

Mechanisms of degradation of cobalt dioxygen complexes

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Abstract - The three types of reactions by which cobalt dioxygen complexes become converted irreversibly to inert complexes having no affinity for dioxygen are described: 1, conversion to an inert cobalt(III) complex with separation of hydrogen peroxide; 2, oxidative dehydrogenation of the coordinated ligand by coordinated dioxygen; 3, oxygen insertion into the coordinated ligand. Examples of the first and second reaction types are given in some detail but experimental examples of coordinated dioxygen insertion into coordinated substrate are not yet available for cobalt(III) complexes, although such reactions do occur with appropriate organic substrates. Degradation reactions of type 1 seem to occur with very thermodynamically stable oxygen complexes or complexes with ligands which resist oxidative attack. Promotion of ligand dehydrogenation by reaction with coordinated oxygen involves very specific steric and conformational requirements and are characterized by very high deuterium isotope effects indicating direct transfer of hydrogen to coordinated oxygen.

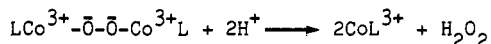
INTRODUCTION

All dioxygen complexes undergo irreversible degradation reactions to form inert complexes that have no affinity for dioxygen. This type of reaction occurs for all dioxygen complexes regardless of the nature of the metal ion and the ligand involved. The three reaction types observed are listed in Table 1 with illustrative examples. In some cases the degradation rates may be very slow, and in other cases they are so rapid as to make it difficult to isolate or work with the dioxygen complex under consideration. The factors that control the tendencies of oxygen complexes to undergo such reactions at various rates are not well understood and it is still not possible to predict whether a particular dioxygen complex would be stable or labile toward such degradation reactions. Also it is not possible to predict with certainty which type of degradation reaction a newly synthesized dioxygen complex would undergo, but it is certain that some such reaction does take place. In case of cobalt, reaction type 3 has not yet been observed in its dioxygen complexes, however, it is a very common reaction for other metal dioxygen complexes, and many cobalt dioxygen complexes have been observed to insert one or two of its coordinated dioxygens into an appropriate organic substrate. Therefore it is considered only a matter of time before examples of type 3 degradation reactions of cobalt dioxygen complexes are discovered.

TABLE 1. Spontaneous irreversible conversion of binuclear cobalt dioxygen complexes to inert complexes

1. Metal-centered oxidation

Conversion to the inert Co(III) complexes of the original ligand with release of H₂O₂



2. Oxidative dehydrogenation of the coordinated ligands



3. Oxygen insertion into coordinated ligand



The rates of the degradation reactions in Table 1 must be controlled and be sufficiently slow if the dioxygen complex is to be employed as an oxidant or as a catalytic intermediate for the oxidation of organic substrates. The ability to design and synthesize dioxygen complexes having extended, useful lifetimes in aqueous solution would be invaluable for the study of oxygenase and oxidase models or for the development of dioxygen carriers useful for separation processes and oxygen manufacture. However, the number of degradation reactions of dioxygen complexes subjected to detailed studies thus far is relatively limited, and it is not yet possible to predict with certainty whether a proposed oxygen carrier would be sufficiently resistant to oxidative degradation reactions and have a sufficiently long lifetime in solution to be useful for separation processes or for the study of oxidation processes as oxidase and oxygenase enzyme models. There are some interesting leads in the literature indicating a relationship between thermodynamic stability of the oxygen complex and its kinetic lability with respect to degradation reactions. Thus it has been pointed out (ref. 1) that the most successful cobalt dioxygen complex developed up to the present time for the production of oxygen through oxygenation and deoxygenation cycling is the so-called cobalt "fluomine" complex having relatively low dioxygen affinity (the resistance of the salcomine Schiff base ligand to oxidative attack by coordinated oxygen has been increased by fluorine substitution in the aromatic ring, but this also results in further reduction in dioxygen affinity). On the other hand, in investigating cobalt dioxygen complexes containing a series of polyamine ligands as catalysts for the oxidation of ditertiarybutylphenol, the usefulness as catalysts of the weaker complexes having low dioxygen affinity was impaired by the fact that they underwent relatively rapid degradation reactions in solution and therefore had lifetimes too short for kinetic studies of their catalytic activities (ref. 2).

SURVEY OF DEGRADATION REACTIONS OF COBALT DIOXYGEN COMPLEXES

The cobalt dioxygen complexes on which detailed degradation studies have been carried out are listed in Table 2 with an indication of the types of reaction involved. Of the ligands listed the one that undergoes the most rapid degradation reaction is glycyglycine, which becomes dehydrogenated at an appreciable rate at 25°C, under the same conditions as those employed for potentiometric equilibrium measurements, thus greatly complicating the quantitative determination of oxygenation equilibrium constants. On the other hand, the dioxygen complex formed from dipyrindyl, and from the aliphatic polyamines TETREN, EPYDEN, and MXBTRIEN, do not become dehydrogenated but undergo metal-centered oxidation at elevated temperatures to form inert cobalt(III) complexes and hydrogen peroxide. All of the remaining ligands, which contain chelating pyridyl groups, form dioxygen complexes which degrade to dehydrogenation products which have coordinated imines with double bonds conjugated with the aromatic rings. These reactions have rather specific steric requirements, probably because the reactions seem to take place with intramolecular hydrogen transfer from the carbon atoms alpha to the pyridine rings directly to coordinated dioxygen. Although the dioxygen complexes having the highest thermodynamic stabilities do not undergo oxidative dehydrogenation, the ease of the dehydrogenation reaction is essentially a property of the ligand, and is very dependent on ligand conformation in the dioxygen complex.

It is not expected that the glycyglycine-containing cobalt dioxygen complex in Table 2 would fit in with the stabilities and degradation rates of the other dioxygen complexes listed, because the ligand donor groups are quite different. Although the thermodynamic stability of the oxygen-free complex is very high, it has a low oxygenation constant and undergoes rapid dehydrogenation at room temperature. The low oxygenation constant is considered due to both the presence of negative donor groups in the complex $\text{Co}(\text{H}_2\text{L})_2^{2-}$ and to octahedral coordination by the two terdentate ligands.

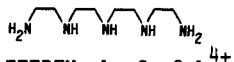
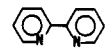
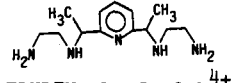
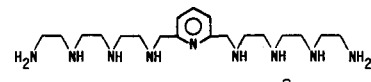
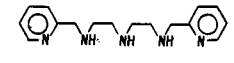
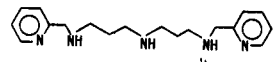
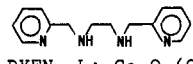
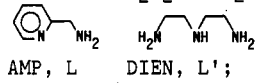
While conjugation with an aromatic ring seems to promote dehydrogenation to produce an imine double bond, this is in itself not sufficient, as is indicated by the lack of oxidative dehydrogenation of MXBTRIEN.

For a more detailed account of the factors involved in the tendency of the a coordinated ligand to undergo dehydrogenation by reaction with coordinated dioxygen, the experimental evidence for the degradation reactions of the dioxygen complexes containing EPYDEN and PYDIEN are now presented. It is again noted that oxygen insertion of the coordinated ligand has not yet been observed with cobalt dioxygen complexes, although there does not seem to be any obvious reason for the lack of such a reaction. It is therefore thought that such examples will eventually be found.

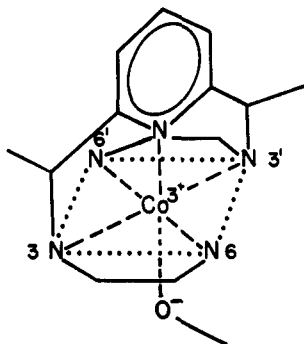
METAL-CENTERED DEGRADATION OF THE COBALT EPYDEN DIOXYGEN COMPLEX

The lack of oxidative dehydrogenation of EPYDEN is of interest because superficially it seems to have all of the properties of those ligands, such as PYDIEN, PYEN, PYDPT and AMP, which do undergo this type of degradation. Metal-centered oxidation to form the cobalt(III) complex of the unchanged ligand and hydrogen peroxide has been rationalized on the basis of the folded conformation of the coordinated ligands, indicated by formula 1 (ref. 8,9). It is seen that the formation of the conjugated trigonal imine group resulting from dehydro-

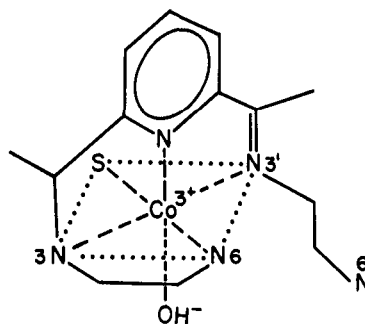
TABLE 2. Degradation studies of cobalt dioxygen complexes

Ligand and Formula of Dioxygen Complex	Oxygenation Constant $P_{1/2}^{-1}, \text{atm}^{-1}$	Degradation rate constants Conditions	Reaction Products	Ref.
$\text{H}_2\text{NCH}_2\text{CONHCH}_2\text{COOH}$ glycylglycine, GG, HL; $\text{Co}_2\text{O}_2(\text{H}_{-1}\text{L})_2$	7.5×10^2	$43 \times 10^{-5} \text{ s}^{-1}$ 25°C, pH 11.31	$\text{HN}=\text{CHCONHCH}_2\text{COOH}$	3,4 5,15
 TETREN, L; $\text{Co}_2\text{O}_2\text{L}_2^{4+}$	9.1×10^9	$12.5 \times 10^{-5} \text{ s}^{-1}$ 35°C, pH 11.0	$\text{CoL}^{3+}, \text{H}_2\text{O}_2$	6,16
 Dipyrityl; $\text{Co}_2\text{O}_2(\text{OH})\text{L}_4^{3+}$	$3.4 \times 10^{1*}$	$10.6 \times 10^{-5} \text{ s}^{-1}$ 25°C, pH 2.02	$\text{CoL}_2^{3+}, \text{H}_2\text{O}_2$	7,8
 EPYDEN, L; $\text{Co}_2\text{O}_2\text{L}_2^{4+}$	$6.8 \times 10^{8*}$	$29 \times 10^{-5} \text{ s}^{-1}$ 35°C, pH 10.98	$\text{CoL}^{3+}, \text{H}_2\text{O}_2$	9,10
 MXBTRIEN, L; $\text{Co}_2\text{O}_2(\text{OH})\text{L}^{3+}$	$4.0 \times 10^{7*}$	$20 \times 10^{-5} \text{ s}^{-1}$ 50°C, pH 11.0	$\text{Co}_2(\text{OH})\text{L}^{5+}, \text{H}_2\text{O}_2$	11
 PYDIEN, L; $\text{Co}_2\text{O}_2\text{L}_2^{4+}$	3.4×10^5	$53 \times 10^{-5} \text{ s}^{-1}$ 35°C, pH 11.10	$\text{Co}_2(\text{H}_{-2}\text{L})_2^{4+}, \text{H}_2\text{O}$	6
 PYDPT, L; $\text{Co}_2\text{O}_2\text{L}_2^{4+}$	6.8×10^1	880×10^{-5} 35°C, pH 10.56	$\text{Co}_2(\text{H}_{-2}\text{L})_2^{4+}, \text{H}_2\text{O}$	6
 PYEN, L; $\text{Co}_2\text{O}_2(\text{OH})\text{L}_2^{3+}$	$23 \times 10^{5*}$	$21 \times 10^{-5} \text{ s}^{-1}$ $3.5 \times 10^{-5} \text{ s}^{-1}$ 35°C, pH 11.9	$\text{Co}(\text{H}_{-2}\text{L})^{2+}, \text{H}_2\text{O}$	12
 AMP, L DIEN, L'; $\text{Co}_2\text{O}_2\text{L}_2\text{L}'^{4+}$	3.9×10^7	$550 \times 10^{-5} \text{ s}^{-1}$ $61 \times 10^{-5} \text{ s}^{-1}$ 35°C, pH 11.05	$\text{CoL}^{2+}, \text{NH}_3, \text{H}_2\text{O}$ N CHO	13,14

* at pH 7.00



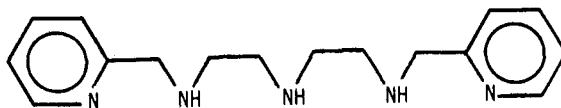
1 Proposed conformation of the EPYDEN cobalt dioxygen complex



2 Dehydrogenation product of 1 (not formed)

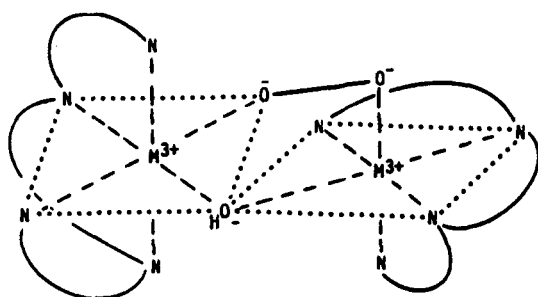
genation, indicated by formula 2, could not take place without breaking a cobalt-nitrogen coordinate bond and therefore would be a highly energetic process.

For the cobalt dioxygen complex PYDIEN, formula 3, the crystal structure reported by Timmons et al. (ref. 17) clearly indicates that the coordinated ligand could generate a coordinated and conjugated trigonal imine group with little or no strain, thus providing a low-energy pathway for dehydrogenation.

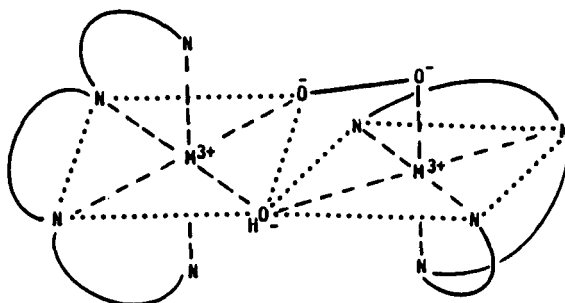


3 PYDIEN

The sensitivity to ligand conformation of the degradation reaction involving dehydrogenation of the coordinated ligand by coordinated dioxygen is indicated by the recent work of Basak and Martell (ref. 13,14) in which the rate determining steps were found to have very high kinetic deuterium isotope effects (~6-8). The proposed activated complex, illustrated for PYEN by 4 involves simultaneous proton and electron transfer involving both the coordinated dioxygen and the coordinated ligand, and thus would be very sensitive to the relative positions of these coordinated entities. The conformation indicated by 4 provides the closest approach for the reaching groups. Evidence was also reported (ref. 13) for a more slowly reacting species which could have a ligand conformation such as the one shown in 5, which has similar H-O transfer distance but the wrong conformation for facile dehydrogenation. Other possible solution species have longer distances between the alpha hydrogens and coordinated oxygen and therefore would be expected to undergo hydrogen transfer more slowly than 4.



4 Both pairs of coplanar rings cis to dioxygen



5 Both ligands folded

One of the advantages of studying the degradation reactions of cobalt dioxygen complexes is the fact that most of these complexes are stable enough in solution at room temperature to be isolated and characterized before the kinetics of degradation are studied, usually at somewhat elevated temperatures. The catalysis of the dehydrogenation of several polyamines by metal ions other than cobalt have been reported by a number of investigators. In these cases intermediate dioxygen complexes were not isolated or identified, but the nature of the reactions, and the fact that the presence of dioxygen is required, leads to the conclusion that highly reactive dioxygen complexes with short lifetimes are formed as intermediates.

Investigations by Curtis (ref. 18) and Busch et al. (ref. 19,20,21) show that macrocyclic complexes of Ni(II), Cu(II), and Fe(II) react with dioxygen to form products in which oxidative dehydrogenation of the coordinated ligand occurs. Analogous Co(III) complexes of polyamines have been observed to be resistant to dehydrogenation, indicating that a dioxygen complex may be involved as an unstable intermediate in the dehydrogenation of the ligand and reduction of the metal center. Nelson and coworkers (ref. 22) have attributed the dehydrogenation to the formation of an intermediate peroxy-bridged binuclear copper dioxygen complex. Additional examples of dehydrogenation reactions of metal-polyamine complexes by molecular oxygen, presumably through intermediate dioxygen complex formation include complexes of osmium(II) (ref. 23), nickel(II) (ref. 20,24-29), ruthenium(II) (ref. 30-36), copper(II) (ref. 22,26,37), and iron(II) (ref. 18,19,38,39). Dehydrogenation of the cobalt polyamine complexes by molecular oxygen reported by Nemeth and Simandi (ref. 40) and by Black and Hartshorn (ref. 26) probably involve reasonably stable intermediate dioxygen complexes, although such complexes were not identified in their investigations.

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