The Kinetics and Mechanism of Oxidation of Vanillin by Diperiodatonickelate(IV) in Aqueous Alkaline Medium

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The title reaction was investigated in aqueous alkaline medium. A first order dependence in diperiodatonickelate (IV) (DPN) and an apparent fractional order in both vanillin and alkali were obtained. Periodate has a retarding effect on the reaction. The effect of added products and the ionic strength of the reaction medium have no significant effect on the reaction rate. A decrease in the dielectric constant of the medium decreases the rate of reaction. Effects of temperature on the rate of reaction were studied. A mechanism based on experimental results was proposed, and constants involved in the mechanism were evaluated. A good agreement between the observed and calculated rate constants at different experimental conditions was obtained.

Key Words: Oxidation; Vanillin, Kinetics, DPN

Introduction

The use of diperiodatonickelate (IV) (DPN) as an oxidant in alkaline medium is recent and limited to a few cases[1−6] by the fact that its solubility and stability in aqueous medium is very low. Reduction of nickel (IV) complexes has received considerable attention in order to understand the nature of intermediate oxidation states of nickel such as nickel (III). Indeed, stable nickel (III) complexes are known[7−9]. Moreover, when nickel (IV) periodate is the oxidant it needs to be known which of the species is the active form of oxidant, since multiple equilibria between the different nickel (IV) species are involved.

Vanillin is a very popular flavoring in the food industry, and is useful in the synthesis of drugs; 40% of vanillin is consumed in manufacturing drugs such as Aldomet, L-dopa and Trimethaprim. Vanillin is also used in the perfume and metal-plating industries. Vanillin has both aldehydic and phenolic groups and is capable of undergoing many types of reactions. In view of the lack of literature on oxidation of vanillin by DPN and in view of multiple equilibria embracing the different Ni(IV) periodate species and the complexity of the title reaction, a detailed study of the reaction was undertaken.

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Experimental

All chemicals used were of reagent grade. Doubly distilled water was used throughout the work. Solution of vanillin (s.d.fine chem) was prepared by dissolving an appropriate amount of sample in distilled water. The solid complex nickel (IV) periodate was prepared as described by Ray[10]. Aqueous solution of DPN was obtained by dissolving the solid complex in 1.0 mol dm^{-3} KOH solution. The Ni(IV) in alkaline solution was estimated gravimetrically[11] after reducing it to Ni(II) and precipitating Ni(II) as its dimethyl glyoxime complex. Potassium hydroxide and potassium nitrate were employed to maintain the required alkalinity and ionic strength respectively.

The oxidation of vanillin by DPN was followed under pseudo-first order conditions where [vanillin] was in excess over [DPN] at 23 $\pm$0.1°C unless otherwise stated. The reaction was initiated by mixing thermally equilibrated solutions of DPN and vanillin of required concentrations. The latter solution contained the required amounts of potassium hydroxide, potassium nitrate and potassium metaperiodate. The total concentration of hydroxide ions was calculated considering the potassium hydroxide in DPN as well as the potassium hydroxide additionally added. Similarly, the total metaperiodate concentration was calculated by considering the metaperiodate present in the DPN solution and that additionally added. The reaction was followed by measuring the absorbance of the unreacted DPN in the reaction mixture in the 1 cm quartz cell in the thermostatted compartment of a Hitachi 150-20 spectrophotometer, at 410 nm, where other constituents of the reaction do not absorb significantly. The obedience of Beer's law by DPN at 410 nm in the concentration range of 2.0 x 10^{-5} to 2.0 x 10^{-4} mol dm^{-3} under constant metaperiodate and alkali concentration was studied earlier and the molar absorbance coefficient 'ε' was 7500 $\pm$ 375 dm^3 mol^{-1} cm^{-1} at this wavelength. The first order constants, k$_{obs}$,were obtained from the plots of log $(a - x)$ versus time, where 'a' and 'x' are the initial concentration and change in concentration of diperiodatonickelate (IV) at time 't' respectively. The plots were linear to about 85% completion of the reaction and the rate constants were reproducible within $\pm$5% .

Regression analysis of experimental data to obtain the regression coefficient r and standard deviation S of points from the regression line was performed using a Pentium-III personal computer.

Results

Stoichiometry

Different reaction mixtures with different sets of concentrations of reactants, where [Ni(IV)] was in excess over [Vanillin] at constant ionic strength and alkali, were kept for about 4 hours at 23$\pm$0.1^o C in a closed vessel. The remaining [DPN] was assayed spectrophotometrically by measuring the absorbance at 410 nm. The results indicated that one mole of DPN consumed one mole of vanillin as in equation (1):

$$\text{(1)}$$
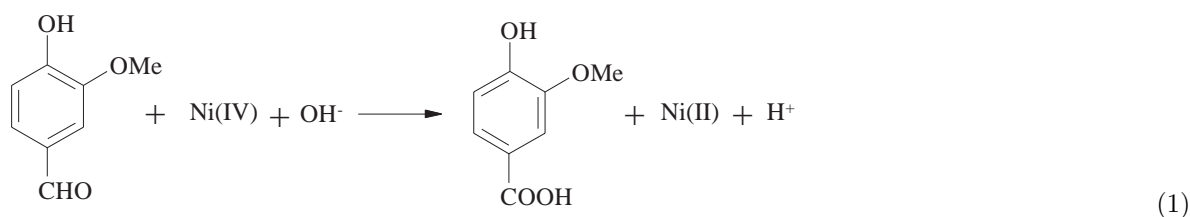
The stoichiometric ratio suggests that the main reaction products are vanillic acid and Ni(II). The acid was confirmed by spot test[12] and by its IR spectrum, which showed bands at 3025 and 1733 cm^{-1} due to OH and C=O stretching respectively. Ni (II) was confirmed by its dimethyl glyoxime complex.

Reaction orders

The order with respect to [Vanillin] and [alkali] was found by log k_{obs} versus log concentration plots; these orders were obtained by varying the concentration of reductant and alkali in turn while keeping the others constant.

Effect of [diperiodatonickelate (IV)]

The concentration of diperiodatonickelate(IV) was varied in the range 1.0×10^{-5} to 8×10^{-5} mol dm^{-3} at fixed [Vanillin], [OH^-] and ionic strength. The non-variation in the pseudo-first order rate constants at various concentrations of DPN indicates that the order in [DPN] was unity (Table 1). This was confirmed by the linearity of plots of log [DPN] versus time (r>0.9993, S<=0.019) up to 85% completion of the reaction.

Table 1. Effect of variation of [DPN], [Vanillin], [OH^-] and [IO_4^-] on oxidation of Vanillin by DPN at 23°C, I = 1.0 mol dm^{-3}.

[DPN] x 10^5 mol dm^{-3}	[Vanillin]x10^4 mol dm^{-3}	[OH^-] mol dm^{-3}	[IO_4^-] x 10^4 mol dm^{-3}	k_{obs} x 10^3 s^{-1} Exptl.*	Calcd.*
1.0	8.0	0.2	0.2	5.42	5.05
2.0	8.0	0.2	0.2	5.35	5.05
4.0	8.0	0.2	0.2	5.39	5.05
6.0	8.0	0.2	0.2	5.45	5.05
8.0	8.0	0.2	0.2	5.33	5.05
6.0	6.0	0.2	0.2	4.25	3.99
6.0	8.0	0.2	0.2	5.45	5.05
6.0	20	0.2	0.2	11.4	10.7
6.0	40	0.2	0.2	17.3	16.9
6.0	60	0.2	0.2	20.0	19.9
6.0	8.0	0.1	0.2	4.54	4.39
6.0	8.0	0.2	0.2	5.45	5.05
6.0	8.0	0.4	0.2	5.94	5.50
6.0	8.0	0.7	0.2	6.20	5.87
6.0	8.0	1.0	0.2	6.45	6.23
6.0	8.0	0.2	0.5	4.03	3.80
6.0	8.0	0.2	1.0	2.73	2.68
6.0	8.0	0.2	2.0	1.66	1.70
6.0	8.0	0.2	4.0	0.93	0.97
6.0	8.0	0.2	5.0	0.75	0.60

*Experimental and Calculated.

Effect of [Vanillin]

The substrate, vanillin was varied in the range 6.0×10^{-4} to 6.0×10^{-3} mol dm^{-3} at 23°C, keeping all other reactant concentrations and conditions constant (Table 1). The k_{obs} values increased with increases

in concentration of vanillin, indicating an apparent less than unit order dependence on [substrate].

Effect of alkali concentration

The effect of [alkali] on the rate of reaction was studied at constant concentrations of vanillin and DPN and with ionic strength at 1.0 mol dm^{-3}. The rate constants increased with increases in [alkali] (Table 1).

Effect of periodate:

The effect of $[IO_4^-]$ was observed by varying the concentration from 5x10^{-5} to 5x10^{-4} mol dm^{-3}, keeping all other reactant concentrations constant. It was found that the added periodate retarded the rate, and the order in periodate was inverse fractional.

Effect of Ionic Strength and Effect of Solvent Polarity

The effect of ionic strength was studied by varying the potassium nitrate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.2 to 2.0 mol dm^{-3} at constant concentrations of DPN, vanillin and alkali. It was found that ionic strength had negligible effect on the rate of the reaction.

The relative permittivity (ε_T) effect was studied by varying the *t*-butyl alcohol-water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids as in earlier work[13]. There was no reaction of the solvent with the oxidant under the experimental conditions used. The rate constants, k$_{obs}$, decreased with the decrease in the dielectric constant of the medium. The plot of log k$_{obs}$ *vs.* $1/\varepsilon_T$ was linear (Figure 1) (r > 0.9994, S<=0.029).
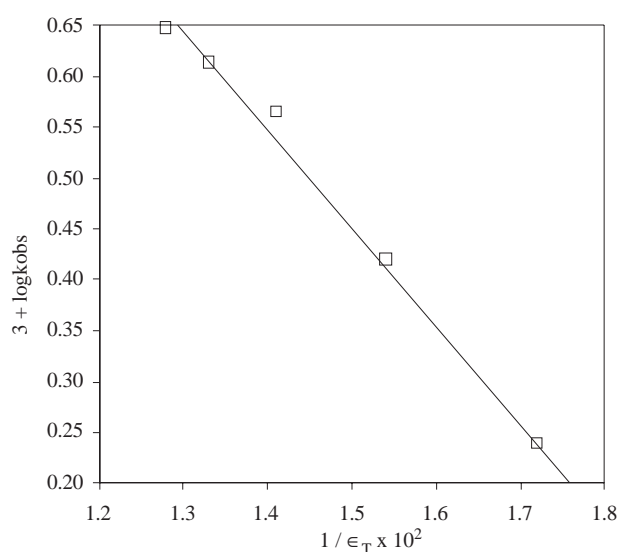

Figure 1. Plot of logk$_{obs}$ versus $1/\varepsilon_T$

Effect of Initially Added Products

The initially added products such as Ni (II) and vanillic acid did not have any significant effect on the rate of the reaction.

Test for Free Radicals

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 24 hours in an inert atmosphere. On dilution with methanol, white precipitate of polymer was formed, indicating the presence of free radicals in the reaction.

Effect of Temperature

The rate constants, k, of the slow step of the mechanism were obtained from the intercepts of the plots of $1/k_{obs}$ vs. $1/[\text{vanillin}]$ (r>0.9996, S<=0.021) at different temperatures and used to calculate the activation parameters (Table 2). The values of k (s^{-1}) are given in Table 2 (a). Above 36°C, we were unable to follow the reaction since the initial reaction was fast. The corresponding activation parameters are shown in Table 2.

Table 2. Activation parameters for the oxidation of Vanillin by DPN in aqueous alkaline medium.

(a) Effect of temperature

Temp. in °C	k x 10^2 s^{-1}
23	3.64
27	5.26
33	6.67
36	9.09

(b) Activation parameters with respect to slow step of Scheme 1

Ea kJ mol^{-1}	LogA	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}
55±3	7.2±0.4	-116±6	52±3	87±4

Discussion

The water soluble Ni(IV) periodate complex is reported[5,6,14−17] to be [Ni $(HIO_6)_2$ $(OH)_2]^{6-}$, although periodate is involved in multiple equilibria depending on the pH employed. Under the conditions of high pH as maintained in this study, periodate is likely to exist[6] as $[H_3IO_6^{2-}]$. Hence, the species of Ni(IV) in alkali can be expected to be [Ni $(H_3IO_6)_2$ $(OH)_2]^{2-}$ (DPN).

The rate increase with increases in alkalinity and the rate decrease with increases in [periodate] (Table 1) suggest that the equilibria of different Ni(IV) periodate complexes as in equations (2) and (3) are important. It may be expected that monoperiodatonickelate (IV) (MPN) is more important in the reaction than the (DPN). The inverse fractional order in $[IO_4^-]$ may also be due to this reason.

$$[\text{Ni}(H_3IO_6)_2(OH)_2]^{2-} + OH^- \xrightleftharpoons{K_1} [\text{Ni}(H_3IO_6)(H_2IO_6)(OH)_2]^{3-} + H_2O \qquad (2)$$

$$[Ni(H_3IO_6)(H_2IO_6)(OH)_2]^{3-} \underset{}{\overset{K_2}{\rightleftharpoons}} [Ni(H_2IO_6)(OH)_2]^- + H_3IO_6^{2-}$$

(3)
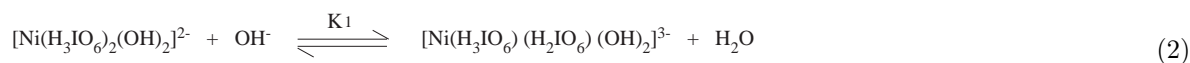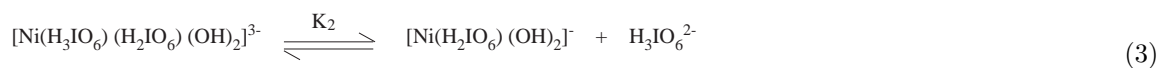
Therefore, MPN might be the main active form of the oxidant. A free radical intervention is to be accounted for, since addition of acrylonitrile results in polymerization.

The reaction between DPN and vanillin shows the first order dependence on [DPN] and fractional order dependence on both [vanillin] and [OH$^-$]. The fractional order in [vanillin] presumably results from a complex formation between the oxidant and substrate prior to the formation of the products. Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-VIS spectra of the vanillin, DPN and a mixture of both. A bathochromoic shift of about 8 nm from 413 to 421 nm of DPN was observed. Indeed, it is to be noted that a plot of $1/k_{obs}$ versus $1/$[vanillin] (r>0.9997, S<=0.021) shows a straight line with a non-zero intercept (Figure 2). Such a complex formation between the oxidant and substrate has been observed in other studies[5,14,15,18.] All experimental results indicate a mechanism of the type as given below in Scheme 1.
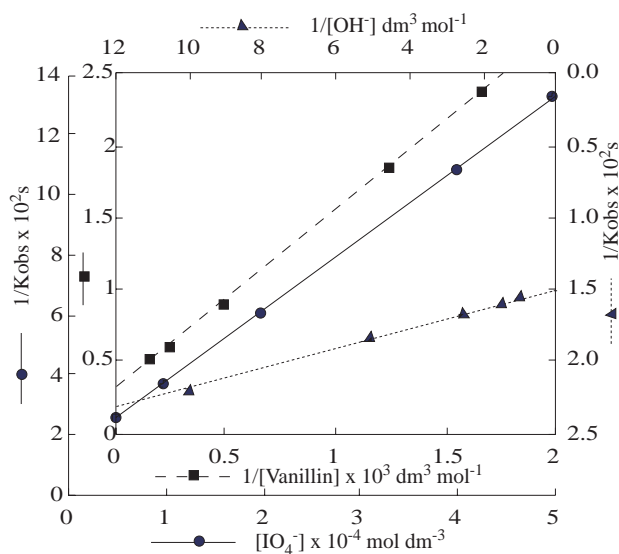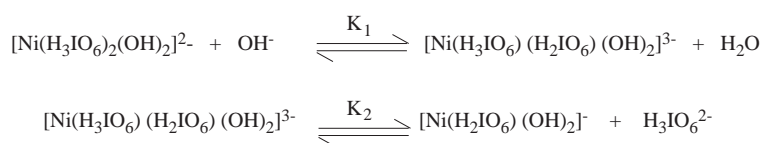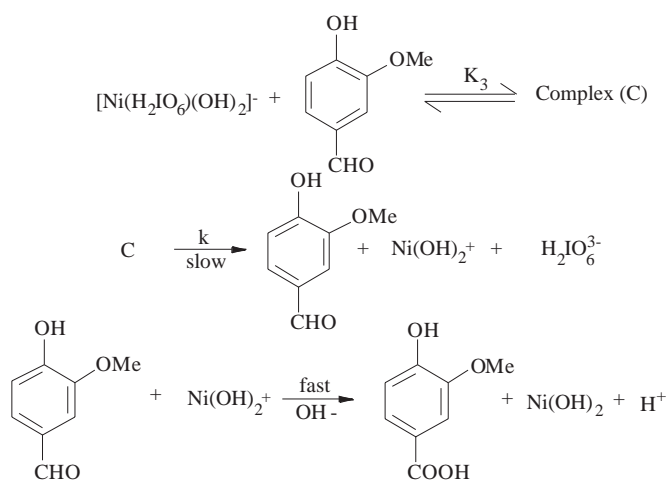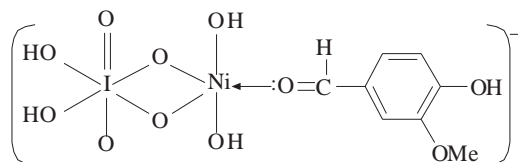

Figure 2. Verification of rate law (5)

(Condition as in Table 1

$$[Ni(H_3IO_6)_2(OH)_2]^{2-} + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Ni(H_3IO_6)(H_2IO_6)(OH)_2]^{3-} + H_2O$$

$$[Ni(H_3IO_6)(H_2IO_6)(OH)_2]^{3-} \underset{}{\overset{K_2}{\rightleftharpoons}} [Ni(H_2IO_6)(OH)_2]^- + H_3IO_6^{2-}$$

Scheme 1

The probable structure of complex (C) is

Scheme 1 leads to the rate law equation (4):

$$\text{Rate} = -\frac{d[\text{Ni(IV)}]}{dt} \tag{4}$$

$$= \frac{kK_1K_2K_3[\text{Ni(IV)}]\,[\text{Vanillin}]\,[\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-]\,[\text{H}_3\text{IO}_6^{2-}] + K_1K_2\,[\text{OH}^-] + K_1K_2K_3[\text{Vanillin}]\,[\text{OH}^-]} \tag{5}$$

Therefore,

$$k_{obs} = \frac{kK_1K_2K_3\,[\text{Vanillin}]\,[\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-]\,[\text{H}_3\text{IO}_6^{2-}] + K_1K_2\,[\text{OH}^-] + K_1K_2K_3[\text{Vanillin}]\,[\text{OH}^-]} \tag{6}$$

Equation (5) can be arranged to (6), which is suitable for verification

$$\frac{1}{k_{obs}} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_1K_2K_3[\text{Vanillin}]\,[\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_2K_3[\text{Vanillin}]} + \frac{1}{kK_3[\text{Vanillin}]} + \frac{1}{k} \tag{7}$$

According to equation (6), other conditions being constant, the plots of $1/k_{obs}$ versus $1/[\text{OH}^-]$ (r>0.9988, S<=0.045), $1/[\text{vanillin}]$ (r>0.9997, s<=0.021) and $[\text{H}_3\text{IO}_6^{2-}]$ (r>0.9992, S<=0.051) should be linear as shown in Figure 2. From the slopes and intercepts, the values of K_1, K_2, K_3 and k were derived as 2.5 ± 0.1 dm^3 mol^{-1}, $1.9\pm0.1\times10^{-4}$ mol dm^{-3}, 270 ± 13 dm^3 mol^{-1} and $3.64\pm0.18 \times 10^{-2}$ s^{-1} respectively. The values of K_1 and K_2 are in agreement with earlier values[6]. The negligibly small effect of ionic strength on the reaction is presumably due to the fact that the reaction takes place between a neutral and charged species (Scheme 1). The effect of solvent on the reaction rate is described elsewhere[19]. The plot of $1/k_{obs}$

versus $1/\varepsilon_T$ gives a straight line (r>0.9995, S<=0.029) (Figure 1) with a negative slope, which supports the proposed mechanism given in scheme 1.

The mechanism is also supported by moderate values of activation parameters (Table 2). A high negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants[20]. The modest value of enthalpy of activation and the higher rate constants 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[21-24].

References

1. D. H. Macartney, A. McAuley, **Inorg. Chem. 22,** 2062, (1983)

2. S. Acharya, G. Neogi, R. K. Panda, D. Ramaswamy, **Int. J. Chem. Kinet. 14,** 1253, (1982)

3. A. G. Lappin, M. C. Laranjeira, O. L. Youdi, **J. Chem. Soc. Dalton Trans.** 721, (1981).

4. M. A. A. Siddiqui, Ch. S . Kumar, U. Chandraiah, S. Kandlikar, **Indian J. Chem., 30A**, 849, (1991).

5. S. M. Tuwar, S. T. Nandibewoor, J. R. Raju, **J. Indian Chem. Soc. 69,** 651, (1992).

6. S. T. Nandibewoor, G. H. Hugar, **Polish J. Chem., 71**, 1572, (1997).

7. S. Bhattacharya, B. Saha, A. Datta, P. Banerjee, **Coord Chem. Rev. 47,** 170, (1970).

8. R.T. Haines and A. McAuley, **Coord. Chem. 39**, 79**,** (1981).

9. K. Nag, A. Chakravarthy, **Coord Chem. Rev. 33**, 87, (1980).

10. P. Ray, **"Inorganic Synthesis",** Vol. 5, ed. Therald Moellar, p. 201, McGraw-Hill, New York, 1957.

11. G. H. Jeffery, J. Bassett, J. Mendham, R. C. Denney, **"Vogel's Text Book of Quantitative Chemical Analysis",** 5th ed. p.181, ELBS Longman, Essex, UK, 1991.

12. F. Feigl **"Spot Tests in Organic Analysis"**, p. 332, Elsevier Scientific Publishers, 1975.

13. G. H. Hugar, S. T. Nandibewoor, **Trans. Met. Chem. 19,** 215, (1994).

14. G. H. Hugar, S. T. Nandibewoor, **Indian J. Chem. 32A**, 1056, (1993).

15. N. N. Halligudi, S. M. Desai, S. T. Nandibewoor, **Int. J. Chem. Kinet. 31,** 789, (1999).

16. M. R. Kembhavi, A. L. Harihar, S. T. Nandibewoor, **J. Indian Chem. Soc. 76**, 79, (1999).

17. A. L. Harihar, M. R. Kembhavi, S. T. Nandibewoor, **Inorg. React. Mech. 1**, 145, (1999).

18. J. Devi, S. Kothari, K. K. Banerji, **Indian J. Chem. 29A,** 241, (1995).

19. E. S. Amis, "**Solvent effects on reaction rates and mechanism",** Academic Press, New York, 1966.

20. A. Weissberger, **"Investigation of Rates and Mechanism of Reactions"** in **Techniques of Chemistry,** Vol. 4, ed. E. S. Lewis Wiley, p. 421, Interscience Publication, New York, 1974.

21. A. Sutin, **Ann. Rev. Phys. Chem. 17,** 119, (1966).

22. M. Lancaster, R. S. Murray, **J. Chem. Soc. A,** 2755, (1971).

23. M. Martinez, M. Pitarque, R. V. Eldik, **J. Chem. Soc. Dalton Trans.** 2665, (1996).

24. A. L. Harihar, M. R. Kembhavi, S. T. Nandibewoor, **Monatshefte fur Chemie 131,** 1129, (2000).