Cobalt Complexes: Correlation of Redox Potential With Effectivity as Oxygenation Catalysts

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Summary The redox potential of a series of cobalt(II) chelates correlates with their properties as either oxygen carriers or phosphine oxidation catalysts.

The recent report[1] of a correlation between oxygen binding strength and redox potential for a number of oxygen-carrying cobalt chelates prompts us to report a related correlation that we have observed. Cobalt complexes were being studied as catalysts for the oxygenation reaction [equation (1)]. The reaction rate was measured under

$$2\ \mathrm{Ph_3P} + \mathrm{O_2} \longrightarrow 2\mathrm{Ph_3PO} \qquad (1)$$

standard conditions (70°, 1 atm O_2, 76 mM Ph_3P in acetonitrile) by g.l.c. analysis of Ph_3P and Ph_3PO. Various metal compounds were added at 2 mM concentration. Without added metal compounds, only 2—4% of the Ph_3P was oxidized after 48 h. The addition of some metal chelates had no effect on the rate, but certain others, particularly cobalt chelates, greatly increased the rate of reaction, *e.g.* with an active catalyst at 2 mM concentration, 50% of the phosphine could be oxidized within 60 min. Rate data are given in the Table, along with the half-wave potential for the first oxidation wave observed for the cobalt species. The half-wave potentials were measured on 2 mM solutions of the complex in acetonitrile containing 100 mM Et_4NClO_4, under argon, with a platinum button rotating at 3000 r.p.m. The values are reported relative to a saturated calomel electrode ($E_{\frac{1}{2}}$ *vs.* S.C.E.).

The data show that the cobalt complexes may be divided into three groups, according to their redox potential and catalytic effectivity.

Group 1 contains the oxygen carriers Co(acacen) and Co(salen), and their pyridinated derivatives. Their low potentials readily allow transfer of an electron from cobalt to oxygen to form a Co^{III} superoxide adduct[2] at low temperatures, but at room temperature and above these compounds are easily destroyed by exposure to oxygen in solution.[3] These compounds, and presumably those reported earlier,[1]

Table. Oxidation rates and redox data for cobalt chelates

	Cobalt(II) complex $[R^1C(=X)CH=C(Y)R^2]_2Co{\cdot}L$					$E_{\frac{1}{2}}$/V	Ph_3P Oxidation rate/mM min^{-1}
	R^1	X	Y	R^2	L		
(I)	Me	O	O	Me		1·01	0·49
(II)	Me	O	O	Me	$2H_2O$	0·95	0·57
(III)	Me	O	O	Ph	$2H_2O$	1·03	0·42
(IV)	Ph	O	O	Ph	$2H_2O$	1·01	0·07
(V)	Bu^t	O	O	Bu^t		0·92	0·06
(VI)	Me	O	O	Me	bipyridyl	0·46	a
(VII)	Me	NH	O	CF_3		0·66	0·32
(VIII)	Me	NMe	O	CF_3		1·14	a
(IX)	Me	O	O	CF_3		1·75	a
(X)	Me	O	O	OBu^t		1·28	0·003
(XI)	Me	O	O	Me	$LiClO_4$	(1·46)[b]	a
(XII)	$Co(ClO_4)_2{\cdot}6H_2O$					>2·0	a
(XIII)	Co(salen)					0·20	a
	Co(salen) + 0·4% pyridine					−0·02	a
(XIV)	Co(acacen)					0·16	a
	Co(acacen) + 0·4% pyridine					−0·01	a

[a] Oxidation rate less than or equal to uncatalysed control (<0·001 mM/min). [b] $E_{\frac{1}{2}}$ measured in MeCN with 50 mM Et_4NClO_4 and 50 mM $LiClO_4$.

do not catalyse the reaction under standard conditions, nor do they catalyse reaction (1) at 0° in toluene–pyridine under 1 atm O_2, where they exist in solution largely as the superoxide adduct.

Group 2 compounds, also ineffective as catalysts for reaction (1), have rather high redox potentials, and hence would have little tendency to interact in any way with molecular oxygen in solution. The chelates in this group are characterized by having electronegative substituents such as CF_3 directly on the chelate ring. These cause an increase in the redox potential compared to an alkyl substituent. However, replacing an oxygen donor with an imino donor in the chelate has the opposite effect on the redox potential.

Group 3 contains all cobalt chelates tested which were effective as catalysts. They are characterized by redox potentials in a range between groups 1 and 2, that is, neither so high as to preclude metal–oxygen interaction, nor low enough to allow facile oxidation. However, not all complexes with redox potentials in this range are necessarily active, or equally active. For example, although the acetyl- and benzoyl-acetone complexes (I), (II), and (III) are the most active of those cobalt complexes tested, the related dibenzoyl- and dipivaloylmethane-complexes [(IV) and (V)] are significantly less effective as catalysts despite their similar redox potentials. This probably relates more to the square planar–tetrahedral equilibrium known[4] for four-co-ordinate cobalt(II) complexes in solution, than to the trends in redox potential. In fact the redox potentials of these four complexes are ordered according to the electron-withdrawing (phenyl) or electron-donating (alkyl) effects of the groups R^1 and R^2, as observed[5] previously with copper chelates. The configurational equilibrium of β-diketone and β-ketoimmine complexes of cobalt (II) is such that increasingly bulky ligands increasingly disfavour the square-planar forms both in solution and in the solid state.[4]

The catalysed reaction is unaffected by small amounts of water or alcohols, and is only slightly inhibited by 2,6-di-t-butylphenol. However, it is strongly inhibited by co-ordinating agents such as pyridine, DMF, and 2,2′-bipyridyl. Catalysis of reaction (I) by $Co(acac)_2$ (I) was not affected by 100mM tetra-ethylammonium perchlorate (TEAP) but 50 mM $LiClO_4$ completely inhibited the catalysis. We propose that in this case the lithium ion becomes chelated[6] by the ligand donor oxygens of the cobalt complex. By acting as a Lewis acid, the bound lithium ion decreases the availability of electron density on the complex thus reducing the likelihood of a cobalt–oxygen interaction. This is substantiated by the sharp increase in the redox potential of $Co(acac)_2$ in the presence of $LiClO_4$ (XI).

These findings, together with the geometrical and redox potential criteria which the catalytically active complexes meet, are consistent with the assumption that an inner sphere metal–oxygen interaction is a necessary part of the catalytic reaction. Further work on the mechanism of the catalytic reaction is in progress.

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