

KINETICS AND MECHANISM OF THE CHEMICAL OXIDATIVE POLYMERIZATION OF *p*-SEMIDINE

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A potentiometric study of the kinetics of the oxidative polymerization of p-semidine (N-phenyl-1,4-benzenediamine) established that the oxidation of this diamine by ammonium peroxodisulfate proceeds without autocatalysis. The reaction rate is independent of the acidity of the medium. A mechanism is proposed for the oxidative polymerization of p-semidine.

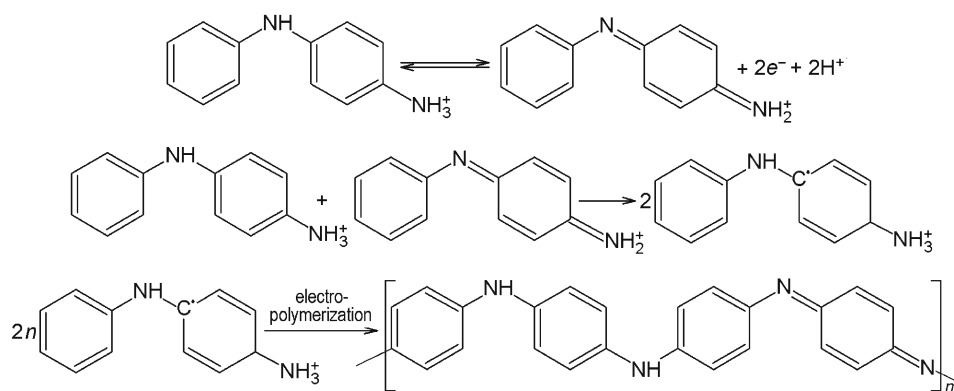
Key words: *p-semidine, oxidative polymerization, kinetics, mechanism.*

Despite considerable progress in the study of the kinetics and mechanism of the oxidative polymerization of aromatic amines [1-6], some aspects have not been sufficiently investigated. Thus, there is yet no definitive elucidation of the details of the mechanism and kinetics of the oxidative polymerization of *p*-semidine (*N*-phenyl-1,4-benzenediamine), which is formed as an intermediate in the oxidative polymerization of aniline [7-9]. Various workers [8, 9] have proposed that the mechanism of the oxidative polymerization of *p*-semidine involves two-electron oxidation of this diamine to give *N*-phenylquinonediimine, followed by the oxidation of *p*-semidine by this diimine to give a radical intermediate, which is converted to polyaniline in accord with an electrophilic mechanism [2] for oxidative polymerization (Scheme 1) [9]. The latter step is given only schematically and the chain growth mechanism was not entirely clear. Hence, an additional investigation of this reaction was carried out by means of chemical kinetics in order to better understand its mechanism.

EXPERIMENTAL

Since protons are released into the reaction system during the oxidation of aromatic amines [1-6], the extent of conversion of *p*-semidine is readily monitored using a pH-meter. We employed an IPL-311 instrument with precision of 0.005 pH unit. A sample of 0.184 g (0.001 mol) *p*-semidine was dissolved in 10 mL freshly-prepared 0.4 M hydrochloric acid with heating and rapid stirring. A solution of 2.28 g (0.01 mol) ammonium peroxodisulfate in 90 mL distilled water was also prepared. These solutions were held at constant temperature for 30 min and then mixed in a reactor equipped with an electrode, which had been subjected to prior argon flushing. The kinetic measurements were carried out at 25, 30, 35, and 40 °C, recording the pH of the reaction medium until a constant value was established. The product of the oxidation of *p*-semidine was characterized by IR spectroscopy using a Nicolet-380 Fourier IR spectrometer. All the absorption bands were in accord with the IR spectrum of polyaniline obtained under analogous conditions for the oxidation of aniline [5].

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Scheme 1. Mechanism for the oxidative polymerization of *p*-semidine according to Khudaish et al. [9].

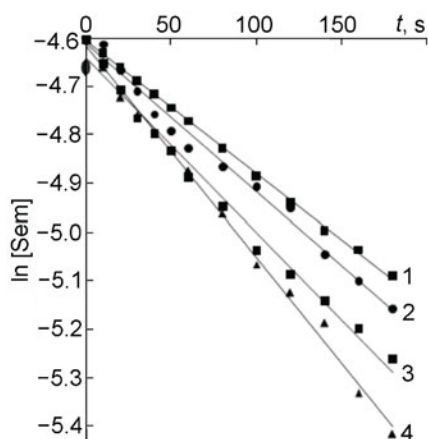


Fig. 1. Kinetic curves for the oxidation of *p*-semidine as plots of $\ln [\text{Sem}]$ vs. t at 1) 25 °C, 2) 30 °C, 3) 35 °C, and 4) 40 °C. $[\text{Sem}]_0 = 0.01 \text{ M}$, $[(\text{NH}_4)_2\text{S}_2\text{O}_8]_0 = 0.1 \text{ M}$.

RESULTS AND DISCUSSION

The experimental pH values of the reaction system are related to the current *p*-semidine concentration by the equation

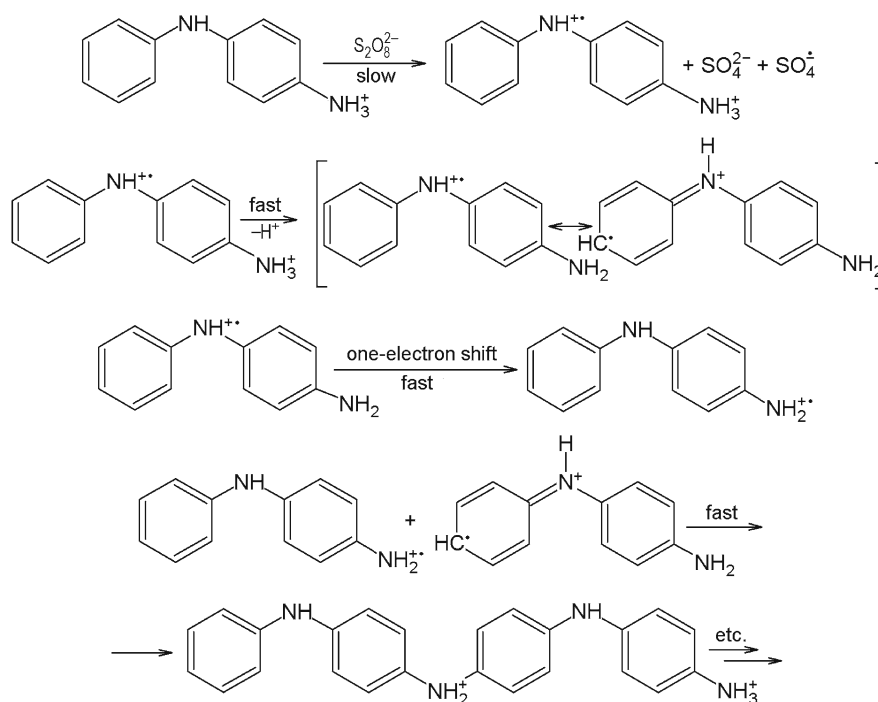
$$[\text{Sem}] = [\text{Sem}]_0 - (10^{-\text{pH}} - [\text{H}^+]_0)/g \quad (1)$$

where $[\text{Sem}]$ and $[\text{Sem}]_0$ are the current and initial *p*-semidine concentrations, respectively, $[\text{H}^+]_f$ and $[\text{H}^+]_0$ are the final and initial proton concentrations in the reaction system, respectively, $g = ([\text{H}^+]_f - [\text{H}^+]_0)/[\text{Sem}]_0$ is the molar amount of protons released per mole oxidized aromatic amine.

The dependence of the current *p*-semidine concentrations on elapsed time gives a linear plot for $\ln [\text{Sem}]$ vs. t (Fig. 1).

In light of the ten-fold excess of ammonium peroxydisulfate in the reaction system and the first-order behavior relative to the *p*-semidine concentration (Fig. 1), the kinetics for the oxidation of this aromatic amine obeys pseudo-first-order kinetics:

$$-d[\text{Sem}]/dt = k[\text{Sem}][\text{Ox}]_0 \quad (2)$$



Scheme 2. Radical-cation mechanism for the oxidative polymerization of *p*-semidine.

The integral form of Eq. (2) is as follows:

$$\ln [\text{Sem}] = \ln [\text{Sem}]_0 - k[\text{Ox}]_0 t \quad (3)$$

where k is the rate constant for the oxidation of *p*-semidine by the peroxodisulfate ion, $[\text{Ox}]_0$ is the initial concentration of ammonium peroxodisulfate in the reaction system, and t is the elapsed time.

The rate constants for the oxidation of *p*-semidine by ammonium peroxodisulfate determined from the slope of the curves plotted as $\ln [\text{Sem}]$ vs. t (Fig. 1) are $(2.70 \pm 0.14) \cdot 10^{-2} \text{ L}/(\text{mol} \cdot \text{s})$ for 298 K, $(3.10 \pm 0.16) \cdot 10^{-2} \text{ L}/(\text{mol} \cdot \text{s})$ for 303 K, $(3.60 \pm 0.18) \cdot 10^{-2} \text{ L}/(\text{mol} \cdot \text{s})$ for 308 K, and $(4.30 \pm 0.21) \cdot 10^{-2} \text{ L}/(\text{mol} \cdot \text{s})$ for 313 K. The activation energy for the oxidation of *p*-semidine is $24 \pm 4 \text{ kJ/mol}$.

In contrast to the case of *p*-semidine, the oxidation of aniline, *m*-semidine, and *o*-semidine in acidic aqueous solution proceeds autocatalytically [1-5], while the reaction rate obeys the following equation [1]:

$$-d[\text{M}]/dt = K_a k_1 [\text{M}][\text{Ox}]/[\text{H}^+] + k_2 [\text{P}][\text{M}] \quad (4)$$

where k_1 and k_2 are rate constants, $[\text{M}]$ is the current concentration of the salt form of the monomeric aromatic amine, $[\text{P}] = [\text{M}]_0 - [\text{M}]$ is the concentration of polymer product, $[\text{M}]_0$ is the initial monomer concentration, and K_a is the acidity constant of the conjugate acid monomer.

Comparison of Eqs. (1) and (4) reveals two features of the oxidation of *p*-semidine. Firstly, the rate of *p*-semidine oxidation is independent of the acidity of the reaction medium, while the initial rate in the oxidation of aniline decreases with increasing proton concentration [6]. Secondly, the oxidation of aniline is an autocatalytic reaction [1-5], while the oxidation of *p*-semidine proceeds under identical conditions without autocatalysis.

The oxidation of aromatic amines is possible only for their basic forms [1-6]. Thus, the lack of dependence of the *p*-semidine oxidation rate on the acidity of the medium is attributed to the circumstance that only the primary amino group is protonated ($\text{p}K_{a2} = 5.2$ [10]), while the secondary amino group ($\text{p}K_{a1} = -0.71$ [10]) is almost completely unprotonated in the pH

range studied ($\text{pH} > 0.5$). Thus, while aniline is virtually completely protonated at $\text{pH} < 2$ and oxidation is possible only for the basic form present in only a very low equilibrium concentration (less than 0.25%), only the primary amino group is protonated in the oxidation of *p*-semidine and the unprotonated secondary amino group is active in the oxidation reaction.

The lack of autocatalysis indicates the impossibility of an electrophilic mechanism in the oxidation of *p*-semidine, which is generally accepted to account for the autocatalytic polymerization of aniline [2]. A likely mechanism for the oxidation of *p*-semidine to give its oligomeric forms in accord with the kinetic data is given in Scheme 2 and involves the participation of radical-cation intermediates. Furthermore, the lack of autocatalysis in the oxidation of *p*-semidine indicates direct involvement of the aniline moiety in chain growth. Since the oxidative polymerization of aniline is autocatalytic [1-5] and *p*-semidine (a dimer of aniline) is an intermediate in the oxidation of aniline [7-9], the oxidative copolymerization of aniline and *p*-semidine is an autocatalytic process. However, the oxidative homopolymerization of *p*-semidine proceeds without autocatalysis, indicating the participation of monomeric aniline in the chain growth steps.

Thus, we have shown that, in contrast to the oxidative polymerization of aniline, the oxidation of *p*-semidine by the action of ammonium peroxodisulfate proceeds without autocatalysis and the reaction rate is independent of the acidity of the medium.

The lack of autocatalysis in the oxidation of *p*-semidine points to a difference between the electrophilic mechanism of oxidation polymerization of aniline and the radical-cation mechanism for the corresponding polymerization of *p*-semidine and also is evidence for the direct participation of aniline in the chain growth steps.

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