THE INVESTIGATION OF THE REACTION KINETICS OF o-PHENYLENEDIAMINE AND m-PHENYLENEDIAMINE IN THE PRESENCE Ag(I)

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ABSTRACT

o- and m-phenylenediamines yield product through oxidative bonding in the presence of metals. Oxidative bonding products are azo dyes that are formed through a coloration reaction.

In this study, a visible spectrophotometric and differential methods have been developed for the reaction kinetics of o-phenylenediamine and m-phenylenediamine in the presence of Ag (I). Optimum conditions fort the reaction were established as pH=6 at λ=450 nm. When the oxidation of o-phenylenediamine and m-phenylenediamine by Ag (I) investigated, it was observed that in this reaction the following rate formula was found in this reaction:

$$V = k\,[Ag^+]^{0.5}\,[o\text{-phenylenediamine}]^2\,[m\text{-penylenediamine}]^{0.5}$$

The rate equation demonstrates that one molecule of m-phenylenediamine and four molecule o-phenylenediamine react with one molecule Ag (I).

Keywords: o-phebylenediamine, m-phenylenediamine, Spectrophotometry, Differential method, Reaction Kinetic

INTRODUCTION

The o-, m- and p- Phenylenediamines ($C_6H_4(NH_2)_2$), are the nitrogen analogs of the three dihydroxybenzenes ($C_6H_4(OH)_2$), pyrocatechol, resorcinol and hydroquinone, respectively; in fact, these hydroxy compounds are used as intermediates for the preparation of some of the phenylenediamines. These structural similarities have their counterpart in chemical reactivities. For instance, the ortho-

and para classes are very good reducing agents and used as antioxidants, while the meta compounds couple readily with diazotizedamines, forming useful dyes. Of the six possible tolylendiamines (toluendiamines or toluylendiamines), only one of the meta isomers and para isomer are commercial available [1].

The oxidation occurs quantitavely and proceeds in the presence of Cu(II) [2, 3], Ag(I) [4, 5]. Co(II) ions behaving as autooxidation catalysts. It is known that aromatic amines are suitable for the investigation. In the former study, 3,4-diaminobenzenesulfonic acid (DBS) [6, 7] was oxidised by the effect of catalytic Co(II) between a pH range of 7.4-8.4. The rate formula was found as follows:

$$V = k \, [Co^{+2}] \, [DBS] \, [O_2]$$

There is no reaction at pH < 7.4 and the reaction rate increases with the increasing pH. The oxidation product is 3,4-diiminobenzenesulfonic acid. The kinetics of these reactions related with o-phenylenediamine and m-phenylenediamine in the presence of Cu (II) were also investigated by using spectrophotometrical and differantial methods in this study.

In this study, the reactions related to o-phenylenediamine and m-phenylenediamine in the presence of Ag (I) [8] were investigated using spectrophotometric [9-15] and differential methods [16-18]. When the reactions of o-phenylenediamine and m-phenylenediamine in the presence of Ag (I) were investigated, it was observed that the following rate formula was found:

$$V = k \, [Ag^+]^{0.5} \, [\text{o-phenylenediamine}]^2 \, [\text{m-penylenediamine}]^{0.5}$$

The result of the reactions between Ag (I) and o- and m-phenylenediamine mixtures it was found out that there is an oxidation by means of complexation. And as a result of oxidation, a diazo compound occured from amines and Ag (I) was reduced to elemental form.

EXPERIMENTAL
Investigation of the reaction conditions

Relative wideness of o-phenylenediamine was calculated from pH = 0 to 14 (K_1= 0.251, K_2 = 1.82x10^{-5}) (Figure 1). During this investigation, o-phenylenediamine is taken as two protons (H$_2$A, α_0), and protons progrewing disappear in two steps. First proton disappears at the pH = 3 (HA$^-$, α_1), while second proton disappears at pH > 7 (A$^=$, α_2).

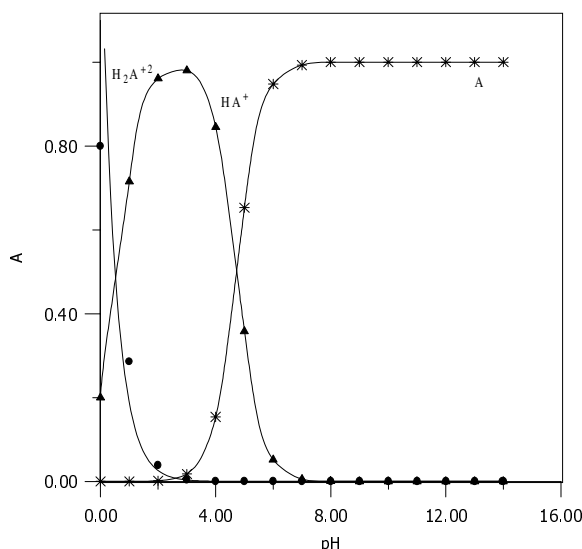**Figure 1.** *Relative wideness of o-phenylenediamine*

o-Phenylenediamine exhibited an absorption at $\lambda = 442$ nm at pH = 3 and it also showed an absorption $\lambda = 424$ nm at pH > 7.

Determination of the wavelength for the study

For determining the wavelength which would be used in the following reaction, various solutions including o-phenylenediamine, m-phenylenediamine and Ag (I) between pH = 5-10, were prepared in the proportion of 1:1:1 and the spectra were measured after waiting 10 minutes.

As a result of the investigation in various pH range, the oxidation product showed an absorption at $\lambda = 450$ nm and the absorbance was fixed after pH > 5. As a working medium, an absorbance value of $\lambda = 450$ nm and a pH value of 6 were chosen.

Dependence of the reaction rate to the Ag(I) concentration

A graphic of log v_o = f(log [Ag$^+$]) was drawn (Figure 2) related with the investigation of the effect of the Ag (I) concentration to the reaction rate which is related with the reaction of o- phenylenediamine and m-phenylenediamine by Ag (I). The equation obtained is log v_0 = -2.865 + 0.536log C. The straight line is $n_1 = 0.536 \approx 0.5$.
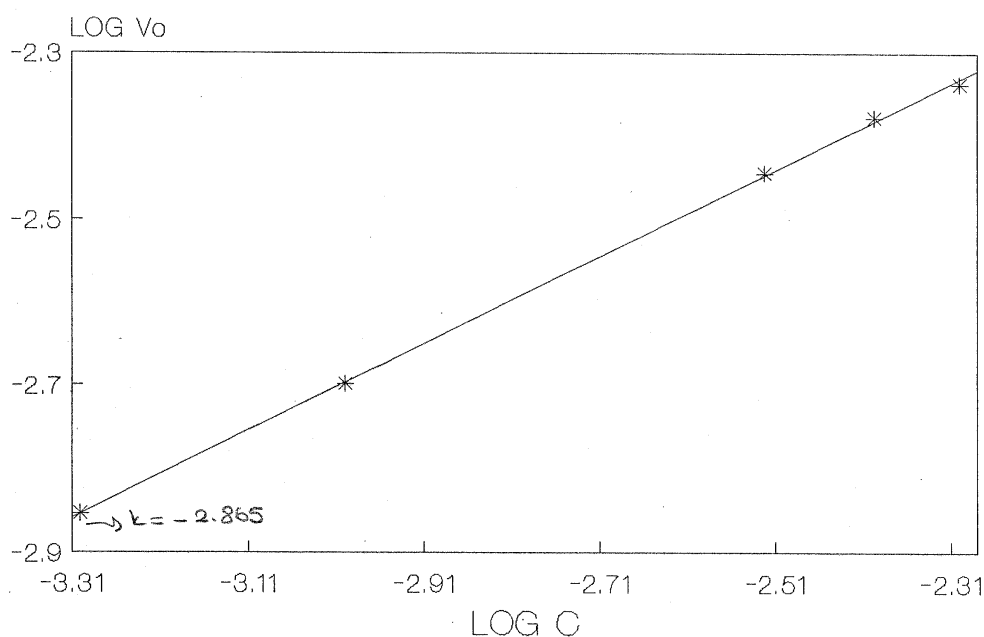
Figure 2. $\lambda = 450$ nm, $C_{o\text{-}phen} = 1x10^{-3}M$, $C_{m\text{-}phen} = 1x10^{-3}M$, $C_{Ag}^{+} = 0.5x10^{-3}$ - $5x10^{-3}M$, $pH = 6$

Dependence of the reaction rate to the o-phenylenediamine concentration

A graphic of log v_0 = f(log [o-phen]) was drawn (Figure 3) related with the investigation of the effect of the o-phenylenediamine concentration to the reaction rate which is related with the reaction of o-phenylenediamine and m-phenylenediamine by Ag (I). The equation obtained is log v_o = -2.900 + 1.977 log C. The straight line is n_2 = 1.9770 ≈2.
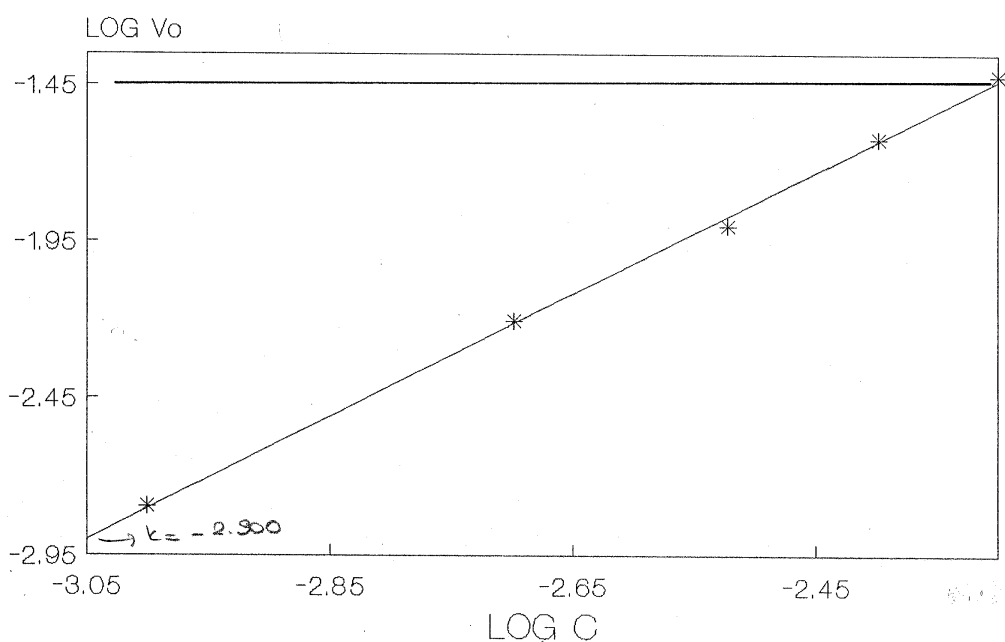

Figure 3. $\lambda = 450$ nm, $C_{o\text{-}phen} = 1x10^{-3}$ - $5x10^{-3}M$, $C_{m\text{-}phen} = 1x10^{-3}M$, $C_{Ag}^{+} = 1x10^{-3}M$, $pH = 6$

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Dependence of the reaction rate to the m-phenylenediamine concentration

A graphic of log v_0 = f(log [m-phen]) was drawn (Figure 4) related with the investigation of the effect of the m-phenylenediamine concentration to the reaction rate which is related with the reaction of o-phenylenediamine and m-phenylenediamine by Ag (I). The equation obtained is log v_o = -2.730 + 0.5427 log C. The straight line is n_3= 0.5427 ≈0.5
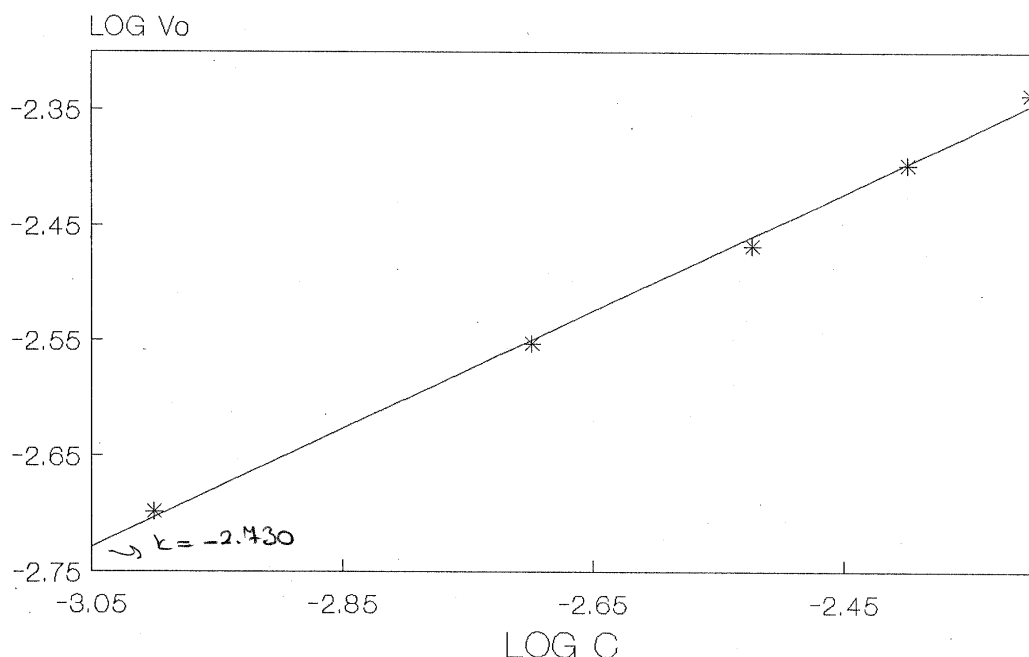

Figure 4. *λ = 450 nm, $C_{o\text{-}phen}$ = $1x10^{-3}$M, $C_{m\text{-}phen}$ = $1x10^{-3}$- $5x10^{-3}$M, C_{Ag}^{+} = $1x10^{-3}$M, pH = 6*

RESULTS

Following the investigation of the dependence of reaction rate Ag (I) concentration at pH = 6 the gradient was found as n_1 = 0.5 (Figure 2). However, in the investigation of the dependence reaction rate to o-phenylenediamine concentration the gradient was found as n_2 = 2 (Figure 3) and the dependence reaction rate to m-phenylenediamine concentration the gradient was found as n_3 = 0.5 (Figure 4) .

Considering this, the rate equation related with the oxidation of o-phenylenediamine and m-phenylenediamine by Ag (I), is found as the following equation ie.

$$V = k \, [Ag^+]^{0.5} \, [\text{o-phenylenediamine}]^2 \, [\text{m-penylenediamine}]^{0.5}$$

The rate equation demonstrates that one molecule of m-phenylenediamine and four molecule o-phenylenediamine react with one molecule Ag (I).

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