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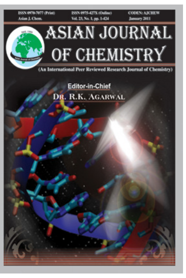

Kinetics and Mechanism of Oxidation of N-Methyldiethanolamine by Dihydroxydiperiodatonickelate(IV) in Alkaline Liquids

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The kinetics of oxidation of N-methyldiethanolamine (MDEA) by diperiodatonickelate(IV) (DPN) in alkaline liquids at a constant ionic strength has been studied spectrophotometrically in the temperature range of 293.2–313.2 K. The reaction shows first order dependence on [DPN] and fractional order with respect to [MDEA]. The observed rate constant (k_{obs}) decreased with increasing [IO_4^-] and increased with increasing [OH^-]. The added salts did not affect the rate. A mechanism involving the diperiodatonickelate(IV) (DPN) as the reactive species of the oxidant has been proposed. The rate constants of the rate-determining step and the activation parameters were calculated.

Key Words: Dihydroxydiperiodatonickelate(IV), Kinetics, Mechanism, N-methyldiethanolamine.

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 many fields. Transition metals in a higher oxidation state can generally be stabilized 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. Ni(IV) complexes have been employed as oxidizing agents for the investigation of some organic compounds such as tetrahydrofurfuryl alcohol[4], L-leucine[5], 4-hydroxycoumarin[6], gabapentin[7], *etc.*

N-Methyldiethanolamine (MDEA) is an important and widely used class of organic compounds. It has been widely applied as desulfurization emulsifier for oil gases, acidic gas absorber and pH control agent. In the presence of activator reagents, MDEA can effectively remove the carbon dioxide from the synthetic ammonia. In addition, MDEA can also be used as the semi-products of pesticides and textile auxiliaries, the intermediate of anticancer agent chlormethine hydrochloride, fiber additives and dry-promoter for the paint. The kinetics and mechanisms of oxidation of MDEA can provide some valuable information for chemical industry and organic synthesis.

EXPERIMENTAL

All the reagents used were of A.R. grade. All solutions were prepared with double distilled water. The solution of oxidation was prepared[8] and standardized[9] by the method reported earlier. Its UV spectrum were found to be consistent with that reported in the literature. The concentration of dihydroxydiperiodatonickelate(IV (DPN) was derived from its absorption at 410 nm. The solution of oxidation was always freshly prepared before use. The ionic strength (μ) was maintained by adding KNO_3 solution and the pH of the reaction mixture was adjusted with a KOH solution. The kinetic measurements were performed on a UV-Vis spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell holder kept at constant temperature (± 0.1 ºC) by circulating water from a thermostat (DC-2010, Baoding, China).

Kinetics measurements: The kinetic measurements was described elsewhere[10]. The product of oxidation was identified as the corresponding aldehyde and Ni(II) by spot test[11].

RESULTS AND DISCUSSION

Evaluation of pseudo-first order rate constants: Under the conditions of $[MDEA]_0 >> [Ni(IV)]_0$, the plots of $\ln (A_t-A_\infty)$ *versus* time were straight lines, details of the evaluation are described in our previous work[12].

Rate dependence on the MDEA concentration: At constant temperature, k_{obs} values increase by increasing the concentration of MDEA while keeping the [Ni(IV)], [OH^-], [IO_4^-] and μ constant. The order with respect to MDEA was fractional. The plots of $1/k_{obs}$ *vs.* 1/[MDEA] were straight lines with a positive intercept (Fig. 1).

Rate dependence on the IO_4^- concentration: At constant [Ni(IV)], [MDEA], [OH^-], μ and temperature, the experimental results indicate that k_{obs} decreases while increasing the $[IO_4^-]$. The order with respect to $[IO_4^-]$ was negative fractional and the plot of $1/k_{obs}$ *vs.* $[IO_4^-]$ was linear (Fig. 2).

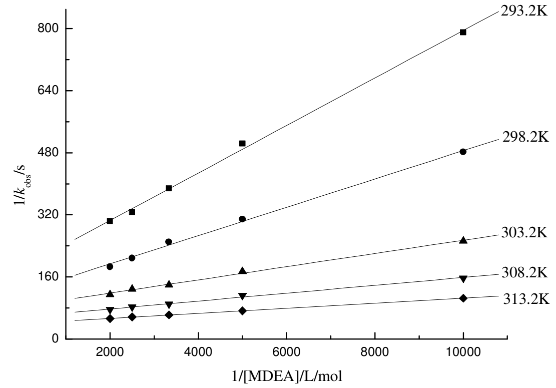

Fig. 1. Plots of $1/k_{obs}$ *versus* 1/[MDEA] (r ≥ 0.997). $[Ni(IV)] = 3.20 \times 10^{-6}$ M, $[IO_4^-] = 5.00 \times 10^{-4}$ M, $[OH^-] = 1.48 \times 10^{-2}$ M, $\mu = 3.53 \times 10^{-2}$ M

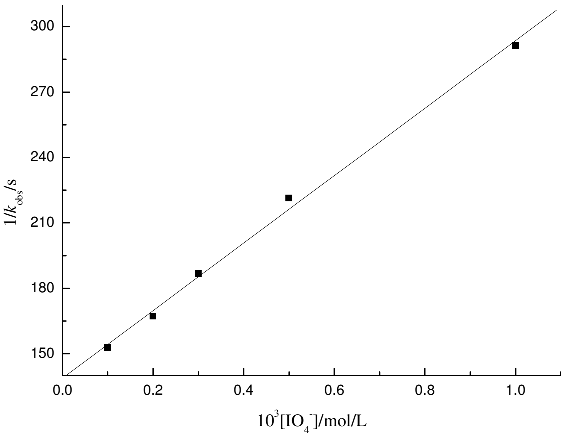

Fig. 2. Plot of $1/k_{obs}$ *versus* $10^3[IO_4^-]$ at 298.2 K (r = 0.998). $[Ni(IV)] = 3.20 \times 10^{-6}$ M, $[OH^-] = 1.48 \times 10^{-2}$ M, $[MDEA] = 3.00 \times 10^{-4}$ M, $\mu = 3.08 \times 10^{-2}$ M

Rate dependence on the OH^- concentration: At constant [Ni(IV)], [MDEA], $[IO_4^-]$, μ and temperature, k_{obs} values increased with the increase in $[OH^-]$. The order with respect to $[OH^-]$ was fractional and the plot of $1/k_{obs}$ *vs.* $f([OH^-])/[OH^-]$ was linear (Fig. 3).

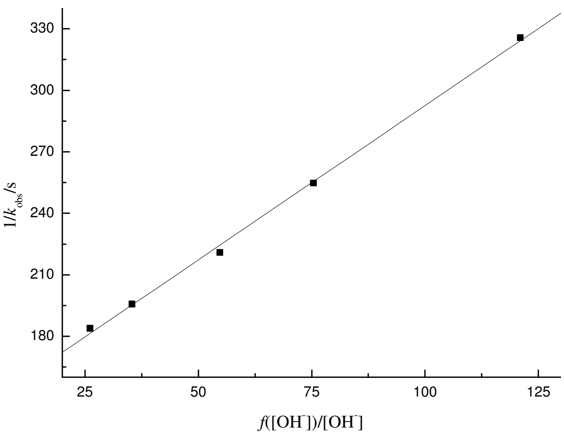

Fig. 3. Plot of $1/k_{obs}$ *versus* $f([OH^-])/[OH^-]$ at 298.2 K (r = 0.999). $[Ni(IV)] = 3.20 \times 10^{-6}$ M, $[IO_4^-] = 5.00 \times 10^{-4}$ M, $[MDEA] = 3.00 \times 10^{-4}$ M, $\mu = 3.53 \times 10^{-2}$ M

Rate dependence on the ionic strength: With other fixed conditions, the reaction rate dose not change by the addition of KNO_3 solution (Table-1),which indicate there is no salt effect.

TABLE-1
RATE DEPENDENCE ON IONIC STRENGTH AT 298.2 K

10^2 μ/M	1.53	2.53	3.53	4.53	5.53
$10^3 k_{obs}/s^{-1}$	4.42	4.40	4.47	4.45	4.44

$[Ni(IV)] = 3.20 \times 10^{-6}$ M, $[OH^-] = 1.48 \times 10^{-2}$ M, $[MDEA] = 3.00 \times 10^{-4}$ M, $[IO_4^-] = 5.00 \times 10^{-3}$ M

Reaction mechanism: In alkaline solution, equilibria (1-3) were observed and the corresponding equilibrium constants at 298.2 K were determined by Aveston[13].

$$2IO_4^- + 2OH^- \rightleftharpoons H_2I_2O_{10}^{4-} \qquad \log \beta_1 = 15.05 \qquad (1)$$

$$IO_4^- + OH^- + H_2O \rightleftharpoons H_3IO_6^{2-} \qquad \log \beta_2 = 6.21 \qquad (2)$$

$$IO_4^- + 2OH^- \rightleftharpoons H_2IO_6^{3-} \qquad \log \beta_3 = 8.67 \qquad (3)$$

The distribution of all species of periodate in alkaline solution can be calculated from the equilibriums (1-3). The dimer $H_2I_2O_{10}^{4-}$ and IO_4^- species can be neglected, the main iodic acid species is $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. According to the literature, the main existent form of oxidant was $[Ni(OH)_2(H_2IO_6)_2]^{4-}$ over the experimental concentration range of OH^-.

Neglecting the concentration of ligand dissociated from Ni(IV), the main species of periodate are $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$, here:

$$[IO_4^-]_t \cong [H_3IO_6^{2-}] + [H_2IO_6^{3-}] \qquad (4)$$

Eqns. 5 and 6 can be obtained from eqns. 2, 3, 4:

$$[H_2IO_6^{3-}] = \frac{\beta_3[OH^-]}{\beta_2 + \beta_3[OH^-]} \cdot [IO_4^-]_t = f([OH^-]) \cdot [IO_4^-]_t \qquad (5)$$

$$[H_3IO_6^{2-}] = \frac{\beta_2}{\beta_2 + \beta_3[OH^-]} \cdot [IO_4^-]_t = \phi([OH^-]) \cdot [IO_4^-]_t \qquad (6)$$

Here, $[IO_4^-]_t$ represents the concentration of original over all periodate ions which is approximately equal to the sum of $[H_2IO_6^{3-}]$ and $[H_3IO_6^{2-}]$. In the $[OH^-]$ range used in this work, the main specie of periodate is $H_2IO_6^{3-}$. Based on the discussion, the formula of the Ni(IV) periodate complex may be represented by either $[Ni(OH)_2(H_3IO_6)_2]^{2-}$ or the less protonated ionic species $[Ni(OH)_2(H_2IO_6)_2]^{4-}$. We preferred to use the latter to represent dihydroxydiperiodatonickelate(IV) because it is close to that suggested by Mukherjee[14].

Based on the above discussion, the following reaction mechanism was proposed:

$$\underset{(I)}{[Ni(OH)_2(H_2IO_6)_2]^{4-}} + OH^- \overset{K_1}{\rightleftharpoons} \underset{(II)}{[Ni(OH)_2(HIO_6)]^{2-}} + H_2IO_6^{3-} + H_2O \qquad (7)$$

$$\underset{(II)}{[Ni(OH)_2(HIO_6)]^{2-}} + R \overset{K_2}{\rightleftharpoons} \text{Complex} \qquad (8)$$

$$\text{Complex} \xrightarrow{k} Ni(II) + \text{Product} \qquad (9)$$

$R = MDEA = CH_3N(CH_2CH_2OH)_2$

Here, reaction (9) is the rate-determining step. The oxidation products of MDEA is the corresponding aldehyde.

$[Ni(IV)]_t = [I]_e + [II]_e + [complex]_e =$

$$[\text{complex}]_e\left(1+\frac{1}{K_2[R]}+\frac{[H_2IO_6^{3-}]}{K_1K_2[OH^-][R]}\right)$$

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

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

As the rate of the disappearance of $[Ni(IV)]_t$ was monitored, the rate of the reaction can be derived as:

$$-\frac{d[Ni(IV)_t]}{dt}=k[\text{complex}]_e$$

$$=\frac{kK_1K_2[OH^-][R]}{[H_2IO_6^{3-}]+K_1[OH^-]+K_1K_2[OH^-][R]}[Ni(IV)]_t \quad (10)$$

$$\therefore k_{obs}=\frac{kK_1K_2[OH^-][R]}{[H_2IO_6^{3-}]+K_1[OH^-]+K_1K_2[OH^-][R]} \quad (11)$$

$$\frac{1}{k_{obs}}=\frac{1}{k}+\frac{f([OH^-])[IO_4^-]_t+K_1[OH^-]}{kK_1K_2[OH^-]}\cdot\frac{1}{[R]} \quad (12)$$

$$\frac{1}{k_{obs}}=\frac{1+K_2[R]}{kK_2[R]}+\frac{f([OH^-])}{kK_1K_2[OH^-][R]}\cdot[IO_4^-]_t \quad (13)$$

$$\frac{1}{k_{obs}}=\frac{1+K_2[R]}{kK_2[R]}+\frac{[IO_4^-]_t}{kK_1K_2[R]}\cdot\frac{f([OH^-])}{[OH^-]} \quad (14)$$

In this report, eqn. 12 shows that the order in (MDEA) should be fractional order and $1/k_{obs}$ *vs.* 1/[reductant] should be linear, eqn. 13 shows that the plot of $1/k_{obs}$ *vs.* $[IO_4^-]$ should also be linear and eqn. 14 shows that the plot of $1/k_{obs}$ *vs.* $f([OH^-])/[OH^-]$ should also be linear too. The rate equations derived from the reaction mechanisms are consistent with present experimental results. The activation energy and the thermodynamic parameters (298.2 K) were evaluated by the previously published method[15] (Table-2).

TABLE-2
RATE CONSTANTS (k) AND ACTIVATION PARAMETERS OF THE RATE-DETERMINING STEP

T/K	293.2	298.2	303.2	308.2	313.2
10^3 k/s^{-1}	5.46	8.28	11.85	17.47	24.82
Thermodynamic activation parameters (298.2 K)	E_a=57.63 kJ mol^{-1}, $\Delta H^{\neq}$=55.15 kJ mol^{-1}, $\Delta S^{\neq}$=-99.97 J K^{-1} mol^{-1}				
The plots of ln k *vs.* 1/T have following intercept (a) slope (b) and relative coefficient (r). a = 18.44, b = -6932, r = 0.9999					

Conclusion

Among various species of Ni(IV) in alkaline liquids, monoperiodatonickelate is considered as the active species for the title reaction. The rate constant of the rate-determining step and activation parameters with respect to the rate-determining step of the reaction were computed. The overall mechanistic sequence described here is consistent with product studies, mechanistic studies and kinetic studies.

REFERENCES

1. W.J. Niu, Y. Zhu, K.C. Hu, C.L. Tong and H.S. Yang, *Int. J. Chem. Kinet.*, **28**, 899 (1996).
2. T.S. Shi, *Sci. China, Ser. B Chem.*, **12**, 471 (1990).
3. U. Chandraiah, C.P. Murthy and K. Sushama, *Indian J. Chem.*, **28A**, 162 (1989).
4. Z.T. Li, F.L. Wang and A.Z. Wang, *Int. J. Chem. Kinet.*, **24**, 933 (1992).
5. R.T. Mahesh, P.D. Pol and S.T. Nandibewoor, *Monatsh. Chem.*, **134**, 1341 (2003).
6. R.S. Shettar and S.T. Nandibewoor, *J. Mol. Catal. A: Chem.*, **234**, 137 (2005).
7. C.V. Hiremath, D.C. Hiremath and S.T. Nandibewoor, *J. Mol. Catal. A: Chem.*, **269**, 246 (2007).
8. L.C.W. Baker, H.G. Mukerjee, S.B. Sarkar and B.K. Choudhury, *Indian J. Chem.*, **21A**, 618 (1982).
9. C.P. Murthy, B. Sethuram and T.N. Rao, *Z. Phys. Chem. (Leipzig)*, **287**, 1212 (1986).
10. J.H., Shan, H.M. Liu, S. Y. Huo, L. Fan and S.G. Shigang, *Transition Met. Chem.*, **31**, 999 (2006).
11. F. Feigl, Spot Tests in Organic Analysis, Elsevier Publishing Co, New York, p. 208 (1956).
12. J. Qian, M.Z. Gao, J.H. Shan, S.G. Shen and H.W. Sun, *J. Guangxi Normal Univ.*, **21**, 248 (2003).
13. J. Aveston, *J. Chem. Soc. A*, 273 (1969).
14. H.G. Mukherjee, B. Mandal and S. De, *Indian J. Chem.*, **23A**, 481 (1984).
15. J.H. Shan and T.Y. Liu, *Acta Chim. Sinica*, **52**, 1140 (1994).