THE OXIDATIVE COUPLING OF o- AND m-PHENYLENEDIAMINES IN THE PRESENCE OF SOME TRANSITION METALS

(RESEARCH)

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ABSTRACT

The reactions which are related to with o- and m-phenylenediamine in the presence of silver(I), copper(II) and gold(III) were investigated in this study by using spectrophotometric and differential methods. As a result of the measurements, no reaction was seen between silver(I) and m-phenylenediamine, between copper(II) and m-phenylenediamine, between gold(III) and o-phenylenediamine and between o- and m-phenylenediamine in the presence of gold(III).

When the oxidation of o-phenylenediamine by silver(I) was investigated, it was observed that in this reaction the ratio of o-phenylenediamine to silver(I) was 1:1 and the ratio formula as follows,

$$V = k\ [Ag^{+}]^{0.5}\ [\text{o-phen}]^{0.5}$$

The rate equations show that one o-phenylenediamine molecule reacts with one silver(I) ion. Since there is one electron transfer in the oxidation reaction, monoimine is formed.

When the ternary systems of o-phenylenediamine and m-phenylenediamine were investigated in the presence of silver(I), the ratio formula was found to be as follows,

$$V = k\ [Ag^{+}]^{0.5}\ [\text{o-phen}]^{0.5}\ [\text{m-phen}]^{0.5}$$

According to this equation, one silver(I) ion reacts with four o-phenylenediamine molecules and one m-phenylenediamine molecule. Repeated experiments yield the same result, but this situation cannot be explained with the available information.

When the oxidation of o-phenylenediamine by copper(II) was investigated, it was observed that in this reaction the ratio of o-phenylenediamine to copper(II) was 1:1 and the ratio formula was found as follows,

$$V = k\ [Cu^{2+}]\ [\text{o-phen}]$$

The rate equations show that one o-phenylenediamine molecule reacts with one copper(II) ion. Since there is one electron transfer in the oxidation reaction, monoimine is formed.

When the ternary systems of o-phenylenediamine and m-phenylenediamine were investigated in the presence of copper(II), it was observed that in this reaction the ratio of o-phenylenediamine to copper(II) was found as 1:1 and no reaction m-phenylenediamine was observed and the ratio formula was found as follows

$$V = k\ [Cu^{2+}]\ [\text{o-phen}]$$

The rate equation shows that one copper(II) ion reacts with one o-phenylenediamine molecule but does not react with one m-phenylenediamine molecule.

When the oxidation of o-phenylenediamine by gold(III) was investigated, it was observed that in this reaction the ratio of o-phenylenediamine to gold(III) was 1:1 and before pH 4, the ratio formula was found as follows,

$$V = k\ [Au^{3+}]^{0.5}\ [\text{o-phen}]^{0.5}$$

The rate equations show that one o-phenylenediamine molecule reacts with one gold(III) ion. Since there are two electron transfers in the oxidation reaction, it can be said that there must be at least two steps, and the experimentally determined rate equation belongs to the slowest rate-determining step. Because there are two electron transfers, diamine is formed.

When the ternary systems of o-phenylenediamine and m-phenylenediamine were investigated in the presence of gold(III), it was observed that in this reaction the ratio of o-phenylenediamine to gold(III) was found as 1:1 and no reaction m-phenylenediamine was observed and the ratio formula was found as follows

$$V = k\ [Au^{3+}]\ [\text{o-phen}]$$

The rate equation shows that one gold(III) ion reacts with one o-phenylenediamine molecule but does not react with one m-phenylenediamine molecule. The ratio formulas showed that the reactions took place in various phases.

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INTRODUCTION

The phenylenediamines are an organic compound with the formula $C_6H_8N_2$ [1]. This aniline derivative is a white solid, although samples may darken due to air oxidation. It is primarily used as a component of engineering polymers and composites. The phenylenediamine can be referred to as:

o-phenylenediamine or OPD, a chemical compound $C_6H_4(NH_2)_2$
m-phenylenediamine or MPD, a chemical compound $C_6H_4(NH_2)_2$
p-phenylenediamine or PPD, a chemical compound $C_6H_4(NH_2)_2$
N,N-dimethyl-p-phenylenediamine or DMPD
N,N,N′,N′-tetramethyl-p-phenylenediamine or TMPD, used in microbiology

Ortho, meta, and para phenylenediamines ($C_6H_4(NH_2)_2$) are nitrogen analogs of dihydroxybenzene ($C_6H_4(OH)_2$), hydroquinone, pyrocatechol, and resorcinol, respectively. In fact, these hydroxy compounds are used as intermediates in the preparation of some phenylenediamines. These structural similarities are also reflected in their chemical reactivities. For example, ortho and para classes are very good reducing agents and are used as antioxidants, while meta compounds readily combine with diazotized amines to form useful dyes [1].

o-, m-, and p-phenylenediamines and their various derivatives form dyes by undergoing oxidative coupling reactions with various oxidizing agents. Because the reaction proceeds quantitatively, the amount of oxidizing agent can be determined spectrophotometrically or potentiometrically by measuring the silver(I) and copper(II) absorption of the resulting dye. Determination of transition metals is also possible using these methods. The fact that gold is generally rare in its pure form, and in other cases contains transition metals such as Fe, Cu, and Ni, causes interference from these elements in the determination process. Ions of these transition metals can form complexes in the determination process due to the low selectivity of the ligands used. This situation creates significant problems, especially in samples extracted by dissolving them from minerals. Although some studies have been conducted taking advantage of gold's strong oxidizing property, these studies are based on complex formation. Robertus and Levin [2] showed that in an anhydrous medium with the oxidizing effect of silver(I) ions gives a coupling product of o-, m- and p-phenylenediamines. Since silver(I), copper(II) and gold(III) ions are in the same group, it was thought that a highly selectable, sensitive and simple spectrophotometric determination method could be given for the coupling reactions that these metal ions can give with o-, m- and p-phenylenediamines. In particular, the fact that no reagents other than amines are needed during the experiments has been an advantage for the method to be applied.

In this study, the coupling reactions of o-, m- and p-phenylenediamines in the presence of silver(I), copper(II) and gold(III) ions were investigated spectrophotometrically using the differential method, and the reaction mechanisms were attempted to be elucidated.