSO₅·0.5·KHSO₄·0.5·K₂SO₄) has been widely utilized as a source of HSO₅⁻ ions that yield into SO₄^{•-} radical anions. In order to be efficient, the Oxone[®] should be activated. In our previous work, pillared montmorillonite impregnated with cobalt, was found to be efficient catalyst in catalytic oxidation of tartrazine in the presence of Oxone[®] [2]. The process was monitored using UV-Vis spectroscopy. It was found that changes in UV-Vis spectra were the result of tartrazine decolorization as well as formation of oxidative products. In this paper quantum chemical calculation were applied in order to assign newly formed peaks in UV-Vis spectra to defined products of tartrazine degradation.

EXPERIMENTAL

The 2 μm fraction of clay rich in montmorillonite was pillared with aluminium, impregnated with cobalt. The obtained catalyst was fully characterized [2]. The catalytic test was performed by stirring (300 rpm) tartrazine solution (C₀ = 50 mg dm⁻³) in the presence of 0.130 mmol Oxone[®] and 10 mg of catalyst [2]. The experiments were conducted at 50 °C at unadjusted pH (pH = 3.6). The sampling was performed at a predetermined periods of time (5, 10, 20, 30, 60, 120 and 240 min). The supernatant was separated from the catalyst by centrifugation and the obtained solution was monitored by using UV-Vis spectrophotometry (Thermo Scientific Evolution 220 UV-Vis Spectrophotometer).

All theoretical calculations were performed with the Gaussian 09 program package [3]. Structures of all investigated tartrazine forms were optimized with Density functional theory (DFT), by using the TPSS-D3 functional and 6-31g basis set. Time dependent density functional theory (TD-DFT) has been employed to compute the absorption spectra. To determine the level of theory which achieves the best agreement of experimental with calculated UV-Vis spectra, several functionals (cam-B3LYP, M06-2X, and TPSS-D3) and two basis sets (aug-cc-pVDZ and def2-TZVP) were used.

The calculations were performed using restricted formalism, the tight convergence criteria and without any symmetry constraints. The effect of water, as solvent, was simulated using the Solvation Model based on Density (SMD).

RESULTS AND DISCUSSION

Experimentally obtained UV-Vis spectra after selected reaction times are given in Figure 1a. The only change in spectra of starting solution (0 min) up to 60 min of reaction, was diminishing of the characteristic peaks at 257 nm and 426 nm. Besides these changes, a new peak at 231 nm appeared after 120 min of reaction, Later on, after 240 min of reaction the intensity of this peak decreased along with formation of another additional peak at 275 nm.

The possible reaction pathways were analyzed in order to estimate the origin of 231 nm and 275 nm peaks. Afterwards, for each potential product of the reaction, the theoretical UV-Vis spectra obtained by quantum chemical calculations were established (Figure 1b).

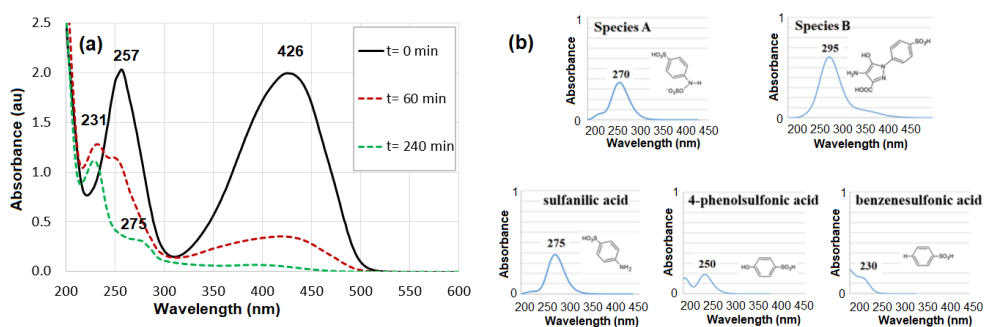


Figure 1. Experimental UV-Vis spectra for degradation of tartrazine (a) and calculated UV-Vis spectra of its oxidation products (b).

In the proposed mechanism $\text{SO}_4^{\cdot-}$ radical anion attacked the N atom of the azo group of tartrazine bonded to the benzene ring, producing a sulfate tartrazine derivative. Degradation started with the azo bond cleavage by $\text{SO}_4^{\cdot-}$ radical anion [4] (Figure 2). In this manner, two products were formed: sulfanilic acid derivative (species A) and the derivative of benzenesulfonic acid with pyrazole ring as substituent (species B).

After NH_3 and CO_2 release from species B and degradation of pyrazole ring, the sulfanilic acid might be formed. Further degradation sulfanilic acid can lead among other products into formation of 4-phenolsulfonic and benzenesulfonic acid. In calculated spectra of species B the peak was estimated at 300 nm. This peak was not pronounced in the experimental spectra, indicating the fast degradation of this product. The spectra of species A and sulfanilic acid have peaks at 270 nm and 275 nm, respectively. Therefore, the experimentally obtained peak at 275 nm can be assigned to these two species. The occurrence of the peak at 230 nm could be assigned to 4-phenolsulfonic and benzenesulfonic acid since they showed peak at around 230 nm in calculated spectra.

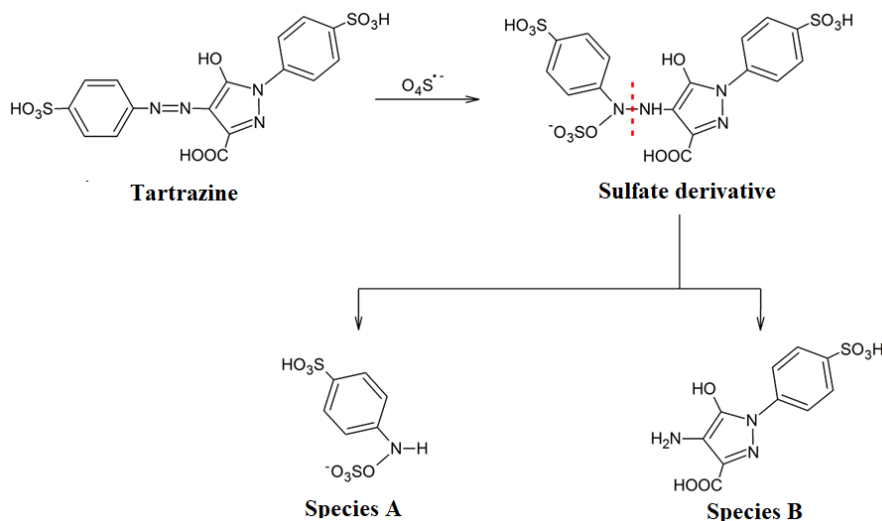


Figure 2. The first step of main reaction path of tartrazine degradation i.e. the azo bond cleavage.

CONCLUSION

Oxidative degradation of tartrazine by $\text{SO}_4^{\bullet-}$ radical anions was monitored by UV-Vis spectroscopy. In the first period of the reaction (up to 60 min) the only registered change in spectra was diminishing of the tartrazine originated characteristic peaks at 257 nm and 426 nm. After 120 min and 240 min of the catalytic reaction additional peaks at 231 nm and 275 nm, respectively, were monitored. The possible reaction pathways were analyzed in order to estimate the origin of 231 nm and 275 nm peaks. For each potential product of reaction quantum-chemical calculations were performed and theoretical UV-Vis spectra were calculated. The combination of TPSS-D3 method and aug-cc-pVDZ basis set was found to be the most appropriate. Based on calculated UV-Vis spectra peak at 275 nm can be assigned to sulfanilic acid derivatives. On the other hand, peak at 231 nm can be the result of further degradation of derivative of the benzenesulfonic acid with pyrazole ring as substituent. The products of degradation for which the calculated UV-Vis spectra had maxima in vicinity of 231 nm were 4-phenolsulfonic and benzenesulfonic acid. The quantum chemical calculations have proven beneficial for the identification of the products of tartrazine degradation.

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