

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 (NO_2^-) in aqueous media have been studied at 30°C , $I=0.25\text{ M}$ (LiCl), $[\text{H}^+]=3.0\times 10^{-4}\text{ M}$. 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 $-d[\text{ros}]/dt = a[\text{H}^+][\text{ros}][\text{NO}_2^-]$. 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 (NO_2^-) are well known. Nitrite ions have been observed to reduce riboflavine¹, ascorbic acid² and enzymes from cucurbita-pepo³. In the reduction of riboflavine, H_2O_2 was obtained as the product while NH_3 was the product for the reaction involving ascorbic acid and enzyme from cucurbita-pepo. Dolcetti and Peloso⁴ studied the reduction of Pt [Co-phenylene-bis-dimethylarsine Br_2]²⁺ by NO_2^- 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 NO_2^- were reported by Fraser et al.⁵, Yatsimirski and Badarina⁶, Meyerstein and Mulac⁷, Nakahara and Takabayashi⁸. These reactions demonstrate NO_2^- 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 NO_2^- ion.

EXPERIMENTAL

Reagents

*Author for correspondence

Present address: Chemistry Department

Federal College of Education, Zaria, Nigeria.

Nigerian Journal of Chemical Research, Vol 3, 1998

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 Corning Spectronic 20 colorimeter by observing the decrease in the absorbance of ros at its characteristic wavelength, $\lambda_{\text{max}} = 545\text{nm}$. All kinetic measurements were carried out under pseudo-first order conditions with NO_2^- concentration in excess over the ros concentration at 30°C and 0.25 M (LiCl) ionic strength. The pseudo-first order plots of $\log(A_t - A_\infty)$ versus time were made. From the slope of the plots the pseudo-first order rate constant (k_1) was determined. The second order rate constant (k_2) was obtained from k_1 as $k_1/[\text{NO}_2^-]$. 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 $1.0-10.0 \times 10^{-4}\text{ M}$ while the concentrations of ros and NO_2^- were kept constant. The reaction was carried out at 30°C and $I=0.5\text{ M}$ (LiCl). The results are presented in Table 1.

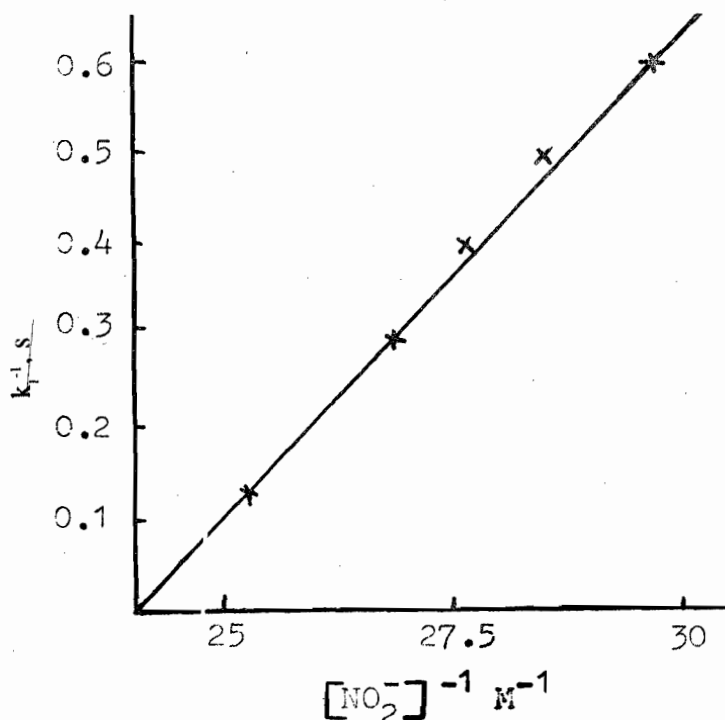
The effect of ionic strength

The effect of ionic strength on the rate of the reac-

Table 1: Pseudo-first order and second order rate constants for the reaction of rosaniline and NO₂⁻ I = 0.25 M (LiCl), T = 30°C, λ_{max} = 545 nm, [ros] = 4 × 10⁻⁴ M.

[NO ₂ ⁻]M	[H ⁺]M	[LiCl]M	10 ³ k ₁ s ⁻¹	k ₂ M ⁻¹ s ⁻¹
3.3	3.0	0.25	2.31	9.24
3.5	3.0	0.25	2.88	8.23
4.0	3.0	0.25	2.96	7.40
3.8	3.0	0.25	3.36	6.72
6.0	3.0	0.25	3.84	6.40
8.0	3.0	0.25	4.80	6.00
2.5	1.0	0.25	0.27	1.08
2.5	3.0	0.25	2.35	9.40
2.5	7.0	0.25	5.85	23.40
2.5	10	0.25	11.20	44.80
2.5	30	0.25	0.93	3.72
2.5	30	0.05	1.27	5.08
2.5	30	0.10	1.87	7.48
2.5	30	0.17	2.27	9.08
2.5	30	0.25	2.43	9.72
2.5	30	0.35	2.88	11.52
2.5	30	0.40	3.31	13.24

Fig. 1: Michaelis Menten's Plot for the reaction of rosaniline and NO₂⁻



tion was investigated in the range of I = 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_t vs 1/[NO₂⁻] was executed (Figure 1).

RESULTS AND DISCUSSION

Kinetic measurements

The pseudo-first order plots of log (A_t-A_∞) versus time for these reactions were linear for about 70% of the reaction (A_t, A_∞ 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 [ros]. Plots of log k_t versus log [NO₂⁻] gave a slope of 0.73 showing that the reaction is also first order with respect to [NO₂⁻]. Thus the rate equation for the reaction is

$$-d[ros]/dt = k_2 [RNH_2^+][NO_2^-] \dots \dots \dots (1)$$

The order of one in the oxidant and reductant concentration in this reaction conforms with already reported order for the redox reactions involving NO₂⁻ and other oxidants.^{9,4,5}

Acid dependence studies

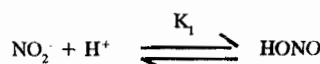
From the result in Table 1, it is observed that the rate constant of the reaction increased with increase in acid concentration. The plot of k₂ vs [H⁺] was linear with no intercept (Figure 2). The acid dependent rate constant k₂ is given as

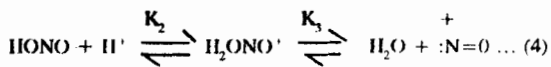
$$k_2 = a[H^+], \quad a = 0.903 \text{ M}^{-2}\text{s}^{-1} \dots \dots \dots (2)$$

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

$$-d[ros]/dt = a[H^+][RNH_2^+][NO_2^-] \dots \dots \dots (3)$$

The nature of acid dependence observed implies that there is a rapid equilibrium between protonated and unprotonated forms of the reductant (NO₂⁻) prior to the rate determining step and that only the protonated form is reactive. This form of acid dependence is expected for NO₂⁻ reactions as the equilibria below have been established¹⁰ for NO₂⁻ in aqueous media:





In these equilibria, the :N=O^+ is assumed to be the reactive specie and it is involved in the reaction mechanism.

The effect of ionic strength

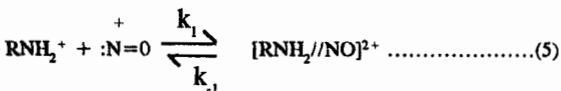
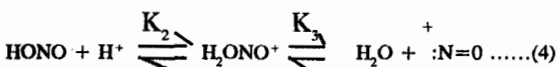
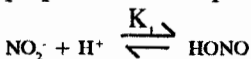
The results in Table 1 show that the rate constant of the reaction increased with increased ionic strength suggesting a positive salt effect. This observation shows that the activated complex is formed from either two ions of like charges or a charged and a neutral reactants.

Intermediate complex formation

No shift in λ_{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 λ_{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 (Ca^{2+} , 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 NO_2^- is probably occurring by the outer sphere mechanism and the mechanism proposed below explains the experimental results:



$$\text{Rate} = k_2 [\text{RNH}_2//\text{NO}]^{2+} \dots (7)$$

$$\frac{-d[\text{RNH}_2//\text{NO}]^{2+}}{dt} = k_1[\text{RNH}_2^+][\text{:N=O}^+] - k_{-1}[\text{RNH}_2//\text{NO}]^{2+} - k_2[\text{RNH}_2//\text{NO}]^{2+} \dots (8)$$

$$[\text{RNH}_2//\text{NO}]^{2+} = \frac{k_1[\text{RNH}_2^+][\text{:N=O}^+]}{k_{-1} + k_2} \dots (9)$$

But from equation (4)

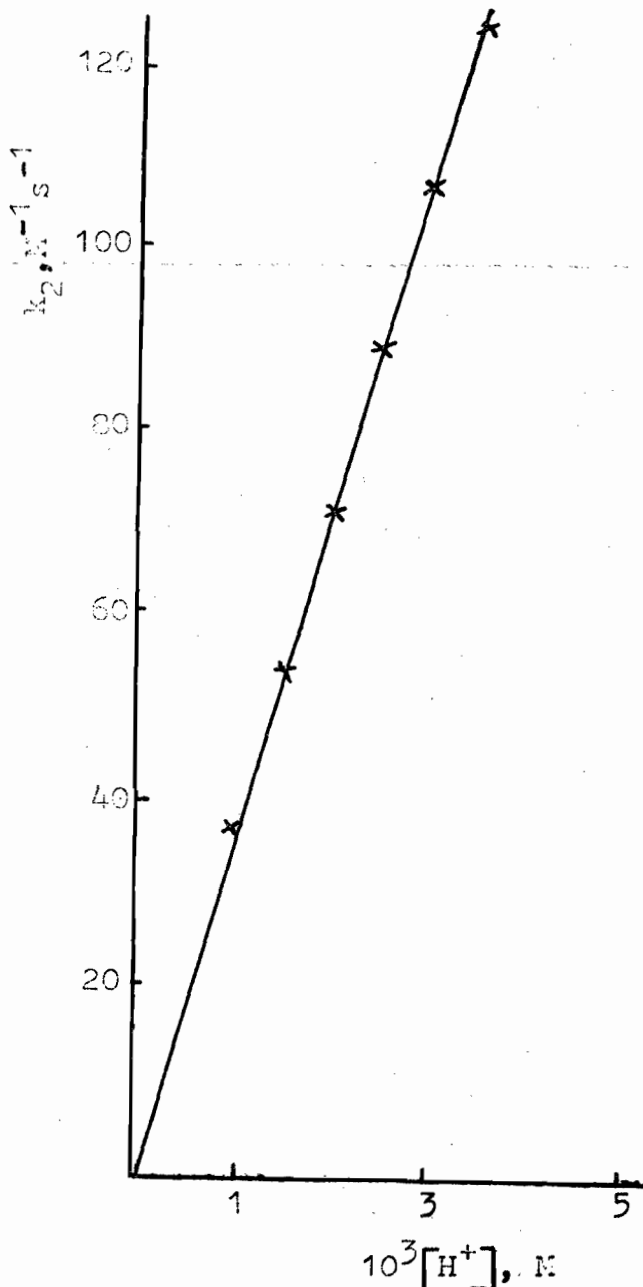


Fig. 2: Plot of k_2 Vs. $[\text{H}^+]$ For the redox reaction between rosaniline and NO_2^-

$$[\text{:N=O}^+] = K_3 K_2 K_1 [\text{H}^+][\text{NO}_2^-] \dots (10)$$

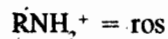
Substituting equation (10) in (9) gives

$$[\text{RNH}_2//\text{NO}]^{2+} = \frac{K_3 K_2 K_1 k_1 [\text{H}^+][\text{RNH}_2^+][\text{NO}_2^-]}{k_{-1} + k_2} \dots (11)$$

Putting equation (11) in (7) gives

$$\text{Rate} = k [\text{H}^+][\text{RNH}_2^+][\text{NO}_2^-] \dots (12)$$

Equation (12) conforms with the observed rate law, equation (3), where $k = \frac{K_3 K_2 K_1 k_1 k_2}{K_1 K_2} = a$ and



REFERENCES

1. Kolesnikov, P.A., Doklady Akado Nauk SS-SR 1960, 133, 1462.
2. Gurevich, A.A. and Trubachev, I.N., Dokl. Akad. Nauk SSSR 1964, 157 (2), 466.
3. Cresswell, C.F., Hageman, R.H., Hewitt, E.J. and Huckleby, D.P., Biochem. J. 1965, 94(1), 40.
4. Dolcetti, G. and Pelso, A., Gazz Chem. Ital., 1967, 97 (10), 1540.
5. Fraser, R.T.M., Lee, R.N. and Hayden K., J. Chem. Soc. A, 1967, 5, 741
6. Yatsimirski, K.B. and Budarina, A.N., Kinet Katal., 1968, 9(2), 422.
7. Meyerstein, D. and Mulac, W.A., J. Phys. Chem. 1968, 72(3), 784.
8. Nakahara, T. and Takabayashi, Y., Jpn. Kakai Tokkoyo Koho Jp 1995, 700972, 4.
9. Lueonok - Burmakina, V.A., Alleva, G.P. and Franchuk, T.M., Zh Neorg. Khim 1968, 13(4) 975.
10. Roberts, J.D. and Caserio, M.C., Basic Principles of Organic Chemistry, 2nd ed., W.A. benamin Inc., USA, 1968.
11. Wilkins, R.G., The Study of kinetics and Mechanism of Reactions of Transition Metal Complexes, Allyn and Bacon Inc., 1974.

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