

Kinetics and Mechanism of the Nickel(II)- and Copper(II)-promoted Reduction of Di-2-pyridyl Ketone with Sodium Tetrahydroborate

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The kinetics of reduction of di-2-pyridyl ketone with NaBH₄ leading to the formation of di-2-pyridylmethanol (dpm) was studied in the presence of Ni^{II} or Cu^{II}. The metal ion-promoted reduction involved two successive intermediates. Based on the visible spectra and kinetic data concerning the intermediates, it is proposed that the first intermediate is the nickel(I) or copper(I) complex of the anion of dpm and that the second intermediate is the corresponding complex of dpm.

Previously, we reported the kinetics and mechanism of the zinc(II)- or cobalt(II)-promoted reduction of di-2-pyridyl ketone (dpk) with NaBH₄ to produce di-2-pyridylmethanol (dpm).¹ In the zinc(II)-promoted reaction the metal ion simply acted as a Lewis-acid catalyst, enhancing the electrophilicity of the carbonyl carbon of dpk by binding the carbonyl oxygen of dpk. On the other hand, kinetic data obtained for the cobalt(II)-catalysed reaction were best explained in terms of rapid initial formation of the cobalt(I) complex of the anion of dpm, protonation of the anionic ligand by the solvent, and oxidation of the cobalt(I) centre by molecular oxygen. In order to gain further insights into the mechanisms of the transition metal-promoted reductions, we extended the mechanistic investigation to the nickel(II)- or copper(II)-promoted reduction of dpk with NaBH₄.

Experimental

The salt Ni(ClO₄)₂·6H₂O was recrystallized from water, and Cu(NO₃)₂·3H₂O purified according to the literature.² Attempts to isolate the complexes of Ni^{II} and Cu^{II} of dpk in high purity were unsuccessful. The preparation or purification of other materials and methods of kinetic measurements were reported previously.¹ Rate measurement was initiated by adding a solution of Ni(ClO₄)₂·6H₂O or Cu(NO₃)₂·3H₂O to a solution of dpk (in 1:2 or 1:3 molar ratio of metal to dpk; change in the molar ratio did not significantly affect the rate constants), and then adding a solution of NaBH₄ in 2,5,8-trioxanonane.

Results and Discussion

As described below, the kinetic features observed for the nickel(II)- or copper(II)-promoted reaction were very similar to those for the cobalt(II)-promoted one. The absorbance changes observed at 240–270 nm for the reduction of dpk with NaBH₄ in the presence of Ni^{II}, Cu^{II} or Co^{II} (ref. 1) were biphasic in the absence of oxygen, and were triphasic in the presence of oxygen. The rapid initial absorbance changes were complete within the manual mixing period of the reaction mixtures. Pseudo-first-order kinetics were observed for the subsequent slow processes. The pseudo-first-order rate constant (*k*₂) for the second process of a biphasic reaction was identical with that of the second process of the corresponding triphasic reaction measured in the

presence of oxygen. The value of *k*₂ decreased when [NaBH₄]₀ was raised. The same decrease in *k*₂ was observed when NaClO₄, NaBF₄, or NH₄PF₆ was substituted for a part of the NaBH₄ added. The shape of the plot of *k*₂ [in the presence of 2.1 mmol dm⁻³ NaBH₄, *k*₂ was 0.063, 0.035 and 0.015 s⁻¹, respectively, for the reactions promoted by Ni^{II}, Cu^{II} and Co^{II} (ref. 1)] against ionic strength was essentially identical for the three metal ions.

The pseudo-first-order rate constant (*k*₃) of the third process of the triphasic absorbance changes observed in the presence of oxygen was not affected by changes in the concentration of NaBH₄ or added electrolytes. The values of *k*₃ measured were 5.2 × 10⁻⁴, 4.2 × 10⁻⁴ and 5.9 × 10⁻⁴ s⁻¹, respectively, for the reactions promoted by Ni^{II}, Cu^{II} and Co^{II}.¹

The spectra of the final products obtained in the presence of oxygen were identical with that of the separately isolated dpm taken in the presence of Ni^{II}, Cu^{II} or Co^{II}.¹ The UV and VIS spectra of dpm in the presence of Cu^{II}, Ni^{II} or Co^{II} (ref. 1) were unaffected by incubation with NaBH₄ for several hours.

The multiphasic absorbance changes observed during the nickel(II)-, copper(II)-, or cobalt(II)-promoted reduction of dpk by NaBH₄ indicate the accumulation of two successive intermediates (see Scheme 1 of ref. 1). The two intermediates are denoted as **1**_M and **2**_M, and the transition state for the conversion of **1**_M into **2**_M as **T**_M. The visible spectra of **1**_{Ni}, **2**_{Ni}, **1**_{Cu} and **2**_{Cu} measured in the absence of oxygen are illustrated in Figs. 1 and 2.

The unique dependence of *k*₂ on [NaBH₄]₀ or the concentration of the added salts has been taken to indicate that the intrinsic rate constant for the *k*₂ step is independent of [NaBH₄]₀ but that the retardation is the result of salt effects.¹ Thus, the transition state **T**_M is in the same oxidation state as **1**_M, as the rate of the conversion of **1**_M into **2**_M is independent of [NaBH₄]₀. The considerable rate-retardation effects exerted by the increase in the total salt concentration indicates that **T**_M is less polar than **1**_M.^{3,4}

The visible spectra of **1**_{Ni}, **2**_{Ni}, **1**_{Cu} and **2**_{Cu} are remarkably different from those of complexes of Ni^{II} or Cu^{II} with dpk or dpm, suggesting that the metal ions of **1**_M and **2**_M are not Ni^{II} or Cu^{II}. The visible spectra of **1**_{Ni} and **2**_{Ni} exhibit strong absorptions that are characteristic of nickel(I) species.⁵⁻⁷ The spectra (Fig. 2) of **1**_{Cu} and **2**_{Cu} show no d-d transition band, indicating the d¹⁰ electronic configuration. In the cobalt(II)-promoted reaction the visible spectra of **1**_{Co} and **2**_{Co} were noticeably different from

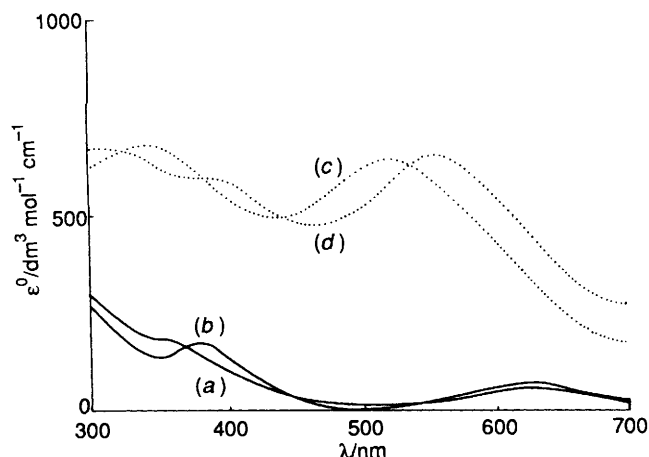


Fig. 1 Visible spectra of $[\text{Ni}(\text{dpk})_n]^{2+}$ (a), $[\text{Ni}(\text{dpm})_n]^{2+}$ (b), 1_{Ni} (c), and 2_{Ni} (d); $[\text{Ni}]_0 = 3.23 \times 10^{-3}$, $[\text{dpk}]_0 = 6.46 \times 10^{-3}$ mol dm $^{-3}$. Molar absorption coefficients were calculated as absorbance/ $[\text{Ni}]_0$. Solvents used: ethanol [(a), (b)] and ethanol containing 14% (v/v) 2,5,8-trioxanonane [(c), (d)]

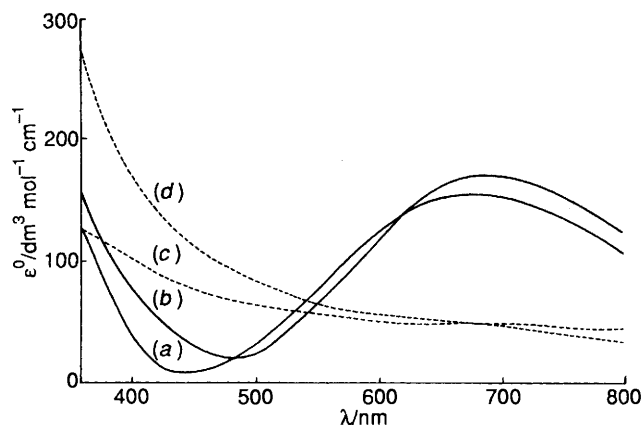
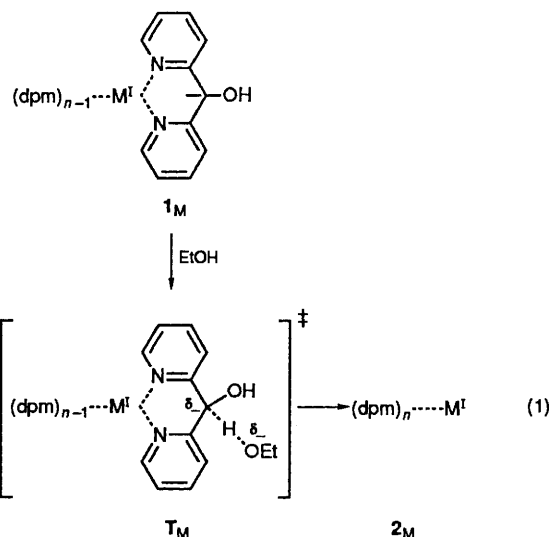


Fig. 2 Visible spectra of $[\text{Cu}(\text{dpk})_n]^{2+}$ (a), $[\text{Cu}(\text{dpm})_n]^{2+}$ (b), 1_{Cu} (c), and 2_{Cu} (d); $[\text{Cu}]_0 = 3.23 \times 10^{-3}$, $[\text{dpk}]_0 = 6.46 \times 10^{-3}$ mol dm $^{-3}$. Molar absorption coefficients were calculated as absorbance/ $[\text{Cu}]_0$. Solvents as in Fig. 1. No d-d band is seen for (c) or (d) beyond 500 nm

those of the cobalt(II) complexes and the intermediates were proposed to be cobalt(I) complexes.¹

Reduction of a dpk molecule requires two electrons and two protons (or a proton and a hydride ion). Thus, the reduction of metal complexes of dpk with NaBH_4 would proceed through several elementary steps involving several intermediates, and elucidation of the whole reaction mechanism is not easy. Some pieces of information, however, are obtained concerning the rate-determining step of the complex reaction. Structures of 1_{M} and 2_{M} consistent with the spectral data and the kinetic data are exemplified in equation (1).¹ Here, 1_{M} and 2_{M} contain Ni^{I} , Cu^{I} or Co^{I} , and, thus, conversion of 1_{M} into 2_{M} does not require NaBH_4 . Dispersed negative charge in T_{M} is consistent with the observed electrolyte effect. Other structures may also be compatible with the results. For example, 1_{M} may contain the oxyanion of dpm, instead of the corresponding carbanion. However, proton transfer to oxyanions is much faster than that to carbanions,^{8,9} and the rate-determining protonation of an



alkoxide ion is less likely. In addition, the carbanion may be unusually stable because it is resonance-stabilized with the negative charge delocalized to the two pyridyl rings.

The metal(I) complex of the anion of dpm is formed by the apparent transfer of one electron and a hydride ion to the metal(II) complex of dpk. Instead of a hydride ion, two electrons and a proton may be involved in the process, and the detailed mechanism is not known at present. Resistance of the metal(II) complex of dpm to reduction by NaBH_4 suggests that the metal(I) species is obtained by the initial reduction by NaBH_4 of M^{II} complexed with dpk.

The k_3 step represents conversion of 2_{M} into the metal(II) complex of dpm in the presence of O_2 . Although little mechanistic information is available at present for this process, resistance of the metal(II) complexes of dpm to the reduction of the metal centres by NaBH_4 suggests that the low oxidation states of the metal ions are not stabilized by the dpm ligand.¹

Acknowledgements

This work was supported by a grant (1989) from the Ministry of Education, Republic of Korea.

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Received 14th September 1990; Paper 0/04200E