Kinetics and Mechanism of Oxidation of Ethylene Glycol Monoethylether by Diperiodatonickelate(IV) in Alkaline Medium

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The kinetics of oxidation of ethylene glycol monoethylether (EGE) by diperiodatonickelate(IV) ion (DPN) was studied by spectrophotometry in alkaline medium. The reaction rate showed first order dependence on Ni(IV) and positive fractional order with respect to EGE. The pseudo-first order rate constants (kobs) increased with the increase of OH^- and decreased with the increase of IO_4^-. Added salts had little effect on the rate and no free radical was detected. Based on these the mechanism including the equilibrium between DPN and EGE was proposed. Furthermore the activation parameters of the reaction were calculated.

Keywords　　　diperiodatonickelate(IV)　ethylene glycol monoethylether　redox reaction　kinetics and mechanism

Introduction

In recent years the study on the highest oxidation state of transition metals has intrigued many researchers. It can provide new and valuable information for certain fields.

Transition metals with a higher oxidation state can generally be stabilized by chelation with suitable polydentate ligands. Metal complexes such as diperiodatocuprate(III)[1] diperiodatoargentate(III)[2] diperiodatonickelate(IV)[3] and nickel(IV) oxime imine[4] are good oxidants in a medium with an appropriate pH value. The use of Ni(IV) as an oxidizing agent is well known in the investigation of some organic compounds such as tetrahydrofurfuryl alcohol[5] 1 4-dioxane[6] ethylene diamine[7] *etc.* In this paper kinetics of oxidation of ethylene glycol monoethylether (EGE) with diperiodatonickelate(IV) ion (DPN) is investigated and mechanism of oxidation is proposed and it is proved that the existent form is less protonated form $[Ni(OH)_2(H_2IO_6)_2]^{4-}$.

Experimental

All reagents used were of A.R. grade. All solutions were prepared with twice-distilled water. Solutions of DPN and EGE were always freshly prepared with stock solution and twice-distilled water before using. The stock solution of DPN in a strong alkaline medium was prepared by the known procedure[8] and standardized with the reported method.[9] Its electronic spectrum was found to be consistent with that reported by Murthy.[9]

The kinetic measurement was described elsewhere.[10] The product of oxidation was the corresponding aldehyde by its characteristic spot test.[11]

Results and discussion

Evaluation of pseudo-first order rate constants k_{obs}

Under the conditions of $[EGE]_0 \gg [Ni(IV)]_0$ the plots of $\ln(A_t - A_\infty)$ versus time t were linear indicating that the reaction is first order with respect to Ni(IV) where A_t and A_∞ were the absorbencies at $t = t$ and $t = \infty$ respectively. The pseudo-first order rate constants k_{obs} were evaluated by the method of least squares. Relative coefficient $r \geqslant 0.999$. To calculate k_{obs}[8—10] A_t values three times more than those at the half-life were used. The k_{obs} in this paper was the averaged value of at least three independent experiments with good reproducibility.

Rate dependence on $[EGE]$ $[OH^-]$ and $[IO_4^-]_{ex}$

At fixed $[Ni(IV)]$ $[OH^-]$ $[IO_4^-]_{ex}$ (ex stands for the additional IO_4^-) ionic strength μ and temperature the plots of $\log k_{obs}$ versus $\log[EGE]$ were linear ($r > 0.99$) and from the slope of such plot the order in $[EGE]$ was found to be fractional order. In addition the plots of $1/k_{obs}$ versus $1/[EGE]$ were also linear (Fig. 1).

At fixed $[Ni(IV)]$ $[EGE]$ $[IO_4^-]$ μ and temperature k_{obs} increased with the increase of $[OH^-]$ (Table 1 the plot of $\ln k_{obs}$ vs. $\ln[OH^-]$ was linear its slope indicated fractional order dependence on $[OH^-]$.

Table 1 $10^2 \, k_{obs} \, s^{-1}$ varying with the different IO_4^-, OH^-, ionic strength μ at 308.2 K

$10^4 \, [Ni \, IV]_T$ mol L^{-1}	[EGE] mol L^{-1}	$10^2 \, [OH^-]$ mol L^{-1}	$10^3 \, [IO_4^-]_{ex}$ mol L^{-1}	μ mol L^{-1}	$10^2 \, k_{obs} \, s^{-1}$
1.485	0.100	1.354	1.838	0.0165	1.13
1.485	0.100	2.396	1.838	0.0165	1.81
1.485	0.100	3.438	1.838	0.0165	2.57
1.485	0.100	4.480	1.838	0.0165	3.27
1.485	0.100	5.522	1.838	0.0165	3.72
1.485	0.100	1.354	1.838	0.0165	1.05
1.485	0.100	1.354	2.838	0.0165	0.85
1.485	0.100	1.354	3.838	0.0165	0.74
1.485	0.100	1.354	4.838	0.0165	0.65
1.485	0.100	1.354	5.838	0.0165	0.59
1.485	0.100	1.354	1.838	0.0165	1.09
1.485	0.100	1.354	1.838	0.0665	1.12
1.485	0.100	1.354	1.838	0.1165	1.22
1.485	0.100	1.354	1.838	0.1665	1.25
1.485	0.100	1.354	1.838	0.2165	1.23
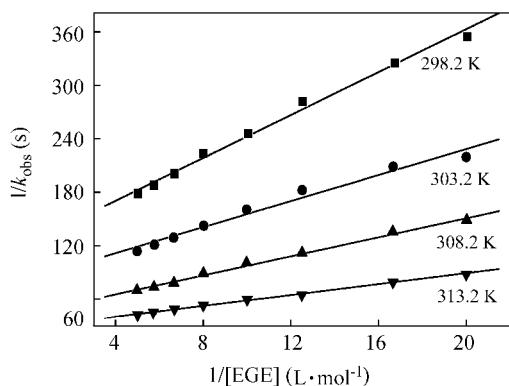
Fig. 1   Plot of $1/k_{obs}$ vs. $1/[EGE]$ at different temperatures. $[Ni \, IV]_T = 1.485 \times 10^{-4}$ mol L^{-1}, $[IO_4^-]_{ex} = 1.838 \times 10^{-3}$ mol L^{-1}, $[OH^-] = 1.354 \times 10^{-2}$ mol L^{-1}, $\mu = 1.651 \times 10^{-2}$ mol L^{-1}.
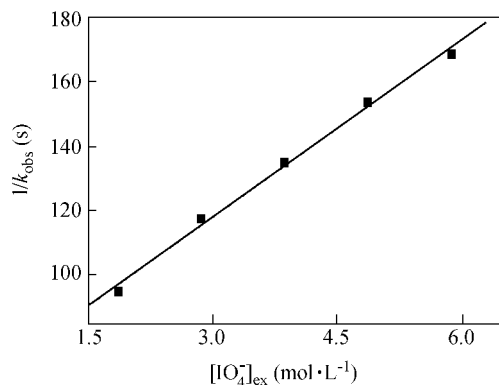
Fig. 2   Plot of $1/k_{obs}$ vs. $[IO_4^-]_{ex}$ at 308.2 K. $[Ni \, IV]_T = 1.485 \times 10^{-4}$ mol L^{-1}, $[EGE] = 0.100$ mol L^{-1}, $[OH^-] = 1.354 \times 10^{-2}$ mol L^{-1}, $\mu = 1.651 \times 10^{-2}$ mol L^{-1}.

At fixed $[Ni \, IV]$, $[EGE]$, $[OH^-]$, μ and temperature, $\ln k_{obs}$ vs. $\ln [IO_4^-]_{ex}$ was linear, its slope revealed the order with respect to IO_4^- to be negative fractional order. In addition, the plot of $1/k_{obs}$ vs. $[IO_4^-]_{ex}$ was linear ($r = 0.998$, Fig. 2).
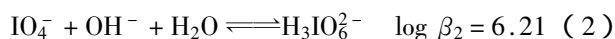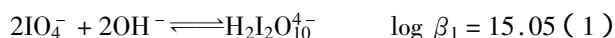
Effect of ionic strength (μ) on rate and free radical detection

Table 1 reveals that the effect of ionic strength μ on the rate is negligible. The addition of acrylonitrile (8% V/V) to the reaction mixture under the protection of nitrogen gas did not alter the rate nor there was any polymerization, showing the presence of free radical in the reaction.

Discussion

In aqueous periodate solution, Eqs. 1—3 were

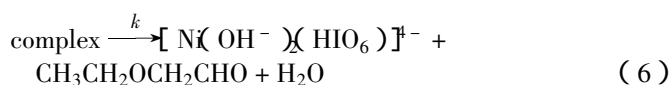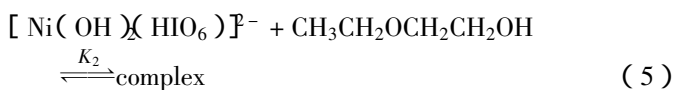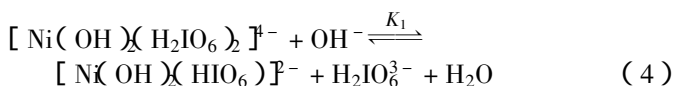detected and the corresponding equilibrium constants at 25 °C were determined by Aveston.[12]

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

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

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

The distribution of all periodate species in aqueous solution was calculated from Eqs. 1—3. The dimmer $H_2I_2O_{10}^{4-}$ and IO_4^- species of periodate can be neglected.[8] The main species of periodate are $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ consistent with the result calculated from Crouthamel's data.[13] Based on such distribution, the formula of Ni (IV) periodate complex 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 close to that suggested by

Mukherjee[14] and will obtain support from kinetic studies.

From the fractional order dependence of k_{obs} on [OH$^-$] it is suggested that OH$^-$ ion would be present in a preequilibrium with DPN. The plot of $1/k_{obs}$ versus [IO$_4^-$] is a line with a positive intercept indicating the presence of 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 plot of $1/k_{obs}$ versus $1/$[EGE] is linear indicating a preequilibrium of forming 1:1 complex between DPN and EGE.

In view of the above discussion, a possible reaction mechanism was proposed

$$[Ni(OH)_2(H_2IO_6)_2]^{4-} + OH^- \xrightleftharpoons{K_1}$$
$$[Ni(OH)_2(HIO_6)]^{2-} + H_2IO_6^{3-} + H_2O \qquad 4$$

$$[Ni(OH)_2(HIO_6)]^{2-} + CH_3CH_2OCH_2CH_2OH$$
$$\xrightleftharpoons{K_2} complex \qquad 5$$

$$complex \xrightarrow{k} [Ni(OH)_2(HIO_6)]^{4-} +$$
$$CH_3CH_2OCH_2CHO + H_2O \qquad 6$$

where Eq. 6 was the rate-determining step.

As the rate of the disapperance of Ni(IV) was monitored and

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

the rate of the reaction can be derived as

$$-\frac{d[Ni(IV)]_T}{dt} = k[complex]_e$$
$$= \frac{kK_1K_2[OH^-][EGE][Ni(IV)]_T}{[H_2IO_6^{3-}] + K_1[OH^-] + K_1K_2[OH^-][EGE]}$$
$$= k_{obs}[Ni(IV)]_T \qquad 7$$

hence

$$k_{obs} = \frac{kK_1K_2[OH^-][EGE]}{[H_2IO_6^{3-}] + K_1[OH^-] + K_1K_2[OH^-][EGE]} \qquad 8$$

Subscripts T and e stand for total concentrations at $t = t$ and at equilibrium, respectively. Neglecting the concentration of ligand dissociated from Ni(IV) and the species of periodate other than $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$, Eqs. 9 and 10 can be obtained from Eqs. 2 and 3

$$[H_2IO_6^{3-}] = \frac{\beta_3[OH^-]}{\beta_2 + \beta_3[OH^-]}[IO_4^-]_{ex} = f[OH^-][IO_4^-]_{ex} \qquad 9$$

$$[H_3IO_6^{2-}] = \frac{\beta_2}{\beta_2 + \beta_3[OH^-]}[IO_4^-]_{ex} = \varphi[OH^-][IO_4^-]_{ex} \qquad 10$$

where $[IO_4^-]_{ex}$ represents the concentration of original overall periodate ion and equals approximately to the sum of $[H_2IO_6^{3-}]$ and $[H_3IO_6^{2-}]$.

Substituting Eq. 9 into Eq. 8, the expression of pseudo-first-order rate constant was got as

$$k_{obs} =$$
$$\frac{kK_1K_2[OH^-][EGE]}{f[OH^-][IO_4^-]_{ex} + K_1[OH^-] + K_1K_2[OH^-][EGE]} \qquad 11$$

Rearranging Eq. 11 leads to Eqs. 12 — 14

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{f[OH^-][IO_4^-]_{ex} + K_1[OH^-]}{kK_1K_2[OH^-]} \cdot \frac{1}{[EGE]} \qquad 12$$

$$\frac{1}{k_{obs}} = \frac{1 + K_2[EGE]}{kK_2[EGE]} + \frac{f[OH^-]}{kK_1K_2[OH^-][GEG]}[IO_4^-]_{ex} \qquad 13$$

$$\frac{1}{k_{obs}} = \frac{1 + K_2[EGE]}{kK_2[EGE]} + \frac{[IO_4^-]_{ex}}{kK_1K_2[EGE]} \cdot \frac{f[OH^-]}{[OH^-]} \qquad 14$$

Eq. 12 shows that the plot of $1/k_{obs}$ versus $1/$[EGE] should have linear relation. From Eq. 13, it is suggested that the plot of $1/k_{obs}$ versus $[IO_4^-]_{ex}$ should be linear, and Eq. 14 shows that the plot of $1/k_{obs}$ versus $f[OH^-]/[OH^-]$ should also be linear (Fig. 3), consistent with the experimental results. If the formula of DPN was $[Ni(OH)_2(H_3IO_6)_2]^{2-}$, Eq. 15 would be obtained instead of Eq. 14.
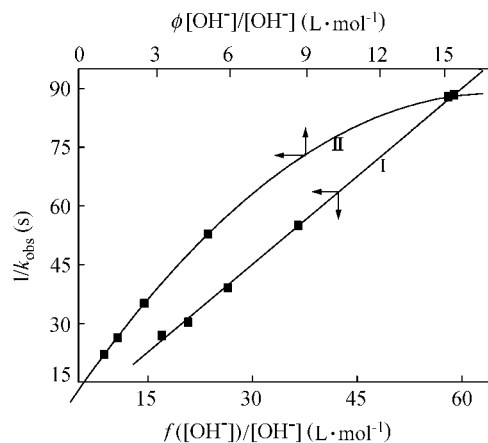

Fig. 3   Comparison of plot of $1/k_{obs}$ vs. $f[OH^-]/[OH^-]$ (curve I) with that of $1/k_{obs}$ vs. $\phi[OH^-]/[OH^-]$ (curve II) at 308.2 K. $[Ni(IV)]_T = 1.485 \times 10^{-4}$ mol L^{-1}, $[IO_4^-]_{ex} = 1.838 \times 10^{-3}$ mol L^{-1}, [EGE] = 0.100 mol L^{-1}, $\mu = 1.651 \times 10^{-2}$ mol L^{-1}.

$$\frac{1}{k_{obs}} = \frac{1 + K_2\ [EGE]}{kK_2\ [EGE]} + \frac{[IO_4^-]_{ex}}{kK_1K_2\ [EGE]} \cdot \frac{\varphi\ [OH^-]}{[OH^-]}$$

(15)

The plot of $1/k_{obs}$ versus $\varphi\ [OH^-]\ /\ [OH^-]$ is shown in Fig. 3 which does not conform to Eq. (15). Therefore, it seems advisable to represent DPN by $[Ni(OH)_2(H_2IO_6)_2]^{4-}$, which consisted with the experimen-

tal observations.

Meanwhile, the plots of $1/k_{obs}$ versus $1/[EGE]$ were linear at different temperatures. From their slopes, the rate-determining step constants k were evaluated and the activation parameters data were obtained (Table 2).[15]

Based on the above results and discussion, the kinetics of oxidation of EGE with DPN is fit for the pseudo-first order. Furthermore, the less protonated form of DPN as activated intermediate was confirmed.

Table 2 Rate constants and activation parameters of rate-determining step

$T\ (K)$	298	303	308	313	Activation parameters at 298—313 K
$10^2\ k\ (s^{-1})$	0.818	1.25	2.28	3.60	$E_a^* = 78.0\ kJ\ mol^{-1}$ $\Delta H_{298}^{\neq} = 75.5\ kJ\ mol^{-1}$ $\Delta S_{298}^{\neq} = -32.1\ J\ K^{-1}\ mol^{-1}$

* $r = 0.999$ intercept $= 26.597$ slope $= -9380.895$ for the linear relation of $\ln k$ vs. $1/T$.

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