Turk J Chem
28 (2004) , 9 – 15.
© TÜBİTAK

Kinetics and Mechanism of Oxidation of *n*–Propanolamine by Dihydroxydiperiodatonickelate(IV) in Alkaline Medium

Jin-Huan SHAN*, **Jing QIAN**, **Ming-Zhu GAO**,
Shi-Gang SHEN, **Han-Wen SUN**
College of Chemistry and Environmental Science, Hebei University,
Baoding 071002-CHINA
Key Laboratory of Analytical Science of Hebei Province
e-mail:qianjinger@yahoo.com.cn

Received 08.07.2003

The kinetics of oxidation of n–Propanolamine ($n-$PA) by dihydroxy diperiodato-nickelate(IV) (DPN) in alkaline medium was studied with spectrophotometry in a temperature range of 293.2-308.2 K. The reaction was found to be pseudo first-order with respect to DPN and fractional order to $n-$PA. The rate conatant k_{obs}, rose with an increase in the concentration of OH^- and a decrease in the concentration of IO_4^-. Added salts did not affect the rate and no free radical was detected. From the evaluation of linear data, a reaction mechanism is proposed which involves a pre-equilibrium of an adduct formation between $n-$PA and dihydroxymonoperiodatonickelate(IV) (MPN), and the activation parameters of the rate-determining step have been calculated.

Key Words: Dihydroxydiperiodatonickelate(IV), n–Propanolamine, Redox reaction, Kinetics and mechanism.

Introduction

In recent years, the study of the highest oxidation state of transition metals has intrigued many researchers. This can provide new and valuable information in some fields. Transition metals in a higher oxidation state can generally be stabilised by chelation with suitable polydentate ligands. Metal chelates such as diperiodatocuprate(III)[1], diperiodatoargentate(III)[2] and diperiodatonickelate(IV)[3] are good oxidants in a medium with an appropriate pH value. The use of DPN as an oxidising agent has been well established in the investigation of various organic compounds such as various amino acids[4]. In our previous works, we have studied the reaction kinetics and mechanism between DPN and β-propylene-glycol(β-PG)[5]. It is useful to perform a further study on this kind of reaction system. In this paper, we study the reaction kinetics and mechanism between DPN and $n-$PA.

---

*Corresponding author

Chemicals and Apparatus

All reagents used were of analytical reagent grade. All solutions were prepared with twice distilled water. Solutions of $[Ni(OH)_2(H_2IO_6)_2]^{4-}$(DPN) and $CH_2NH_2CH_2CH_2OH$ were always freshly prepared before use. The stock solution of DPN in a strong alkaline medium was prepared according to the procedure given by Baker[6] and standardized with the Murthy's[3] method. Its electronic spectrum was consistent with that reported by Murthy. The ionic strength was maintained by adding KNO_3 solution and the pH value was regulated with KOH solution.

Measurements of the kinetics were performed using a UV-8500 spectrophotometer (Shanghai) fitted with a 501 thermostat (±0.1 K,Shanghai). Details of the determinations are described elsewhere [7]. The oxidation product was identified as the corresponding aldehyde by spot test [8].

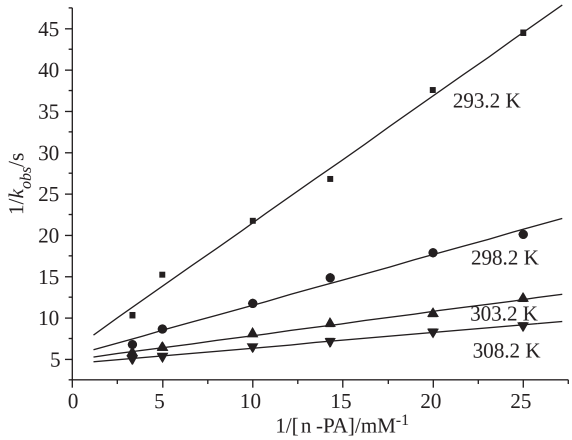
Results and Discussion

Evaluation of pseudo-first-order rate constants

Under the condition of $[n{-}PA]_0 >> [DPN]_0$, the plots of $\ln(A_t\text{-}A_\infty)$ versus time t for more than 3 half lives of the reaction were found to be linear ($r \geq 0.9998$), indicating the order in DPN to be unity. The pseudo-first-order rate constants, k_{obs}, were calculated by the least-squares method. The rate constants reported here are the averages of 3 independent runs. Deviations in duplicate determinations are generally less than ±5%.

The dependence of rate on the concentration of *n*-PA

At constant temperature,k_{obs} values increase by increasing the concentration of $n{-}$PA while keeping the concentration of DPN, OH^-, IO_4^- and μ constant. The order with respect to $n{-}$PA was fractional. The plots of $1/k_{obs}$ versus $1/[n{-}PA]$ were straight lines with a positive intercept ($r \geq 0.995$) (Figure 1).

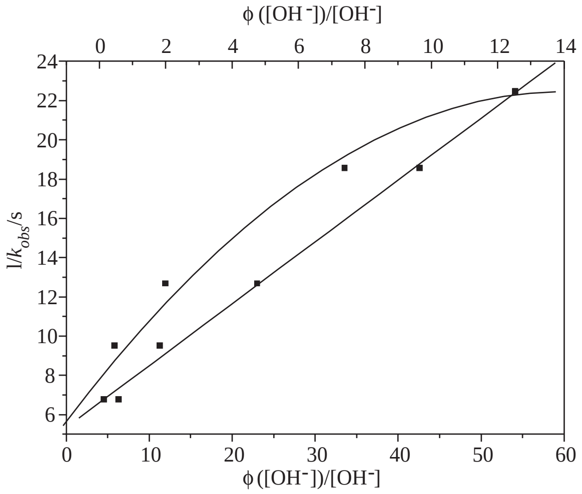


$[DPN] = 6.409 \times 10^{-2}$ mM; $[IO_4^-] = 1.2$ mM; $[OH^-] = 125$ mM; $\mu = 126.3$ mM.

Figure 1. Plots of $1/k_{obs}$ vs $1/[n{-}PA]$ at different temperatures.

The dependence of rate on the concentration of OH^-

At constant temperature,k_{obs} values increase by raising the concentration of OH^- while keeping the concentration of DPN, n−PA, IO_4^- and μ constant.The order with respect to OH^- was fractional. The plot of $1/k_{\mathrm{obs}}$ versus $f([OH^-])/[OH^-]$ was found to be straight linear (r = 0.998) (Figure 2).



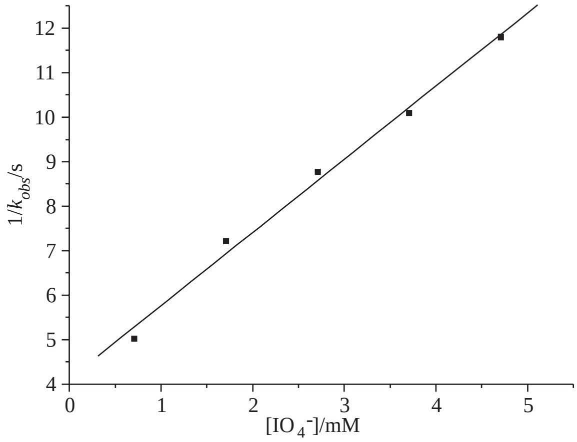
$\phi([OH^-])/[OH^-]$(curve II) at T = 298.2K

[DPN] = 6.409×10^{-2} mM, $[IO_4^-]$ = 1.2 mM, [n−PA] = 15 mM, μ = 156.3 mM.

Figure 2. Comparison of plot of $1/k_{\mathrm{obs}}$ vs. f ($[OH^-]$)/$[OH^-]$ (curve I) with that of $1/k_{\mathrm{obs}}$ vs. ϕ ($[OH^-]$)/$[OH^-]$ (curve II) at T = 298.2 K.

The dependence of rate on the concentration of IO_4^-

At constant [DPN], [n−PA], $[OH^-]$, μ and temperature, the experimental results indicate that k_{obs} decreases while increasing the concentration of IO_4^-. The order with respect to IO_4^- was negative fractional and the plot of $1/k_{\mathrm{obs}}$ versus $[IO_4^-]$ was linear (r = 0.996) (Figure 3).



[DPN] = 4.579×10^{-2} mM; $[OH^-]$ = 123.6 mM; [n−PA] = 25 mM; μ=128.4 mM

Figure 3. Plots of $1/k_{\mathrm{obs}}$ vs. $[IO_4^-]$ at T = 298.2 K

The dependence of rate on the concentration of μ

Table 1 reveals that the effect of ionic strength on the rate is negligible. (Table 1)

Table 1. Rate dependence on ionic strength μ at T = 298.2K.

I/mM	126.3	226.3	326.3	426.3	526.3
$k_{\text{obs}}/\text{s}^{-1}$	0.1042	0.1029	0.1059	0.1048	0.1039

[DPN] = 6.409 × 10^{-2} mM, [n–PA] = 15 mM, [OH^-] = 125 mM, [IO_4^-] = 1.2 mM.

Free radical detection

The addition of acrylonitrile or acrylamide to the reaction mixture under the protection of nitrogen did not alter the rate and there was no polymerisation, showing the absence of free radicals in the reaction.

In the alkaline medium, the dissociative equilibria (1)-(3) of the IO_4^- were detected and the corresponding equilibrium constants were determined at 298.2 K by Aveston[9].

$$2IO_4^- + 2OH^- \rightleftharpoons H_2I_2O_{10}^{4-} \quad \log\beta_1 = 15.05 \tag{1}$$

$$IO_4^- + OH^- + H_2O \rightleftharpoons H_3IO_6^{2-} \quad \log\beta_2 = 6.21 \tag{2}$$

$$IO_4^- + 2OH^- \rightleftharpoons H_2IO_6^{3-} \quad \log\beta_3 = 8.67 \tag{3}$$

The distribution of all periodate species in alkaline solution was calculated from equilibria (1)-(3). In the concentration range of OH^- used in this work, the dimer ($H_2I_2O_{10}^{4-}$) and IO_4^- species of periodate can be ignored (under the condition of [OH^-] = 15.0 - 155mM, [IO_4^-] = 6.41 × 10^{-2} mM, $H_2IO_6^{3-}$: $H_3IO_6^{2-}$: $H_2I_2O_{10}^{4-}$: [IO_4^-] ≅ 1.5:1.0:1.0 × 10^{-4}: 3.7 × 10^{-8}). The main species of periodate $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ are consistent with the result calculated from Crouthamel's data[10] by on Murthy. Based on such distribution and Murthy's argument, the formula of DPN may be represented by either $[Ni(OH)_2(H_3IO_6)_2]^{2-}$ or the less protonated $[Ni(OH)_2(H_2IO_6)_2]^{4-}$. We preferred to use the latter to represent DPN because it is closer to that suggested by Mukherjee[11] and is supported by kinetic studies.

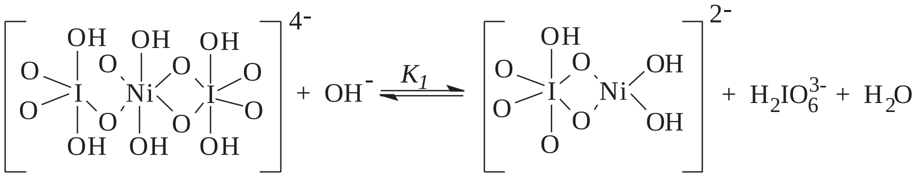
The fractional order dependence of k_{obs}on [OH^-] suggests that OH^- takes part in pre-equilibrium with DPN before the rate-determining step. The plot of $1/k_{\text{obs}}$ vs. [IO_4^-] is linear with a positive intercept indicating a dissociative equilibrium in which the DPN loses a periodate ligand $H_2IO_6^{3-}$ from its coordination sphere, forming a reactive monoperiodatonickelate(IV) complex (MPN). The plots of $1/k_{\text{obs}}$ vs. 1/[n-PA] are linear, indicating a pre-equilibrium forming a 1:1 complex between MPN and n–PA.

In view of the above results and discussion, a plausible reaction mechanism is proposed:

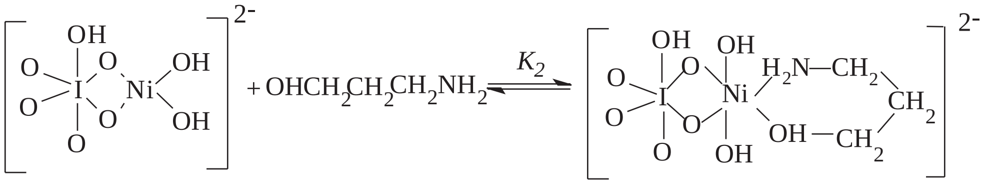
Here, the reaction (6) was the rate-determining step.

$$[\text{Ni(IV)}]_T = [\text{I}]_e + [\text{II}]_e + [\text{complex}]_e = [\text{complex}]_e\left(1 + \frac{1}{K_2[n-\text{PA}]} + \frac{[H_2IO_6^{3-}]}{K_1K_2[OH^-][n-\text{PA}]}\right)$$

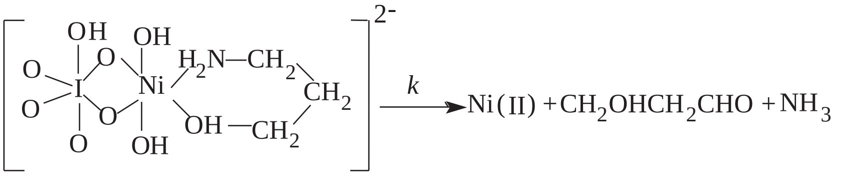
$$[\text{complex}]_e = \frac{K_1K_2[OH^-][n-\text{PA}]}{[H_2IO_6^{3-}] + K_1[OH^-] + K_1K_2[OH^-][n-\text{PA}]}[\text{Ni(IV)}]_T$$



(4)



(5)



(6)

Subscripts T and e stand for total concentration and concentration at equilibrium respectively.

As the rate of the disappearance of DPN was monitored, the rate of the reaction can be derived as:

$$-\frac{d\mathrm{Ni}(IV)_T}{dt} = k[\mathrm{complex}]_e = \frac{kK_1K_2[\mathrm{OH^-}][n-\mathrm{PA}]}{[\mathrm{H_2IO_6^{3-}}]+K_1[\mathrm{OH^-}]+K_1K_2[\mathrm{OH^-}][n-\mathrm{PA}]}[\mathrm{Ni(IV)}]_T \tag{7}$$

$$\therefore k_{\mathrm{obs}} = \frac{kK_1K_2[\mathrm{OH^-}][n-\mathrm{PA}]}{[\mathrm{H_2IO_6^{3-}}]+K_1[\mathrm{OH^-}]+K_1K_2[\mathrm{OH^-}][n-\mathrm{PA}]} = k_{\mathrm{obs}}[\mathrm{Ni(IV)}]_T \tag{8}$$

Ignoring the concentration of ligands dissociated from DPN and the species of periodate other than $\mathrm{H_2IO_6^{3-}}$ and $\mathrm{H_3IO_6^{2-}}$, here

$$[\mathrm{IO_4^-}]_{ex} \cong [\mathrm{H_3IO_6^{2-}}]+[\mathrm{H_2IO_6^{3-}}] \tag{9}$$

Equations (10) and (11) can be obtained from (2), (3) and (9):

$$[\mathrm{H_2IO_6^{3-}}] = \frac{\beta_3[\mathrm{OH^-}]}{\beta_2+\beta_3[\mathrm{OH^-}]}\cdot[\mathrm{IO_4^-}]_{ex} = f([\mathrm{OH^-}])\cdot[\mathrm{IO_4^-}]_{ex} \tag{10}$$

$$[\mathrm{H_3IO_6^{2-}}] = \frac{\beta_2}{\beta_2+\beta_3[\mathrm{OH^-}]}\cdot[\mathrm{IO_4^-}]_{ex} = \phi([\mathrm{OH^-}])\cdot[\mathrm{IO_4^-}]_{ex} \tag{11}$$

Here $[\mathrm{IO_4^-}]_{ex}$ represents the original overall entering periodate and approximately equals the sum of $[\mathrm{H_2IO_6^{3-}}]$ and $[\mathrm{H_3IO_6^{2-}}]$.

Substituting Eq. (10) into (8), we arrive at the following equations:

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1+K_2[n-\mathrm{PA}]}{kK_2[n-\mathrm{PA}]} + \frac{[\mathrm{IO_4^-}]_{ex}}{kK_1K_2[n-\mathrm{PA}]}\cdot\frac{f([\mathrm{OH^-}])}{[\mathrm{OH^-}]} \tag{12}$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k} + \frac{f([\text{OH}^-])[\text{IO}_4^-]_{ex} + K_1[\text{OH}^-]}{kK_1K_2[\text{OH}^-]} \cdot \frac{1}{[n-\text{PA}]} \tag{13}$$

$$\frac{1}{k_{\text{obs}}} = \frac{1 + K_2[n-\text{PA}]}{kK_2[n-\text{PA}]} + \frac{f([\text{OH}^-])}{kK_1K_2[\text{OH}^-][n-\text{PA}]} \cdot [\text{IO}_4^-]_{ex} \tag{14}$$

If the formula of DPN were $[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}$, the substitution of Eq. (11) into (8) gives Eq. (15):

$$\frac{1}{k_{\text{obs}}} = \frac{1 + K_2[n-\text{PA}]}{kK_2[n-\text{PA}]} + \frac{[\text{IO}_4^-]_{ex}}{kK_1K_2[n-\text{PA}]} \cdot \frac{\phi([OH-])}{[\text{OH}^-]} \tag{15}$$

The plot of $1/k_{\text{obs}}$ vs. $\phi([\text{OH}^-])/[\text{OH}^-]$ should also be linear, although the linearity was not straight (Figure 2), which substantially refutes Eq. (15). Therefore, it seems reasonable to represent DPN by $[\text{Ni(OH)}_2(\text{H}_2\text{IO}_6)_2]^{4-}$, which is consistent with the experimental observation.

From Eq. (12), the plots of $1/k_{\text{obs}}$ vs. $1/[n-\text{PA}]$ are straight linear and the rate constants of the rate-determining step at different temperatures were obtained from the intercept of the straight line. Eq. (13) shows that the plot of $1/k_{\text{obs}}$ vs. $f([\text{OH}^-])/[\text{OH}^-]$ is straight linear, and Eq. (14) shows that the plot of $1/k_{\text{obs}}$ vs. $[\text{IO}_4^-]$ is straight linear. The rate constants and the activation parameters of $n-$PA were obtained by the method given earlier[12] (Table 2).

Table 2. Rate constants (k) and the activation parameters for the rate-determining step.

	T/K						T/K Activation parameters (298.2K)		
	293.2	298.2	303.2	308.2	313.2	318.2	Ea	$\Delta H^{\#}$	$\Delta S^{\#}$
10^2k /s^{-1}							J·mmol^{-1}	J·mmol^{-1}	J·K^{-1}·mmol^{-1}
β-PG		0.798	1.1	1.6	2.732	3.602	61.61 ± 1.8	59.13 ± 1.8	0.0873 ± 0.0022
$n-$PA	16.22	18.38	20.20	22.29			15.03 ± 0.2	12.55 ± 0.2	0.217 ± 0.0006

The plot of ln$k$ vs.1/T has following intercepts (a) slope (b) and relative coefficient (r)
r = -0.999, a = 4.366, b = -1807.58

Based on the above discussion and comparing this to our previous work[5], the rate-determining step constants of $n-$PA are larger than those of β-PG, and activation energies have an inverse sequence. We conclude that the reaction rate changed with the active group. Since the formation of a hexa-cyclic intermediate adduct compound by DPN and*n*–Propanolamine ($n-$PA) is easier than that of a hexa-cyclic intermediate adduct compound by DPN and β-propylene-glycol (β-PG), the former is more stable, which is consistent with the experimental observation. This phenomenon is consistent with the theory of hard-soft acid-base.

References

1. K.B. Reddy, B. Sethuram and T.N. Rao, **Indian J. Chem. 23A**, 593 (1984).
2. P.J.P. Rao, B. Sethuram and T.N. Rao, **Indian J. Chem. Soc**., **67**, 101 (1990).
3. C. P. Murthy, B. Sethuram, T. N. Rao, **Phys. Chemie, (Leipzig)**, **267**, 1212 (1986).
4. J.H. Shan, H.Y. Wei, S.G. Shen and H.W. Sun, **Indian J. Chem**. **40A**, 865 (2001).

5. J.H. Shan, J. Qian, L.P. Wang, S.G. Shen and H.W. Sun, **Chem. J. on Internet, 5(3)**, 1523 (2003).
6. L.C.W. Baker, H.G. Mukherjee and S.B. Sarkar, **Indian J. Chem**., **21A**, 618 (1982).
7. J.H. Shan, L.P. Wang, S.G. Shen and H.W. Sun, **Turk J. Chem**. **27**, 265-272 (2003).
8. F. Feigl, "**Spot Tests in Organic Analysis**", Elsevier Publishing Co, New York, 1956.
9. J. Aveston ,**J. Chem. Soc. (A)**, 273 (1969).
10. C.E. Crouthamel, H.V. Meek and D.S. Martin **J. Am. Chem. Soc. 71**, 3031 (1949); **73**, 82 (1951).
11. H.G. Mukherjee and B. Mandal, **Indian J. Chem**, **23A**, 426 (1984).
12. J.H. Shan, L.P. Wang, S.G. Shen, H.W. Sun, **Chinese J. Inorg. Chem. 18(9)**, 887 (2002).