

KINETIC INVESTIGATION OF DIAZOTIZATION REACTION IN BENZOTRIAZOLE WITH DEAD-STOP-END-POINT METHOD

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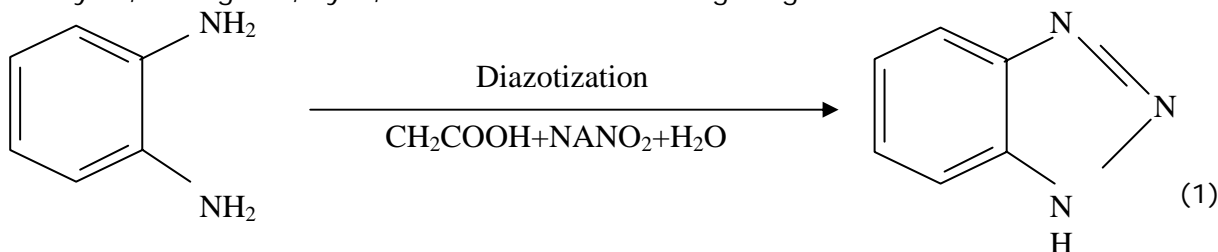
Abstract

Benzotriazole is an organic compound with many industrial applications such as being a main corrosion-inhibiting component of cupric metal. Kinetic investigation of diazotization reaction, which has been performed for the first time in this work, is a key reagent for the industrial scale production of this compound. Benzotriazole is produced through the diazotization of orthophenylenediamine (OPDA) in an aqueous media containing acetic acid and sodium nitrate. Conventional procedures used for the kinetic investigation of the diazotization reactions include biamperometry, amperometry, polarography, spectroscopy in UV area and colorimetry, which cannot be used in the case of the present invention and hence a new electrochemical method called the Dead-Stop-End-Point method was devised. New rate equations based on postulated mechanisms were tested using the experimental data under different temperature, pH and concentration values. The results indicated that the rate equation are first order with respect to orthophenylenediamine and nitroze acid and that the rate constant is a function of the temperature and acetic acid concentration.

Key words: benzotriazole, orthophenylenediamine, diazotization, kinetic, rate equation, electrochemistry.

1. Introduction

Benzotriazole is a heterocyclic derivative the pure form of which produces white needle-like crystals, and is conventionally produced through the diazotization of orthophenylenediamine in aqueous solution containing acetic acid and sodium nitrate (Eq. 1) ^[1,2]. Benzotriazole has many industrial applications including being a main corrosion inhibiting component of cupric metal and other metals, polymerization catalysts, detergents, dyes, cleaners and antifreezing reagents.



Kinetics of orthophenylenediamine diazotization reaction is of great importance in the large-scale production of benzotriazole. The studies carried out on the its kinetic have been mostly based on monoamines ^[3], which are totally different from the case of diamine components in the presence of a totally different acid which is the case with the present invention.

Electrophilic nitrazation of the primary amine groups is the main step of diazotization that converts the produced nitrozeamine to totumer of isonitroze, which in turn converts to diazotization after two successive protonation and dehydration steps. The product has

a high tendency for N_2 elimination, and the system is established only when the $\left(-\overset{+}{N} \equiv \overset{-}{N}-\right)$ reaches a mesomeric electronic system. The diazotization of aromatic diamines yielding a bis-diazonium is also known as bis-diazotization. Under normal conditions the ortho diazotization of aromatic diamines leads to the cyclation of benzo heterocycles. To provide the nitroze reagent for nitrazation through a diazotization mechanism extra acid is required. Depending on the type of acid, one of the following reactions may occur,



Where N_2O_3 and NO^+ are the nitrozing agents in the strong and weak acidic media respectively.

Electrochemical studies of primary aromatic amines in diazotization reactions suffer the shortcoming of requiring an indicator (usually Strach-Iodide Paper) to show the end point. These methods also suffer the time-consuming step of adding sodium nitrate to the reaction medium [4].

Hence a new so-called Dead-Stop physic-chemical electrometric method was used for this purpose through the study of aromatic amines, to be used in rate determination studies of primary aromatic amine diazotization [5]. The basis of this method is to determine nitroze acid HNO_2 in reaction mixture by two polarized platinum electrodes each having a voltage of 0.4 V. The current is detected and used as a find the nitroze concentration due to the fact the nitroze acid oxidation and reduction is an indication of the nitroze concentration. Therefore, the above-mentioned method can be used to measure the rate of the diamine orthophenilin diazotization reaction.

2. Experimental

2.1 Instruments and apparatus

Reaction chamber is a two-layer glassy connected to a circulator (contained a cooling liquid) and equipped with a thermostat and also containing a magnetic stirrer. Two transparent platinum electrodes, connected to a constant voltage source and a galvanometer, are place in the reactor.

2.2 Material preparation and testing procedure

All materials were used of the highest purity available. 99% pure orthophenylenediamine crystals, which were intended for use, were recrystallized for further purification. The deionized water used, had a very low hardness and the acid purity was above 96%.

At first, 50 cm^3 of a water-acid mixture of desired concentration was poured into the reactor and the temperature was adjusted to the desired value through heating or the circulation of the cooling fluid. Next a 0.4 V voltage was applied to the platinum electrodes as a result of which small and highly transient currents were observed. Then 2 cm^3 of a sodium nitrate solution of desired concentration was added to the system in a drop wise manner, in a way that the current was constant, and the current was recorded as soon as the current tolerance was less than $\pm 0.1 \mu A$. Then 2 cm^3 of the amine solution were added to the system and the current was recorded until a steady state was observed. The I-t curves were then recorded using the acquired data.

3. Results and Discussion

Many research studies have been performed on the diazotization kinetics of primary aromatic amines [6,7], through this method. Scholten and Stone's [8] opinion on the nature of the Dead-Stop end point was that it is based on an electrolysis cell with the oxidation of a species at anode and the reduction of same or another material at cathode. When the electrodes are immersed in a nitroze acid solution under a given voltage, gas bubbles evolve on both electrode surfaces, which indicate the flow of electricity in the circuit. The

cathodic reaction is the reduction of nitrozo to nitroze oxide and the anodic one is the oxidation of nitrozo acid to nitrogen dioxide.

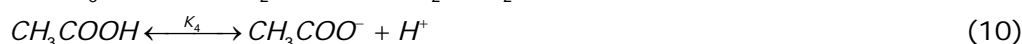
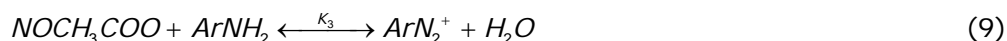
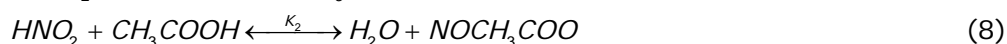


A phenomenon observed during the diazotization reaction of some amines is the emergence of some extra electric current, which is most probably due to the redox pair potential electrolysis produce especially when nitroze group exist. Of course this current dies off before the Dead-Stop end point in all cases.

According to the theory of the Dead-Stop end point method, the current is proportional to the nitroze acid and/or sodium nitrate concentration in reaction medium. If initial point (End point after increasing sodium nitrate) and current are shown by O and I respectively, O-I in each moment is an indication of the completion of the reaction X. Therefore, it is possible to replace concentration terms with the current in the rate equation.

The rate equation was obtained according to the postulated reaction mechanism, which was devised based on the existing theories about diazotization reactions.

The diazotization reactions include several steps that one of is the rate-determining step (RDS). These steps are the amine protonation, and the formation and increase of the nitrozing reagent. If nitrozing reagent is NO^+ , the addition of the nitroze reagent to the amine group is slow and is hence the RDS [9]. During the diazotization reaction of orthophenylenediamine, the nitrozing reagent is NO^+ , due to the balance between the basicity of free amine groups and the acidity of the organic acids. Predicting the different steps of the reaction, the overall rate equation can be obtained. It is also worthy to mention that only one free amine group is attacked by the nitrozing reagent in diazotization reaction.



$$ArNH_2 = K_1 \frac{Ar(NH_3^+)}{[H^+]} \quad (11)$$

$$NOCH_3COO = \frac{[HNO_2][H^+][CH_3COO^-]}{\frac{K_2}{K_4}[H_2O]} \quad (12)$$

The reaction of the nitrozing reagent is the RDS and hence,

$$\frac{dx}{dt} = K_3 [NOCH_3COO] \cdot [ArNH_2] \quad (13)$$

By replacing and rearranging we have,

$$\frac{dx}{dt} = K \cdot [ArNH_3^+] \cdot [CH_3COO^-] \cdot [HNO_2] \quad (14)$$

Where, **a** and **b** are the initial concentrations of orthophenylenediamine and sodium nitrate, respectively. Therefore,

$$a - x = [ArNH_2] + [ArNH_3^+] \approx [ArNH_3^+] \quad (15)$$

$$b - x = [HNO_2] + [NO^+] \approx [HNO_2] \quad (16)$$

$$\frac{dx}{dt} = K \cdot [CH_3COO^-] \cdot [a - x] \cdot [b - x] \quad (17)$$

If $a=b$ then

$$K = \frac{1}{t} \cdot \frac{1}{CH_3COO^-} \cdot \frac{x}{a(a-x)} \tag{18}$$

Replacing the current in eq.18, rate constant was calculated according to eq.19,

$$K = \frac{1}{t} \cdot \frac{1}{CH_3COO^-} \cdot \frac{O-I}{O[O-(O-I)]} \tag{19}$$

A I-t curve for the diazotization of a solution of 0.5 N of orthophenylenediamine and 4N acetic acid at 5°C is shown in Figure 1. Using the current values in Figure 2 and eq.18 Figure 2 is achieved. The rate constant is obtained from the slope of the curve. Using the rate equation obtained based on the postulated mechanism, and by plotting the $\frac{x}{a(a-x)}$ versus time curve for the specified concentrations, a linear plot was achieved indicating that the postulated mechanism is true. The rate constant as a function of acid concentration and temperature was obtained using the slopes of the curves,

$$V = k \cdot [ArNH_3^+] \cdot [HNO_2] \tag{20}$$

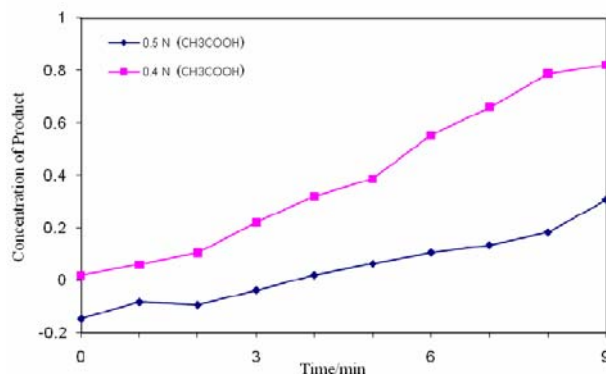
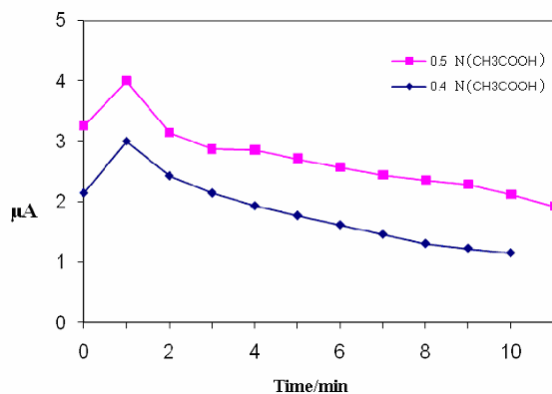


Figure 1: Flow rate vs. time for diazotization of orthophenylenediamine Figure 2: Concentration of product vs. time

Figure 3, illustrates the effect of the acid concentration on the rate constant in $[OPDA]=[NaNO_2]=0.3-0.5$ M and 5°C. As shown in this figure there is a linear relation between the rate constant and the acid concentration.

Figure 4 shows the effect of the temperature on the rate constant. This figure indicates that the rate constant increases by increasing the temperature. It should be noted that the study of these two effects was meant for the production of benzotriazole with higher purity and yield, under the optimum conditions.

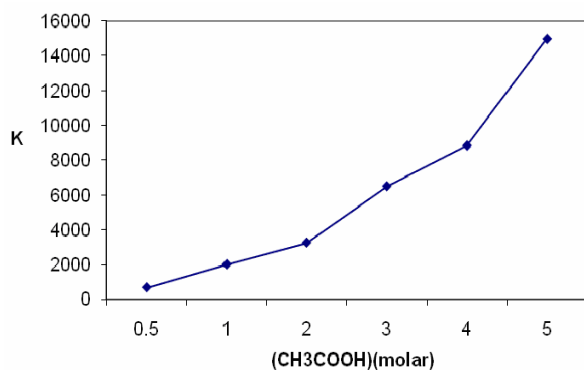


Figure 3: Effect of solvent acidity on rate constant

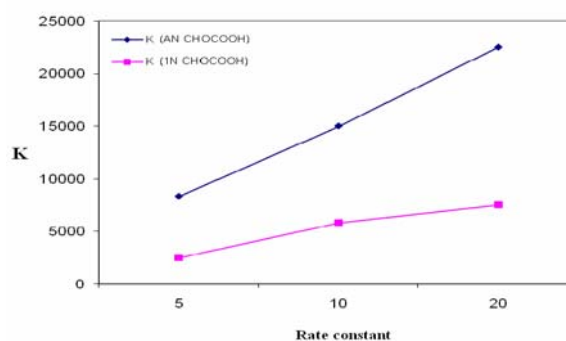


Figure 4: Effect of temperature on rate constant

Conclusion

Based on existing theory in literature about diazotization reactions, the controller step of the reaction is addition of (NO)⁺ agent to amines group. Therefore in this study, a kinetic equation based on mentioned theory was developed. Kinetic equation was developed by integral method. The results showed that rate of reaction corresponding to the concentration of the orthophenylenediamine by first order and concentration of Nitroze acid by first order too. The obtained rate equation is:

$$dX/dt=K(a-X)(b-X), K=1415.163\exp(-13.42/RT) \quad [\text{Acetic acid}=1\text{M}]$$

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