COPPER (II) CATALYZED OXIDATION OF 2-AMINOPHENOL IN AQUEOUS MEDIUM

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abstract: The kinetics of 2-aminophenol oxidation with oxygen from air catalyzed by several copper (II) compounds in aqueous medium was studied using a spectrophotometric method. The catalysts efficiencies in initial conditions were discussed in relation to their states in aqueous solution.

Introduction

The removal or neutralization of organic pollutants from waste waters is usually carried out by advanced oxidation using either strong oxidants like H_2O_2 or O_3 in the presence of high energy sources able to generate HO· or other reactive radicals, or wet air oxidation requiring elevated temperatures and pressures and/or catalysts. If the conventional strong oxidants are replaced by dioxygen from air, at ambient temperature and pressure, the process become simpler and cheaper. The molecular oxygen is however not significantly reactive in this conditions and it requires a catalytic activation.

The transition metal compounds can act as catalysts in many organic oxidation reactions [1]. Copper compounds especially, occupy a major place in oxidation chemistry due to their abundance in natural and biological media [2]. Because of its occurrence in many natural enzymatic processes, the interaction of molecular oxygen with copper in its different oxidation states was also a subject of numerous investigations [3]. The activation of dioxygen for aminophenols oxidation was less studied in the presence of copper (II) salts or its complexes. The oxidation of 2-aminophenol (OAP) to 2-amino-3H-phenoxazin-3-one (APX) in the presence of tyrosinase, a copper containing monooxygenase, is a well-known reaction [4, 5] used as model for the biosynthesis of the powerful antineoplastic agent, actinomycin D [6]. The presence of Cu (II) salts as catalysts in aerated wastewaters containing, OAP as a pollutant has a significant contribution to its natural conversion into less harmful compounds and consequently deserves an increased concern.

Previous work on copper-catalyzed oxidation of OAP [7] as well as studies on enzymatic oxidation [8] validates a model where the formation APX is preceded by the appearance of several active intermediates resulted in successive oxidation, conjugate addition, and tautomerisation reactions, some of them occurring without catalyst assistance. The overall

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stoichiometric equation for OAP oxidation is shown in Fig. 1. Our work provides a comparative study concerning the efficiency of some copper (II) salts and copper (II) complexes in the partial oxidation of OAP.
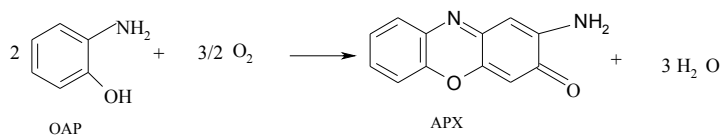

Fig. 1: *Overall equation of 2-aminophenol oxidation to 2-aminophenoxazinone*

The kinetic models reported in literature provide two pathways for *o*-quinone imine formation [7÷9]:

1. The mono-electronic oxidation of OAP (1) to phenoxy radical (2), followed by the disproportionation of radicals to *o*-quinone imine:
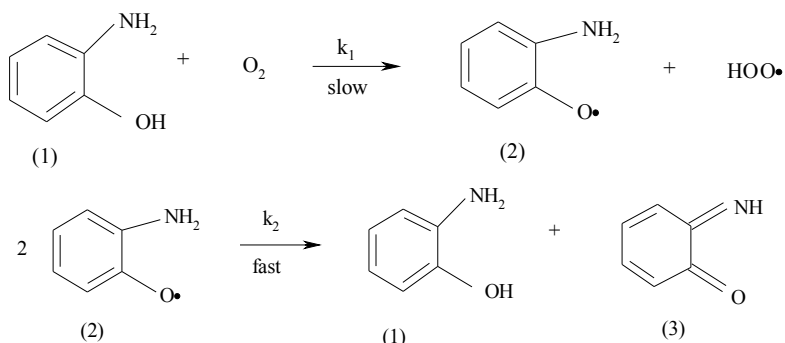

Fig. 2: *Formation of o-quinone imine, via phenoxy radicals*

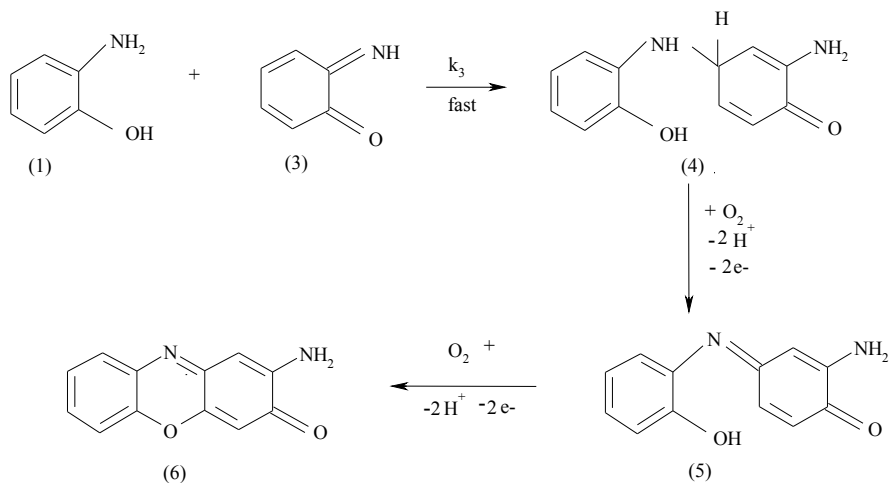The next steps consist in fast conjugate additions, oxidation and tautomerisations, yielding APX (6):

Fig. 3: *Formation of APX by "oxidative" cascade"*

It was shown that in the presence of oxygen from air, in saturated solution, the partial reaction order with respect to OAP is 1 and is also 1 with respect to oxygen [10] according to the proposed model. Earlier studies on cobaloxime-containing biomimic systems confirm the presence of phenoxy free radicals as key intermediates [11], suggesting that this model is realistic.

2. The bi-electronic oxidation of OAP directly to *o*-quinone imine represents the determining rate step. From this stage the reaction follows the pathway previously described. This model is supported by the studies on enzymatic oxidation in the presence of tyrosinase [4] and the chemical oxidation of OAP [12].

Materials and Methods

Materials: OAP was obtained from Aldrich Chemical Co. and APX was prepared according to literature methods [13]. UV-VIS spectra were measured on a JascoW530 spectrophotometer equipped with kinetic software. Argon from Linde was 99.9% and copper salts (II) were of the highest purity grade from Fluka. The glycine-copper (II) complex was prepared according to literature recipes [14, 15].

The oxidation was followed in a bubbling stirred semi-batch reactor using dioxygen from air as oxidizing agent and OAP as substrate in a 3.33 mM solution in the presence of copper chloride (1.66, 1.25, 0.83, 0.62, 0.42, 0.21 mM) at $pH = 4.50$, copper sulphate (1.66 mM) at $pH = 4.95$, copper acetate (1.66 mM) at $pH = 5.50$ and diglycine-copper chloride (0.83 mM) at $pH = 6.00$. The initial concentration of OAP, 3.33 mM, was chosen due to its low solubility in water and of the main reaction product. The air stream was passed through two thermostated saturation vessels containing water in order to avoid the evaporation of the solvent from the reactor. Under these conditions the solution was saturated with air. Kinetic assays were run at 30ºC. The stability of OAP in the absence of oxygen was verified by passing an argon stream through the solution, when no transformation of OAP was observed. APX formation was recorded at 434 nm ($\varepsilon = 23200$ cm$^{-1}\cdot$M^{-1} for APX) (Fig. 4). The pH of each reaction mixture, established after copper salt addition, was also monitored during the oxidation, but no significant variation was observed.
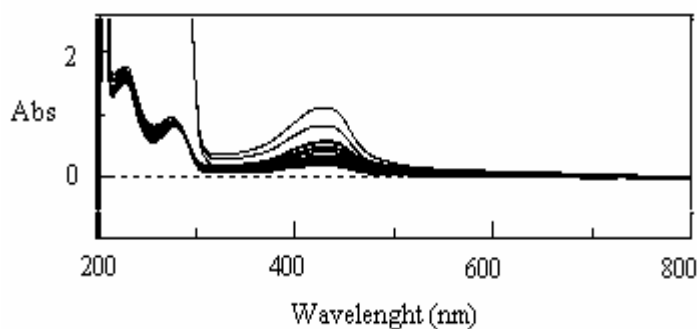

Fig. 4: *Electronic spectra recorded during the oxidation process*

Conditions: $[OAP]_0 = 5$mM, $[CuCl_2] = 1.66$ mM

Results and discussion

The chemical transformation of the substrate was studied by product (APX) analysis. Samples were removed from reactor at different time intervals and the spectra of the reaction mixture were scanned between 200 and 800 nm. The formation of the product can be followed at 434 nm, where the substrate has no absorption. The HPLC analysis of the reaction mixture indicated the formation of APX as the main product. The instant concentration of OAP was calculated from the mass balance. APX is formed through copper catalyzed oxidation of OAP to the *o*-quinone imine.

The experimental curves [OAP] *vs*. time in the presence of different copper catalysts show an increased efficiency of the copper chloride comparing to the other simple salts. The transformation rates in initial conditions (conversion 0.5 – 5%) were calculated from the slope of initial part of the curve [OAP] towards time. The rates of the catalyzed reaction were obtained by subtracting the rates of the non-catalyzed process. [16]. It was previously shown that the overall non-catalyzed process in air-saturated solution is a pseudo-first order one [10]. Consequently, the rate constants of the pseudo - first order processes (k') without catalyst were calculated and their values introduced in the kinetic equation giving the overall transformation rate of OAP:

$$-\frac{\mathrm{d}[OAP]}{\mathrm{d}t} = 2 \cdot r_{\mathrm{cat}} + 2 \cdot r_{\mathrm{non\text{-}cat}} \tag{1}$$

$$r_{\mathrm{cat}} = -\frac{1}{2} \cdot \frac{\mathrm{d}[OAP]}{\mathrm{d}t} - r_{\mathrm{non\text{-}cat}} \tag{2}$$

where $r_{\mathrm{non\text{-}cat}} = k' \cdot [OAP]$.

Since the oxidation was followed at lower conversions, a linear dependence of reaction rate with respect to OAP concentration is expected. This expectation was confirmed by the linear regression on the obtained data (Fig. 5).
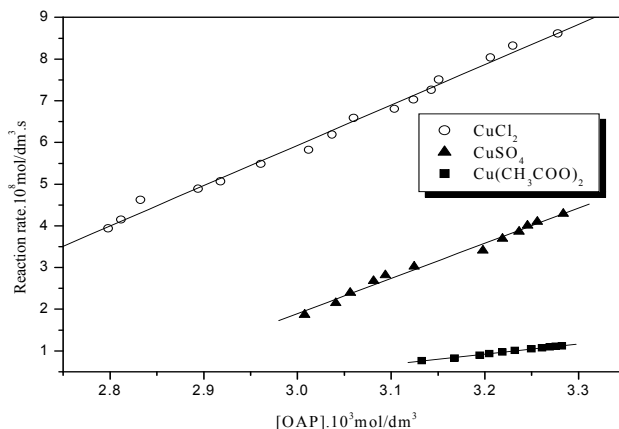

Fig. 5: *Rates of catalyzed reactions vs. OAP concentration*

Conditions: [OAP] = 3.33mM, [CuCl₂,], [CuSO₄], [Cu(Ac)₂] = 1.66 mM

The catalytic efficiency factors, calculated from the proportionality constants divided by catalyst concentration, are summarized in Table 1. The presence of Cu (II) salts induces a pH change of the solution, which is also given in the last column of the table.

Table 1. Catalytic efficiency factors for different copper salts

No	Catalyst	$10^2 k_{cat} \left(dm^3 \cdot mol^{-1} s^{-1} \right)$	pH
1	Cu(CH$_3$COO)$_2$	1.48±0.03	5.40
2	CuSO$_4$	5.08±0.01	4.95
3	CuCl$_2$	5.83±0.00	4.50

The catalytic efficiency introduced by different copper salts can be assigned to anion effects resulting in incomplete dissociation (copper acetate), ion pair formation (copper sulphate) and possibly to some specific interactions.

The complexation of copper ion with glycine, a bidentate ligand, at pH = 6 and 0.83 mM concentration of catalyst, seems to decrease the catalyst efficiency. The efficiency factor is larger for simple copper chloride $k_{cat}^{CuCl_2} = (5.83 \pm 0.00) \cdot 10^{-2}$ dm^3 mol^{-1} s^{-1} as compared to the value of the copper-glycine complex, $k_{cat}^{[Cu(gly)_2]Cl_2} = (1.13 \pm 0.04) \cdot 10^{-2}$ dm^3 mol^{-1} s^{-1}.

The kinetic parameters of OAP oxidation in the presence of mushroom tyrosinase were evaluated in a recent study [17], under the same experimental conditions. The parameters r_{max} and K_M were estimated from the plot of enzymatic reaction rate in initial conditions *vs.* initial concentration of OAP and the selectivity constant k_{enzyme} [18] was calculated as the ratio of r_{max} and K_M ($k_{enzyme} = 1 \cdot 10^{-5}$ s^{-1}) This constant, divided to enzyme concentration (in protein), gives the value of the catalytic efficiency factor: $k_{cat}^{tyr} = 6.58 \cdot 10^2$ dm^3 mol^{-1} s^{-1} for tyrosinase-catalyzed reaction. Since the concentration of catalytic centers is always smaller than the concentration in protein, the calculated value represents the lowest estimate of enzyme efficiency. The enhanced activity of copper complex in tyrosinase reflects the important structural contribution of protein environment.

Conclusions

The oxidation of OAP, a toxic organic pollutant present in wastewaters, with dissolved oxygen from air leading to a less harmful product (APX) is a naturally occurring process, which can be accelerated by different transition metal ions. The copper ions are species often present in natural waters and in the active centers of some oxidative enzymes like tyrosinase. The catalytic effect of copper (II) salts on the oxidation of OAP to APX using oxygen from air is significantly dependent on coordination of Cu^{+2}. In turn, this coordination is a strong function on anion nature as well as on ligand properties. The incomplete dissociation, the ion-pair formation and the interaction with a bidentate ligand like glycine, lower the catalytic efficiency of Cu^{+2}. On the contrary, the Cu^{+2} binding in a flexible environment offered by tyrosinase provides a significant increase of its catalytic efficiency.

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