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Kinetics and Mechanism of the Oxidation of 1,10-Phenanthroline by Diperiodatonickelate(IV) in Aqueous Alkaline Medium

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Summary. The title reaction was investigated in aqueous alkaline medium. A first order dependence on both [diperiodatonickelate(IV)] and [OH^-] and an apparent fractional order in [1,10-Phenanthroline] was obtained. Addition of the reaction product has no effect on the reaction. The effects of dielectric constant, ionic strength, and temperature on the rate of the reaction were studied. A mechanism based on the experimental results is proposed, and the constants involved in the mechanism were evaluated. A good agreement between the observed and calculated rate constants at varying experimental conditions was obtained.

Keywords. Diperiodatonickelate(IV); 1,10-Phenanthroline; Kinetics; Oxidation.

Introduction

The use of diperiodatonickelate(IV) (**1**) as an oxidant in alkaline medium is new and restricted to a few cases [1–4] due to the fact of its limited solubility and stability in aqueous medium. Reduction of Ni(IV) complexes has received considerable attention in order to understand the nature of intermediate oxidation states of nickel, such as Ni(III). Indeed, stable Ni(III) complexes are known [5]. Moreover, when the nickel(IV) periodate complex is the oxidant, it needs to be known which of the species is the active oxidant, since multiple equilibria between the different nickel(IV) species are involved.

1,10-Phenanthroline (**2**) is a well known complexing agent which forms a multitude of coordination compounds with various metal ions. Its use in analytical chemistry as an oxidation-reduction indicator is extensive. *Fedorova et al.* have carried out oxidation of **2** by H_2O_2 in aqueous solution and reported that the oxidation product was 2,2′-bipyridyl-3,3′-dicarboxaldehyde [6]. *Wimmer et al.* have presented a facile synthesis of 2,2′-bipyridyl-3,3′-dicarboxylic acid by vigorous oxidation of **2** by alkaline permanganate without performing any mechanistic study [7]. In view of the lack of reports in literature on the oxidation of **2** (except Refs. [6] and [7]), we investigated the kinetics of the oxidation of **2** by the Ni(IV) periodate complex in order to derive a plausible mechanism.

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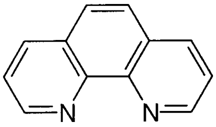
$[Ni(OH)_2(H_3IO_6)_2]^{2-}$

1



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Results and Discussion

Reaction order

The reaction orders were determined from the slopes of logk_{obs} *vs.* log$c$ plots by varying the concentrations of oxidant, reductant, and alkali in turn while keeping the others constant.

Effect of diperiodatonickelate(IV)

The oxidant concentration ([**1**]) was varied from 1.0×10^{-5} to 1.3×10^{-4} mol · dm^{-3} at constant concentrations of **2** and alkali at an ionic strength of 1.5 mol · dm^{-3}. The invariability of *pseudo*-first order rate constants at various concentrations of **1** indicates unity order in [**1**] (Table 1). This was also confirmed from the linearity of the plots of log[**1**] *vs.* time.

Table 1. Effect of [**1**], [**2**], [OH$^-$], and [IO$_4^-$] on the oxidation of **2** by **1** in aqueous alkaline medium at 26°C and $I = 1.5$ mol · dm^{-3} (experimental error: ±5%)

[**1**] × 10^4 mol · dm^{-3}	[**2**] × 10^3 mol · dm^{-3}	[OH$^-$] × 10 mol · dm^{-3}	[IO$_4^-$] × 10^5 mol · dm^{-3}	$k_{obs} \times 10^3$/s^{-1}	
				Expt.	Calc.
0.1	2.0	8.0	2.0	1.59	1.63
0.3	2.0	8.0	2.0	1.60	1.63
0.5	2.0	8.0	2.0	1.57	1.63
1.0	2.0	8.0	2.0	1.60	1.63
1.3	2.0	8.0	2.0	1.61	1.63
1.0	0.5	8.0	2.0	0.75	0.71
1.0	1.0	8.0	2.0	1.11	1.14
1.0	2.0	8.0	2.0	1.59	1.63
1.0	3.0	8.0	2.0	1.90	1.90
1.0	5.0	8.0	2.0	2.28	2.20
1.0	2.0	1.5	2.0	0.31	0.30
1.0	2.0	3.0	2.0	0.62	0.61
1.0	2.0	5.0	2.0	1.10	1.02
1.0	2.0	8.0	2.0	1.59	1.63
1.0	2.0	12.0	2.0	2.50	2.45
1.0	2.0	15.0	2.0	3.00	3.07
1.0	2.0	8.0	0.3	1.63	–
1.0	2.0	8.0	0.5	1.60	–
1.0	2.0	8.0	1.0	1.61	–
1.0	2.0	8.0	1.5	1.59	–
1.0	2.0	8.0	2.0	1.63	–
1.0	2.0	8.0	3.0	1.60	–

Effect of 1,10-phenanthroline

The concentration of **2** was varied from 5.0×10^{-4} to 5.0×10^{-3} $mol \cdot dm^{-3}$ while keeping all other conditions constant. The apparent order in [**2**] was less than unity (Table 1).

Effect of alkali

To study the effect of alkali concentration on the rate of reaction, $[OH^-]$ was varied in the range of 0.15 to 1.5 $mol \cdot dm^{-3}$ at constant concentrations of **1** and **2** at a ionic strength of 1.5 $mol \cdot dm^{-3}$. The order in $[OH^-]$ was found to be unity (Table 1).

Effect of ionic strength

To study the effect of ionic strength, the concentration of potassium nitrate was varied from 0.8 to 3.0 $mol \cdot dm^{-3}$ at constant concentrations of **1**, **2**, and OH^-. It was found that the rate of reaction increases with increasing ionic strength (Fig 1).

Effect of solvent polarity

The relative permittivity (D) effect was studied by varying the percentage of *t*-butanol in water in the reaction medium with all other conditions being kept constant. Attempts to measure the relative permittivity failed; however, it could be computed from the values of the pure liquids [8]. With increasing content of *t*-butanol, a negligible increase in k_{obs} was noted. The inertness of the solvent with respect to the oxidant was also checked under the chosen experimental conditions.

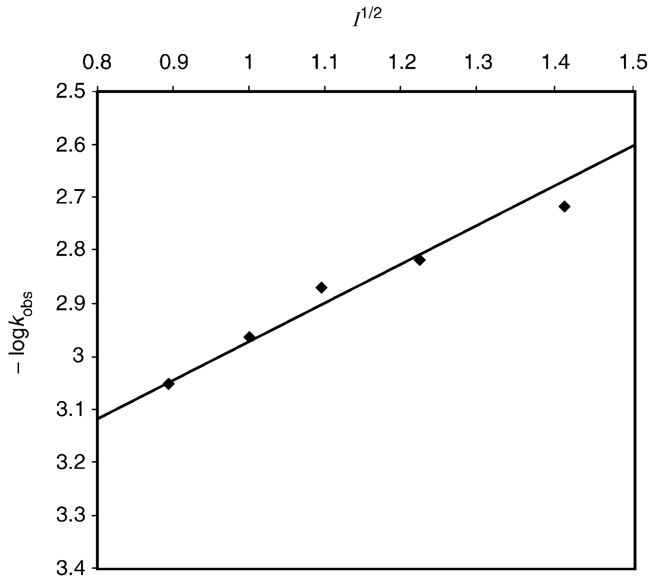


Fig. 1. Plot of $\log k_{obs}$ *vs.* $I^{1/2}$

Effect of periodate

The concentration of KIO_4 was varied in the range of 3.0×10^{-5} to $3.0 \times 10^{-4}\,\mathrm{mol \cdot dm^3}$ keeping all other conditions constant. The results show that there is no effect of periodate concentration on the reaction rate (Table 1).

Effect of initially added product

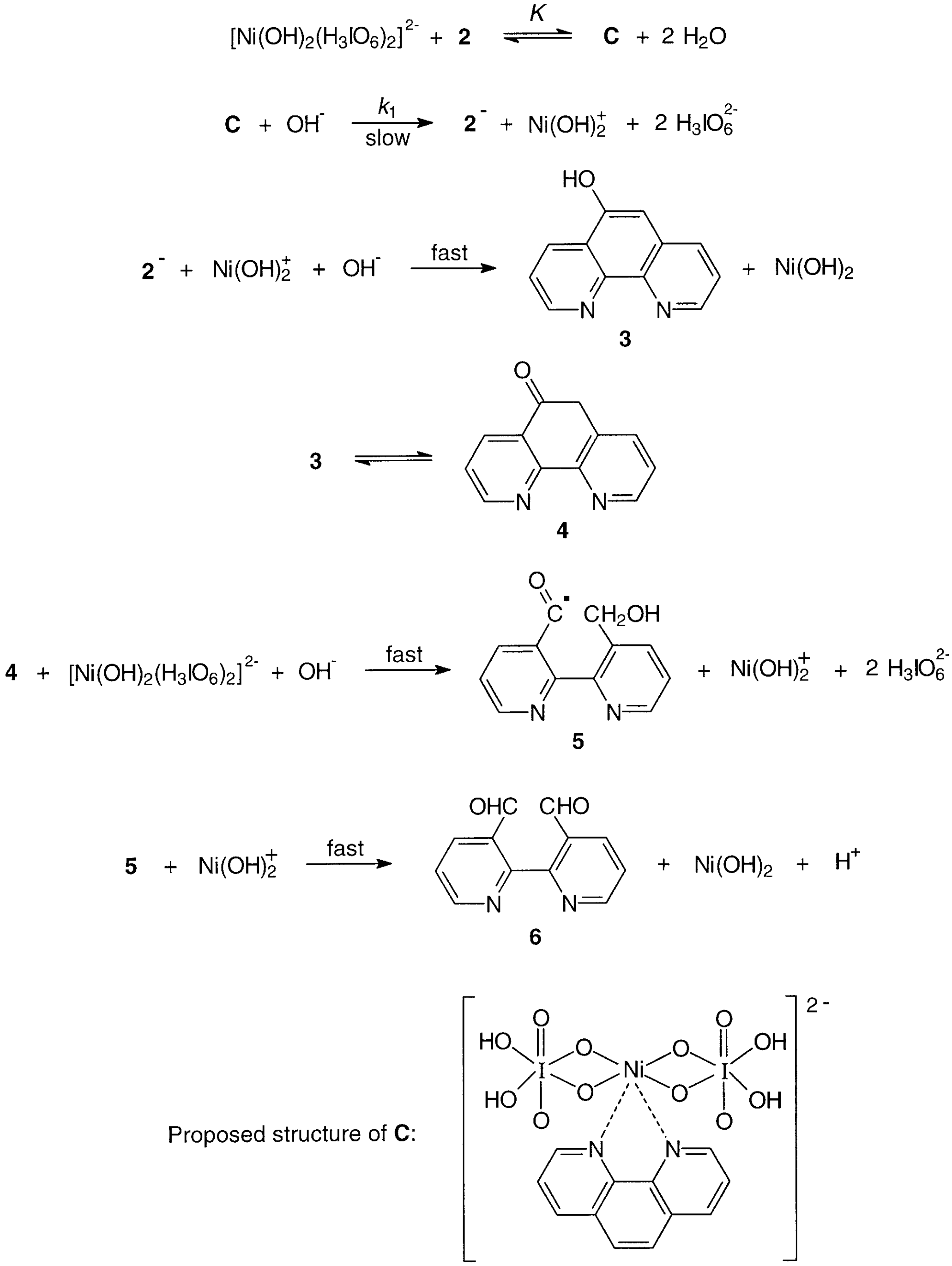
The addition of varying amounts (2.0×10^{-5} to $2.0 \times 10^{-4}\,\mathrm{mol \cdot dm^{-3}}$) of reaction product (Ni(II) in the form of $NiSO_4$) had no significant effect on the rate of reaction.

Test for free radicals

The reaction mixture containing monomeric acrylonitrile was kept in an inert atmosphere for 4 h. Upon dilution with methanol, a precipitate formed indicating the presence of free radicals in the reaction mixture. Blank experiments with either **1** or **2** alone did not induce polymerization under the same conditions as employed for the redox reaction.

The water soluble Ni(IV) periodate complex has been reported to consist of $K_6[Ni(HIO_6)_2(OH)_2]$, [4, 9], although periodate is involved in multiple equilibria depending on the *pH* employed. At high *pH* values as employed in this study, periodate is likely to exist as $H_3IO_6^{2-}$ [4]. Hence, the species of Ni(IV) prevailing in alkaline medium can be expected to be $[Ni(OH)_2(H_3IO_6)_2]^{2-}$ (**1**), a conclusion also supported from earlier results [2, 3].

The reaction between **1** and **2** in alkaline medium displayed a 2:1 stoichiometry of oxidant to reductant with a first order dependence both in [**1**] and $[OH^-]$ and an apparent order of less than unity in [**2**]. In most of the reports related to oxidations with **1** (see *e.g*. Ref. [4]), periodate exhibits a retarding effect, and the reaction order with respect to alkali is less than unity. In view of these observations, monoperiodatenickelate(IV) was considered as the reactive species of the Ni(IV) periodate complex. However, in the present kinetic study different results were obtained, *i.e*. [periodate] has no effect on the rate of the reaction, and the order in $[OH^-]$ was found to be unity. Accordingly, **1** itself is considered to be the active oxidizing species. Based on the observed kinetic results, a mechanism involving complex formation between oxidant and substrate is proposed (Scheme 1). The probable structure of complex **c** is also given in Scheme 1. The observed apparent fractional order in [**2**] may be attributed to the formation of a complex either with alkali or with **1**. In view of the first order dependence of the rate on $[OH^-]$, complex formation involving OH^- is discarded; however, complex formation between **1** and **2** is highly probable. Attempts to obtain UV/Vis spectroscopical evidence for complex formation between **1** and **2** were not successful, no change being observed in the UV/Vis spectra of **1** and a mixture of **1** and **2** at room temperature. However, at 5°C a new band appeared at 320 nm in the UV spectrum of the reaction mixture of **1** and **2**, indicating complex formation at lower temperatures. Analogous complex formation between substrate and oxidant has been reported earlier [10]. It is also known that **2** is a good complexing agent, and complexes of **2** with metal



Scheme 1

ions are well documented in the literature [11]. This complex reacts with OH^- in the rate determining step to give the radical **2**$^{\cdot}$. Subsequently, **2**$^{\cdot}$ reacts in a fast step in presence of OH^- to give **3**, whose keto form **4** reacts with another molecule of oxidant in further fast steps *via* **5** to the products.

Scheme 1 leads to the following rate law:

$$Rate = -\frac{\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = \frac{k \cdot K \cdot [\mathrm{Ni(OH)_2(H_3IO_6)_2}]_{\mathrm{T}}^{2-} \cdot [\mathbf{2}]_{\mathrm{T}} \cdot [\mathrm{OH^-}]}{(1 + K \cdot [\mathrm{Ni(OH)_2(H_3IO_6)_2}]_{\mathrm{f}}^{2-})(1 + K \cdot [\mathbf{2}]_{\mathrm{f}})} \tag{1}$$

The subscripts T and f stand for 'total' and 'free'. In view of the low concentrations of [**1**] used, the term $(1+K\cdot[\mathrm{Ni(OH)_2(H_3IO_6)}]^{2-})$ in the denominator of (**1**) approaches unity. Also, since $[\mathbf{2}] \gg [\mathrm{Ni(OH)_2(H_3IO_6)}]^{2-}$, $[\mathbf{2}]_{\mathrm{f}}$ is almost equal to $[\mathbf{2}]_{\mathrm{T}}$. Omitting the subscripts, the rate law therefore turns into

$$Rate = -\frac{\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = \frac{k \cdot K \cdot [\mathbf{2}][\mathrm{Ni(OH)_2(H_3IO_6)_2}]^{2-}[\mathrm{OH^-}]}{1 + \mathrm{K} \cdot [\mathbf{2}]} \tag{2}$$

Bearing in mind that $[\mathrm{Ni(OH)_2(H_3IO_6)_2}]^{2-} = [\mathbf{1}]$, Eq. (2) can be further simplified to

$$\frac{Rate}{[\mathbf{1}]} = k_{\mathrm{obs}} = \frac{k \cdot K \cdot [\mathbf{2}] \cdot [\mathrm{OH^-}]}{1 + K \cdot [\mathbf{2}]} \tag{3}$$

Equation (3) can be rearranged to the form of Eq. (4) which was used for the verification of the rate law.

$$\frac{[\mathrm{OH^-}]}{k_{\mathrm{obs}}} = \frac{1}{k \cdot K \cdot [\mathbf{2}]} + \frac{1}{k} \tag{4}$$

According to Eq. (4), a plot of $\frac{[\mathrm{OH^-}]}{k_{\mathrm{obs}}}$ *vs.* 1/[**2**] should be linear (Fig. 2). The slope and intercept of this plot led to values of K and k of $672 \pm 34\,\mathrm{dm^3 \cdot mol^{-1}}$ and $3.57 \pm 0.17 \times 10^{-3}\,\mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}}$ at 26°C. These constants were used to calculate the rate constants under varying experimental conditions. There is a reasonable agreement between calculated and observed rate constants (Table 1) which supports Scheme 1. The increase in rate with increasing ionic strength qualitatively explains

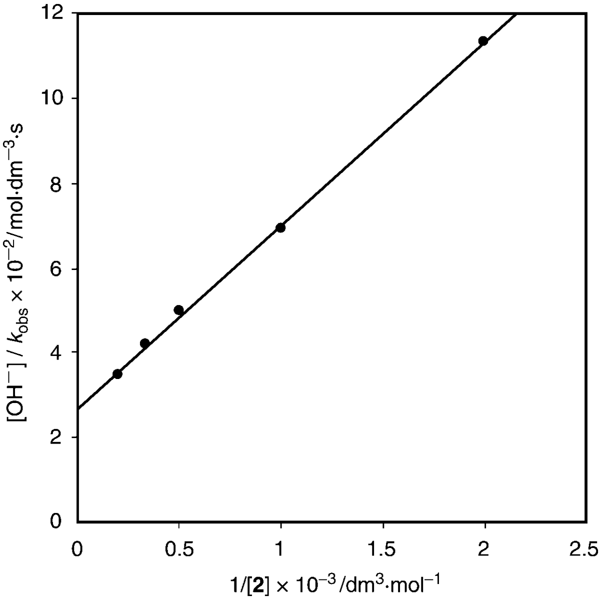


Fig. 2. Plot of $[\mathrm{OH^-}]/k_{\mathrm{obs}}$ *vs.* 1/[**2**] (for conditions, see Table 1)

the participation of two negatively charged species in the rate determining step of Scheme 1. The mechanism is also supported by the low values of the thermodynamic activation parameters. A small negative value of $\Delta S^{\#}$ suggests that the complex is less ordered than the reactants [12], whereas the moderate values of $\Delta G^{\#}$ and $\Delta H^{\#}$ indicate that the activated complex is highly solvated. The observed modest enthalpy of activation and the relatively low value of entropy of activation and the higher rate constant of the slow step of the mechanism indicated that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion was supported by earlier work [13].

Effect of temperature

The rate of reaction was measured at different temperatures under varying concentrations of **2**, keeping all other parameters constant. The rate constant k of the slow step of the mechanism was obtained from the intercept of $[OH^-]/k_{obs}$ *vs.* 1/[**2**], and k was used to calculate the activation parameters. The values of k ($dm^3 \cdot mol^{-1} \cdot s^{-1}$) were $3.57 \pm 0.17 \times 10^{-3}$, $4.0 \pm 0.2 \times 10^{-3}$, $4.5 \pm 0.2 \times 10^{-3}$, and $5.0 \pm 0.3 \times 10^{-3}$ at 26, 31, 36, and 41°C. The activation parameters corresponding to these constants were evaluated as follows: $E_a = 22.7 \pm 1.0\,kJ \cdot mol^{-1}$, $\Delta H^{\#} = 20.2 \pm 1.0\,kJ \cdot mol^{-1}$, $\Delta S^{\#} = -49 \pm 2\,J \cdot K^{-1} \cdot mol^{-1}$, and $\Delta G^{\#} = 15.6 \pm 0.7\,kJ \cdot mol^{-1}$.

Conclusions

Although monoperiodatonickelate(IV) has been considered as the reactive species of the Ni(IV) periodate complex in earlier reports [1–4], **1** itself has to be observed as the active species of the oxidant from the results of the present study. Based on the kinetic results, a mechanism was proposed and verified. Activation parameters with respect to the slow step of the mechanism were computed and explained.

Experimental

Materials

All chemicals used were of reagent grade, and doubly distilled water was used throughout. The solution of **2** (Merck) was prepared by dissolving a weighed amount in distilled hot H_2O. The solid complex **1** was prepared by a standard procedure [14]. The purity of the complex was checked by its UV/Vis spectrum which shows a broad absorption band at 410 nm [4]. The aqueous solution of **1** was obtained by dissolving the solid complex in $1.0\,mol \cdot dm^{-3}$ aqueous KOH at 50°C with stirring. The resulting solution was standardized gravimetrically after reducing Ni(IV) to Ni(II) and precipitating the Ni(II) as its dimethylglyoxime complex [15]. KOH (BDH, Analar) and KNO_3 were employed to maintain the required alkalinity and ionic strength in the solution.

Since periodate is present in excess in **1**, the possibility of oxidation of **2** by periodate in aqueous alkaline medium at 26°C was tested. The progress of the reaction was followed iodometrically [16]. However, it was found that there is no reaction under the experimental conditions employed.

Kinetic measurements

The oxidation of **2** by **1** was followed under *pseudo*-first order conditions where [**2**] was in excess over [**1**] at 26.0±0.1°C unless stated otherwise. The reaction was initiated by mixing the required quantities of previously thermostatted solutions of **2** and **1**, which also contained defined quantities of KOH and KNO_3 to maintain the required alkalinity and ionic strength. The total $[OH^-]$ was calculated considering the KOH in **1** as well as the KOH additionally added. Similarly, the total metaperiodate concentration was calculated by considering the metaperiodate present in the solution of **1** and that additionally added. The progress of the reaction was followed by measuring the absorbance of unreacted **1** in the reaction mixture in a 1 cm cell in a thermostatted compartment of a Hitachi 150–20 spectrophotometer at 410 nm; other constituents of the reaction mixture do not absorb significantly at this wavelength. The obedience of *Beer*'s law for **1** has been validated earlier, and the molar absorption coefficient was found to be $7500 \pm 375\,dm^3 \cdot mol^{-1} \cdot cm^{-1}$. The reaction was followed to more than 90% completion; rate constants were reproducible within ±5%. The first-order rate constants were calculated from the slopes of log[**1**] *vs.* time plots. The plots were linear up to 80% completion of the reaction.

In view of the modest concentration of alkali used, attention was paid on the effect of the surface of the reaction vessel on the kinetics. Use of polythene/acrylic equipment and quartz or polyacrylate cells gave the same results, indicating that surfaces did not play any significant role in the measurements.

Some kinetic runs were carried out in an atmosphere of N_2 to understand the effect of dissolved O_2 on the rate of reaction. No significant difference was observed in the results obtained under N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates. Nevertheless, fresh solutions were used throughout.

Stoichiometry

Different sets of reaction mixtures containing an excess of **1** over **2** with constant $[OH^-]$ and $[KNO_3]$ were kept for 6 h in closed vessels under an N_2 atmosphere. The remaining concentration of **1** was assayed spectrophotometrically at 410 nm. The results indicated a 1:2 stoichiometry as given in Eq. (5). This stoichiometric ratio suggests that the main reaction products are **6** and Ni(II). The presence of aldehyde **6** was confirmed by the formation of its crystalline 2,4-*DNP* derivative [17], a white crystalline precipitate with dimedone [17], and a pink coloured dye upon addition of $NH_2NH_2 \cdot H_2O$. Spectrophotometric comparison with authentic **6** demonstrated about 75% of the product to consist of **6**. The presence of Ni(II) was identified by its dimethyl glyoxime complex.

$$\mathbf{2} + 2\mathrm{Ni(IV)} + 4\mathrm{OH}^- \longrightarrow \mathbf{6} + 2\mathrm{Ni(II)} + 2\mathrm{H_2O} \quad (5)$$

The formed dicarboxaldehyde does not undergo further oxidation under the conditions employed; a test for a probable oxidation product of the aldehyde, *i.e.* acid, was negative [18].

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References

[1] Macartnay DH, McAulley A (1983) Inorg Chem **22**: 2062

[2] Acharya S, Neogi B, Pande RK, Ramaswamy D (1982) Int J Chem Kinet **14**: 1253

[3] Bhattacharya S, Saha B, Datta A, Banerjee P (1998) Coord Chem Rev **47**: 170; Datta A, Bhattacharya S, Banerjee P (1998) Polyhedron **17**: 2313; Lappin AG, Laranjeira, Youdi OL (1981) J Chem Soc Dalton Trans 721

[4] Hugar GH, Nandibewoor ST (1993) Indian J Chem **32A**: 1056; Tuwar SM, Nandibewoor ST, Raju JR (1992) J Indian Chem Soc **69**: 651; Nandibewoor ST, Hugar GH (1997) Polish J Chem

71: 1572; Chandraiah U, Khan JA, Murthy CP, Kandlikar S (1987) Indian J Chem **26A**: 481; Siddiqui MA, Kumar CS, Chandraiah U, Kandlikar S (1991) Indian J Chem **30A**: 489; Chandraiah U, Murthy CP, Kandlikar S (1989) Indian J Chem **28A**: 248; Siddiqui MA, Kumar C, Chandraiah U, Kandlikar S (1991) Indian J Chem **30A**: 849; Harihar AL, Kembhavi MR, Nandibewoor ST (1999) Inorg React Mech **1**: 145; Kembhavi MR, Harihar AL, Nandibewoor ST (1999) J Indian Chem Soc **76**: 79; Harihar AL, Kembhavi MR, Nandibewoor ST (1999) Oxid Commun **22**: 308; Kembhavi MR, Panari RG, Nandibewoor ST (1999) J Soudi Chem Soc **3**: 121

[5] Haines RI, MacAulley A (1981) Coord Chem Rev **39**: 77

[6] Fedorova OS, Berdinicov VM (1979) Izv Akad Nauk SSSR Ser Khim **6**: 1226

[7] Wimmer FL, Wimmer S (1983) Org Prep Proceed Int **15**: 368

[8] Hugar GH, Nandibewoor ST (1994) Transition Met Chem **19**: 215; Nandibewoor ST, Morab VA (1995) J Chem Soc Dalton Trans 483

[9] Crouthamel CE, Hayes AM, Martin DS (1951) J Am Chem Soc **73**: 82

[10] Tuwar SM, Nandibewoor ST, Raju JR (1991) Transition Met Chem **16**: 196; Devi J, Kotari S, Banerji KK (1995) Indian J Chem **34A**: 116; Halligudi NN, Desai SM, Nandibewoor ST (1999) Int J Chem Kinet **31**: 789

[11] Vogel AI (1991) Text Book of Quantitative Chemical Analysis, ELBS, 5th ed. Longman, Essex, p 365; Dulz G, Sutin N (1963) Inorg Chem **2**: 917; Miller JD, Prince RH (1965) J Chem Soc 5749

[12] Mahadevappa DS, Rangappa KS, Gowda NMM, Gowda BT (1982) Int J Chem Kinet **14**: 1183

[13] Sutin N (1966) Ann Rev Phys Chem **17**: 119; Lancaster M, Murray RS (1971) J Chem Soc A 2755; Martinez M, Pitarque M, Eldik RV (1996) J Chem Soc Dalton Trans 2665; Hiremath GA, Timmanagoudar PL, Nandibewoor ST (1998) React Kinet Catal Letts **63**: 403

[14] Ray P (1957) In: Therald M (ed) Inorg Synthesis, vol V. McGraw-Hill, New York, p 201

[15] Vogel AI (1991) A Text Book of Quantitative Chemical Analysis. ELBS Longman, Essex, UK, p 462

[16] Nandibewoor ST, Hugar GH (1999) Oxid Commun **22**: 222; Hiremath GA, Halligudi NN, Nandibewoor ST (2000) Inorg React Mech **1**: 301

[17] Vogel AI (1973) A Text of Practical Organic Chemistry, 3rd ed. ELBS Longman, p 332

[18] Feigl F (1975) Spot Tests in Organic Analysis. Elsevier, New York, p 352

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