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Short communication

Effect of the denticity of tripodal amine ligands containing multiple oximate donors on the catecholase activity of their nickel(II) complexes

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ABSTRACT

The rates of oxidation of 3,5-di-tert-butyl catechol (3,5-DTBC) to 3,5-di-tert-butylbenzoquinone (3,5-DTBQ) by atmospheric dioxygen in the presence of five nickel(II)-polyoximate complexes as catalysts were measured at five different substrate-to-catalyst ratios. In all cases, saturation kinetics were observed at high substrate concentration. Analysis of the data using the Michaelis Menten model reveals rate constant values (k_{cat}) ranging from 120 to 400 h^{-1}, which are comparable to results for other Ni(II)-polyoximate complexes in the literature. For the set of five catalysts examined in this work, those with the fewer number of coordinating groups on their polyoximate ligands showed the highest rates of reaction, while those with the higher number of coordinating groups showed the lowest rates of reaction. These results suggest that greater flexibility and possibly lower hindrance in the coordination sphere of the nickel centers of the catalysts enhance the rate of catalysis.

Catechols (*o*-dihydroxybenzenes), undergo several oxidative pathways in biological systems. In one type of transformation, oxidation by dioxygen (O_2) results in the loss of two electrons and two protons, producing the corresponding *o*-benzoquinone (Fig. 1). This reactivity is promoted by the copper-containing enzyme catechol oxidase, and many synthetic copper complexes exhibit this type of reactivity [1]. Nickel(II) complexes rarely promote the oxidation of substrates using dioxygen as the oxidizing agent. This is in part due to the high energy barrier to the higher oxidations states, Ni(III) and Ni(IV). However, it has been shown that these higher oxidation states are accessible using ligand donor groups such as amidates (deprotonated amides) and oximates (deprotonated oximes) [2]. A dimeric nickel(II) complex of a tripodal amine ligand containing three oximate donors has been shown to oxidize substrates such as triphenyl phosphine [3] and several alcohols and amines [4]. More recently two nickel(II)-oximate complexes, each with four nickel centers, have been shown to catalyze the oxidation of the model substrate 3,5-di-tert-butyl catechol (3,5-DTBC) to the corresponding 3,5-di-tert-butylbenzoquinone (3,5-DTBQ) [5]. In the cases of the oxidation of methanol to formaldehyde and the oxidation of 3,5-DTBC to 3,5-DTBQ, EPR data support that after the initial oxidation of the nickel(II) to nickel(III) by dioxygen, an iminoxyl radical forms by a single electron transfer from an oximate ligand. This ligand-based radical is believed to be the active agent which oxidizes the coordinated substrate. In this work, we are investigating the effect of the coordinating properties of the ligand donor set on the catecholase activity for a set of nickel(II)-polyoximate complexes. Each ligand has a common tripodal amine motif with two pendant oxime donors. The third pendant group off the central amine is varied, containing one of the following: a non-coordinating alkyl or aryl group, a weakly coordinating amide oxygen donor, a strongly coordinating pyridyl nitrogen donor, or a strongly coordinating oxime nitrogen donor (Fig. 2) [6]. Upon deprotonation of the oxime groups, it has been shown in more than one case that these complexes form oximate-bridged dimers [3,4b,7], and it is believed that this is the case for all the complexes of this type. The rate of catalysis of the oxidation of 3,5-DTBC to 3,5-DTBQ by these nickel(II)-polyoximate complexes has been shown to be influenced by the coordination properties of the third pendant group on the ligand.

The metal complexes $[Ni(TRISOXH_3)(NO_3)(H_2O)](NO_3)\cdot H_2O$ [3], $Ni(PRABOH_2)(NO_3)_2$, $Ni(PEABOH_2)Cl_2$ (as the chloride-bridged dimer $[Ni(PEABOH_2)Cl]_2(\mu\text{-}Cl)_2)$), $Ni(PYRABOH_2)Cl_2$, and $Ni(GLABOH_3)Cl_2$ [6] were prepared following published procedures.[1] The substrate 3,5-

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[1] $TRISOHH_3$ = tris(1-propan-2-only oxime)amine; $PRABOH_2$ = *N*-n-propyl-*N*,*N*-bis(1-propan-2-only oxime)amine; $PEABOH_2$ = *N*-(2-phenylethyl)-*N*,*N*-bis(1-propan-2-only oxime)amine; $PYRABOH_2$ = *N*-(pyridine-2-yl)-*N*,*N*-bis(1-propan-2-only oxime)amine; $GLABOH_3$ = *N*,*N*-bis(1-propan-2-only oxime) glycine *N*′-methylamide.

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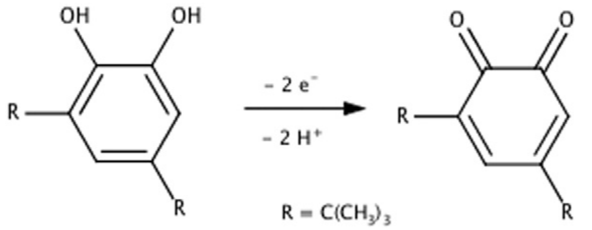

Fig. 1. The oxidation of 3,5-di-tert-butylcatechol (3,5-DTBC) to 3,5-di-tert-butylbenzoquinone (3,5-DTBQ).

DTBC and a standard of 3,5-DTBQ were obtained from Sigma-Aldrich and used without further purification. For each nickel complex listed, five solutions of the complex and the 3,5-DTBC substrate were prepared, such that the amounts of the substrate to the catalyst were in the following ratios: 10:1, 20:1, 40:1, 100:1, and 200:1 (the concentration of the catalyst in the final solutions was 0.000100 M as the monomer, which would be 0.0000500 M as the oximate-bridged dimer upon deprotonation at the start of the reaction). These were prepared by combining 0.250 mL of 0.0100 M stock nickel catalyst solution (calculated as the monomer), with the appropriate volume of 0.100 M 3,5-DTBC solution (0.125 mL, 0.250 mL, 0.500 mL, 1.25 mL, and 2.50 mL) and diluting each to 25.0 mL (all solutions were prepared in methanol under aerobic conditions at room temperature).

To monitor the rate of oxidation of the catechol to the quinone, the growth of the quinone absorbance at 400 nm in the UV–vis spectrum was measured versus time. To 3.00 mL of each solution, a solution of KOH (in methanol) was added to deprotonate the oxime groups of the nickel complex[2] (0.090 mL of 0.010 M KOH for the Ni(TRISOXH_3) complex; 0.060 mL of 0.010 M KOH for the other complexes). The reaction was immediately mixed, and the absorbance at 400 nm was measured every 5 s. The rate of reaction was measured in this manner for three trials of each sample solution. Due to the fact that 3,5-DTBC will air-oxidize under alkaline conditions [8], the rates of the reaction in the presence of the same amount of hydroxide ion (but no nickel catalyst) were measured for each of the substrate concentrations. These rates were significantly lower than those of the reactions in the presence of the nickel catalysts. The rates of the base-only reactions were subtracted to correct the rates of the corresponding nickel-catalyzed reactions [9].

The rate of the formation of the 3,5-DTBQ product for each reaction was determined using the method of initial rates by analyzing the increase in the absorbance at 400 nm. All reactions exhibited saturation kinetics at the higher substrate-to-catalyst ratios. The Michaelis–Menten model of enzymatic kinetics was used in the analysis of the data, and Lineweaver-Burk double-reciprocal plots (data for the reaction using the Ni(PEABO) catalyst are shown in Fig. 3; data for the other catalysts are provided in the Supplementary material) were used to calculate the kinetic parameters K_m, V_{max}, and k_{cat} for the five nickel complexes. The k_{cat} values for the nickel(II)-polyoximate complexes in this study compare closely to those of the two other bridged nickel(II)-polyoximate complexes reported recently [5].

From the results shown in Table 1, a trend is observable between the catalytic rate of each nickel complex (as measured by k_{cat}) and the nature of the third pendant group on the tripodal amine ligand. The two complexes whose third pendant group is a non-coordinating alkyl or aryl group, Ni(PEABO) and Ni(PRABO), have significantly higher k_{cat} values than the other complexes in the work. The two complexes with the lowest k_{cat} values, Ni(TRISOX) and Ni(PYRABO), have strongly coordinating ligand donor groups in the third pendant position. The Ni(GLABO) catalyst, with a weakly coordinating amide oxygen donor group, has a k_{cat} value in the middle of the group. This suggests that the ability of the third pendant group to coordinate to the metal significantly affects the rate of catalysis.

In the report of the oxidation of methanol by dioxygen promoted by the oximate-bridged Ni(TRISOX) dimeric complex [4b], it was proposed that dioxygen could coordinate to both nickel centers of the dimer and oxidize each Ni(II) to Ni(III), which would lead to a bridging peroxide ligand. Subsequently, the formation of iminoxyl radicals on an oximate group of the ligand were identified, supporting the transfer of an electron from the oximate group to return Ni(III) to Ni(II). These oxidizing equivalents in the iminoxyl radicals then could oxidize a coordinated substrate, such as methanol. A similar mechanism was suggested for the Ni(II)-polyoximate complexes that catalyzed the 3,5-DTBC to 3,5-DTBQ oxidations reported earlier, in which ligand-based radicals were also identified [5]. In that proposed mechanism, a ligand pendant arm becomes uncoordinated from each nickel center to allow room in the coordination sphere of each octahedral nickel center for coordination of both dioxygen (and its reduced forms, such as peroxide) and substrate. This proposed pathway is consistent with the trend in the data reported here for the catalytic oxidation of 3,5-DTBC to 3,5-DTBQ.

The catalysts showing the fastest rates already have a vacant position in their six-coordinate nickel coordination spheres (likely filled with easily displaceable monodentate solvent or anion molecules) due to the non-coordinating groups on their third pendant arms. While the 2-phenylethyl group of the PEABO ligand is larger than the propyl group of the PRABO ligand, little difference is observed in their catalytic activities. This suggests that there is little hindrance in the coordination environment caused by the non-coordinating groups. For the subset of complexes with coordinating groups in the third pendant positions, the amide oxygen of Ni(GLABO) (the weakest of the coordinating groups) would be the easiest to displace; this complex shows the fastest rate of catalysis in the subgroup with coordinating groups. Between the two catalysts with the strongest coordinating groups, Ni(PYRABO) and Ni(TRISOX), the Ni(PYRABO) catalyst shows slightly slower rates of reaction. This may be a case of greater steric hindrance caused by the coordinated pyridyl donor group; this is supported by its K_m value, which is the highest in the group and indicates that it has the lowest affinity for the catechol substrate. However, as the Ni(TRISOX) catalyst has the lowest K_m value (and highest affinity for the catechol substrate) in the group, it is possible that catalyst-catechol binding affinity may not be the only factor that is affected by the variation in the ligand/complex structure. It may be that the availability in the coordination sphere of the nickel centers for the proper binding of both dioxygen and the catechol is responsible for the observed effect on the rate of catalysis. Increased flexibility in the dioxygen-catalyst-catecholate complex may result in a more energetically favorable orientation of the dioxygen and/or catechol reactants in the coordination spheres of the nickel centers in the catalyst. It would seem less likely that electronic effects of the additional donor group on the redox potentials of the nickel centers are causing the observed trends, as one would expect the ligand with the most oximate groups, Ni(TRISOX), to have the lowest energy barrier to nickel oxidation. If a major effect on the rate of reaction were the modification of the redox potentials by the ligand donor strengths, this would suggest the possibility that the reaction proceeds by mechanisms involving the reduction of Ni(II) to Ni(I), similar to the dimeric copper systems of catechol oxidase and mimetic systems in which the Cu(II) centers are reduced to Cu(I). This type of reactivity seems unlikely for the nickel system, given that other oxidative reactions (including the oxidation of 3,5-DTBC to 3,5-DTBQ) utilizing these Ni(II)-polyoximate complexes have shown evidence of Ni(III) intermediates. Additionally,

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[2] The oxime groups of each complex must be deprotonated for catalytic activity; in their neutral-oxime forms, the complexes are inactive towards oxygen reactivity. The deprotonated complexes are generated in situ by the addition of hydroxide, as their fully oxime-deprotonated forms have not been successfully isolated.