KINETICS AND MECHANISM FOR OXIDATION OF ROSANILINE MONOCHLORIDE BY NITRITE ION IN AQUEOUS MEDIA

J.F. Iyun and A.D. Onu
Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

ABSTRACT

The kinetics and mechanism of oxidation of rosaniline monochloride (ros) by nitrite ion (NO₂⁻) in aqueous media have been studied at 30°C, I=0.25 M (LiCl), \[\text{NO}_2^- + \text{H}^+ \rightarrow \text{NO}_3^- + \text{H}_2\text{O}\]. The reaction is first order with respect to oxidant and reductant concentrations and the reaction rate showed dependence on acid concentration. The reaction conforms to the rate equation \[\text{d}[\text{ros}]/\text{dt} = k[\text{H}^+][\text{ros}][\text{NO}_2^-]\]. The rate of the reaction increased with increase in ionic strength and decreased as the dielectric constant of the medium increased. Added cations catalyzed the reaction. The result of spectroscopic and kinetic investigation did not indicate intermediate complex formation. A plausible mechanism has been proposed for this reaction.

INTRODUCTION

Redox reactions involving nitrite ion (NO₂⁻) are well known. Nitrite ions have been observed to reduce riboflavin, ascorbic acid and enzymes from cucurbita-pepo. In the reduction of riboflavin, H₂O₂ was obtained as the product while NH₃ was the product for the reaction involving ascorbic acid and enzyme from cucurbita-pepo. Dolce and Pelosi studied the reduction of Pt [Co-phenylene-bis-dimethylarsine Br₂J]⁺ by NO₂⁻ in anhydrous MeOH. The reaction proceeded through a two step inner-sphere mechanism which involves the transfer of two electrons from the reductant to the oxidant.

Redox reactions involving NO₂⁻ were reported by Fraser et al., Yatsimirski and Badarina, Meyerstein and Mulac, Nakahara and Takebayashi. These reactions demonstrate NO₂⁻ either as an oxidant or reductant.

Rosaniline monochloride, a triphenyl methane dye, is used widely as a biological stain. As a dye it is also very useful in the textile industry. Redox reaction of the dye is yet to be established. The kinetic studies of the redox reaction of the dye is therefore necessary for understanding its fading and fastness properties and its uses. In this paper we report our findings on the redox reaction of rosaniline monochloride and NO₂⁻ ion.

EXPERIMENTAL

Reagents

*Author for correspondence
Present address: Chemistry Department
Federal College of Education, Zaria, Nigeria.


Stock solutions of the reactants ros and sodium nitrite were prepared by dissolving known amounts of the reagents in distilled water and making up the solution to known volume. A stock solution of hydrochloric acid was prepared by diluting 36% (specific gravity 1.8) hydrochloric acid and the solution was standardized using sodium carbonate. Stock solutions of lithium chloride, sodium formate, sodium acetate, sodium oxalate, calcium chloride, barium chloride were prepared and standardized gravimetrically. All reagents used were of ‘Analar’ grade.

Kinetic measurements

The rate of the reaction was monitored on a Concav Specrotrophic colorimeter by observing the decrease in the absorbance of ros at its characteristic wavelength, λ_max = 545nm. All kinetic measurements were carried out under pseudo first order conditions with NO₂⁻ concentration in excess over the ros concentration at 30°C and 0.25 M (LiCl) ionic strength. The pseudo-first order plots of log (A_t - A_0) versus time were made. From the slope of the plots the pseudo-first order rate constant (k₁) was determined. The second order rate constant (k₂) was obtained from k₁ as k₂/[NO₂⁻]. The results are presented in Table 1.

Acid dependence studies

The effect of acid on the rate of the reaction was studied within the acid range 1.0-10.0x10⁻⁴ M while the concentrations of ros and NO₂⁻ were kept constant. The reaction was carried out at 30°C and I=0.5 M (LiCl). The results are presented in Table 1.

The effect of ionic strength

The effect of ionic strength on the rate of the reac-
tion was investigated in the range of 1, 0.25-0.40 M (LiCl) while the concentration of other reactants were kept constant. The results are presented in Table 1.

Test for intermediate complex formation
The electronic spectra of the reaction mixture and that of ros alone were compared within 440-470nm. The Michaelis-Menten plot, \(1/k_1 vs 1/[\text{NO}_2^-]\) was executed (Figure 1).

RESULTS AND DISCUSSION

Kinetic measurements
The pseudo-first order plots of \(\log (A_1 - A_2)\) versus time for these reactions were linear for about 70% of the reaction \((A_1, A_2\) are the absorbances of the complex at times \(t\) and the end of the reaction respectively). The linearity of these plots indicates that these reactions are first order with respect to \([\text{ros}]\). Plots of \(\log k\) versus \(\log [\text{NO}_2^-]\) gave a slope of 0.73 showing that the reaction is also first order with respect to \([\text{NO}_2^-]\). Thus the rate equation for the reaction is

\[ -\frac{d[\text{ros}]}{dt} = k_2 [\text{RNH}_2^+] [\text{NO}_2^-] \]  

The order of one in the oxidant and reductant concentration in this reaction conforms with already reported order for the redox reactions involving \(\text{NO}_2^-\) and other oxidants.⁹,⁴,⁵

**Acid dependence studies**
From the result in Table 1, it is observed that the rate constant of the reaction increased with increase in acid concentration. The plot of \(k_2\) vs \([\text{H}^+]\) was linear with no intercept (Figure 2). The acid dependent rate constant \(k_2\) is given as

\[ k_2 = a [\text{H}^+] \]  

Substituting equation (2) in equation (1), the rate of the reaction becomes

\[ -\frac{d[\text{ros}]}{dt} = a [\text{H}^+] [\text{RNH}_2^+] [\text{NO}_2^-] \]  

The nature of acid dependence observed implies that there is a rapid equilibrium between protonated and unprotonated forms of the reductant (\(\text{NO}_2^-\)) prior to the rate determining step and that only the protonated form is reactive. This form of acid dependence is expected for \(\text{NO}_2^-\) reactions as the equilibria below have been established⁶ for \(\text{NO}_2^-\) in aqueous media:

\[ \text{NO}_2^- + \text{H}^+ \rightleftharpoons \overset{k_1}{\text{RNH}_2^+} \]  

---

---

---

---

---

---

---

---
\[
\text{HONO} + \text{H}^+ \rightleftharpoons \text{H}_2\text{ONO}^- \rightleftharpoons \text{H}_2\text{O} + \text{N} = 0 \quad \ldots \ldots \quad (4)
\]

In these equilibria, the \(\text{N} = 0\) is assumed to be the reactive specie and it is involved in the reaction mechanism.

*The effect of ionic strength*

The results in Table 1 show that the rate constant of the reaction increased with increased ionic strength suggesting a positive salt effect. This observation shows that the activated complex is formed from two ions of like charges or a charged and a neutral reactants.

*Intermediate complex formation*

No shift in \(\lambda_{max}\) of ros was observed. Plots of \(1/k_1\) versus \(1/\text{[NO}_2^-]\) gave a straight line which passed through the origin. The lack of shift in the \(\lambda_{max}\) of ros in the spectrum of the reaction mixture and the zero intercept obtained in the Michaelis - Menten plot suggest the absence of intermediate complex formation. In addition, added cations (\(\text{Ca}^{2+}, \text{Ba}^{2+}\)) decreased the rate constant for the reaction. This suggests that substitution of the reactants into their inner coordination shell did not precede electron transfer. The inhibition of the reaction by the cations could be due to coulombic effect as the intervention of positively charged species in between positively charged reactant molecules in the activated complex will lead to the repulsion of the reactants and hence a diminution in rate.

*Mechanism*

On the basis of the evidence so far adduced, the reaction of ros with \(\text{NO}_2^-\) is probably occurring by the outer sphere mechanism and the mechanism proposed below explains the experimental results:

\[
\text{NO}_2^- + \text{H}^+ \rightleftharpoons \text{HONO} \\
\text{HONO} + \text{H}^+ \rightleftharpoons \text{H}_2\text{ONO}^- \rightleftharpoons \text{H}_2\text{O} + \text{N} = 0 \quad \ldots \ldots \quad (4)
\]

\[
\text{RNH}_2^+ + \text{N} = 0 \rightleftharpoons k_1 \frac{\text{RNH}_2^+/\text{NO}_2^+}{\text{RNH}_2^+} \quad \ldots \ldots \quad (5)
\]

\[
\text{Rate} = k_1 \frac{\text{RNH}_2^+/\text{NO}_2^+}{\text{RNH}_2^+} \quad \ldots \ldots \quad (7)
\]

\[
\frac{d[\text{RNH}_2^+/\text{NO}_2^+]}{dt} = k_1[\text{RNH}_2^+][\text{N} = 0] - k_2[\text{RNH}_2^+/\text{NO}_2^+] \quad \ldots \ldots \quad (8)
\]

\[
[\text{RNH}_2^+/\text{NO}_2^+] = \frac{k_1[\text{RNH}_2^+][\text{N} = 0]}{k_1 + k_2} \quad \ldots \ldots \quad (9)
\]

But from equation (4)

\[
10^3[\text{H}^+] = \ldots \ldots \quad (10)
\]

Fig. 2: Plot of \(k_1\) Vs. \([\text{H}^+]\) For the redox reaction between rosaniline and \(\text{NO}_2^-\)

\[
[\text{RNH}_2^+/\text{NO}_2^+] = \frac{K_1K_2K_3[\text{H}^+][\text{NO}_2^-]}{k_1 + k_2} \quad \ldots \ldots \quad (11)
\]

Putting equation (11) in (7) gives

\[
\text{Rate} = k_1 [\text{H}^+] [\text{RNH}_2^+] [\text{NO}_2^-] \quad \ldots \ldots \quad (12)
\]

Equation (12) conforms with the observed rate law, equation (3), where \( k = \frac{K_r K_k K_k K_k}{K_k} \) and 

\[ \text{RNH}_2^+ = \text{ros} \]

REFERENCES


accepted 17/3/99
received 29/10/98