Coordination Chemistry Reviews, 79 (1987) 321–332
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

UTILIZATION OF O_2 FOR THE SPECIFIC OXIDATION OF ORGANIC SUBSTRATES WITH COBALT(II) CATALYSTS

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(Received 19 November 1986)

CONTENTS

INTRODUCTION

The spin-pairing model for the binding of O_2 to transition metal complexes views the bond formation as a combination of two free radicals; the unpaired *d*-electron(s) of the metal complex and the π-antibonding electron(s) of O_2 [1]. The molecular orbital description for the binding of O_2 to a low spin, five coordinate cobalt(II) complex is shown in Fig. 1. For simplicity, the pairing of an electron in the d_z^2 orbital with an electron in the π^* orbital of O_2 is indicated. The spin pairing model was proposed in order to account for inconsistencies in the literature concerning interpretation of the EPR spectra of cobalt-dioxygen complexes by the ionically-bound superoxide model [2]. The sum of the spin density from $^{17}O_2$ hyperfine and cobalt hyperfine values is greater than the spin density that would arise from the one unpaired electron that is present in the system. This fact serves to invalidate the interpretation of EPR spectra using direct delocalization and an ionically bound superoxide species. The spin-pairing model attributes changes in the cobalt hyperfine values to spin polarization of the σ molecular orbital (Fig. 1) by the unpaired electron in the π^* orbital. The charge on

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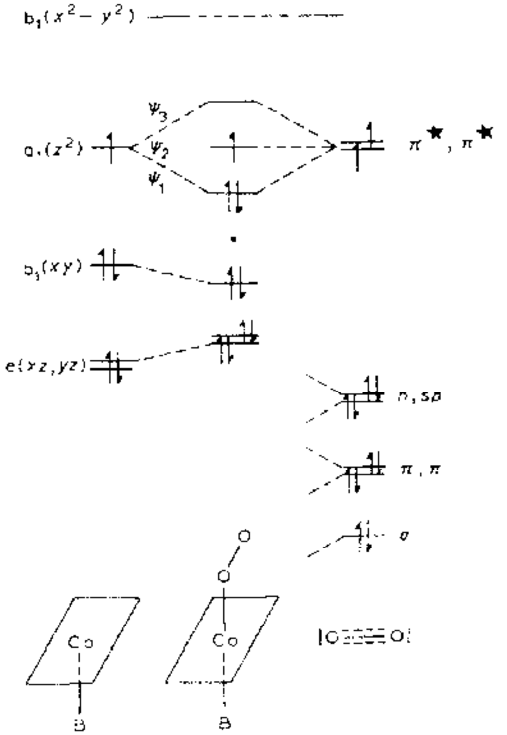


Fig. 1. The molecular orbital diagram for binding O_2 to five coordinate cobalt(II).

O_2 depends mainly on the oxygen and cobalt coefficients in the σ molecular orbital, which can be expressed in simplistic form as $\Psi_I = a\Psi_1(\mathrm{Co},\ d_z^2) + b\Psi_1(O_2,\ \pi^*)$. When $a < b$ O_2 will be negatively charged, when a = b it will be neutral, and when a > b O_2 will be positively charged. In all cases, the unpaired electron resides in a molecular orbital that is essentially oxygen in character. Semi-quantitative estimates, based on an analysis of the cobalt hyperfine values, indicate formation of O_2 adducts in which the extent of electron transfer from cobalt(II) to O_2 ranges from 0.2 to 0.8 of an electron [1a]. The extent of electron transfer is related to the ligand field strength of the ligands that are bound to cobalt(II). Stronger ligands raise the energy of the d_z^2 orbital in the five coordinate complex and hence decrease the cobalt contribution to Ψ_I in the O_2 adduct.

In subsequent work, a correlation between the enthalpy of binding various bases to cobalt(II) complexes and the enthalpy of binding O_2 to five coordinate cobalt(II) complexes was observed [3]. In addition, stronger O_2 binding paralleled increased electron transfer into O_2 and these trends were also nicely rationalized with the spin-pairing model. In Ψ_I, b increases relative to a as the energy of the d_z^2 orbital is raised. This work has led to a "potential energy storing model" to explain cooperativity in hemoglobin [4].

Though confusion continues to exist in the literature, the spin-pairing model is not concerned with the oxidation state of cobalt. Indeed, in some metal-dioxygen systems, oxidation state considerations are found to be misleading. For example, the spin-pairing model views the binding of O_2 to iron(II) as consisting of two spin-pairing interactions of the type shown for cobalt(II), which leads to a metal–oxygen double bond (one σ and one π). The oxidation state formalism for the resulting complex would be iron(IV), with O_2 as a peroxo species. However, the O–O stretching frequency is almost the same for analogous O_2 adducts of cobalt(II) and iron(II), indicating that the electronic nature of the bound O_2 is similar in both adducts irrespective of misleading oxidation state considerations. As expected for the iron–oxygen double bond predicted by the spin-pairing model, the enthalpy of binding O_2 to an iron complex is larger than that of binding O_2 to an analogous cobalt(II) complex [5].

Since the spin-pairing model predicts a range of electron transfer values between cobalt(II) and coordinated O_2, the possibility exists for varying the nucleophilicity of bound O_2. Hence our initial goals were expanded and we sought to determine ways in which coordination to, and reaction of oxygen with metals could be utilized to effect selective oxidations. Our work in this area will constitute the main topic of this review.

COBALT CATALYZED OXIDATIONS

There have been extensive reviews on the catalytic oxidation of organic substrates by transition metal complexes in the presence of molecular oxygen [6,7]. In particular, oxidations involving cobalt complexes have been intensively studied, due in part to their ability to bind dioxygen. Activation, and the subsequent reactivity, of molecular oxygen by transition metal complexes is of particular interest for there are many metalloenzymes in biological systems and investigation of the reactivity of cobalt systems may serve to shed light on this chemistry.

Various modes of reactivity are associated with homogeneous oxidation catalysis involving transition metal complexes [8,9]. In general, four classes are reported: (1) free radical autoxidation; (2) coordination of an organic substrate to a metal center, followed by attack of an oxygen-containing nucleophile; (3) transfer of an oxygen atom from a high valent oxo–metal species; and (4) metal catalysis of hydroperoxide and alkyl hydroperoxide formation and decomposition. We have been interested for some time in the activation of molecular oxygen by cobalt complexes in an attempt to effect selective catalytic oxidation of organic substrates. Two new types of reactions have resulted and we have demonstrated metal–peroxo chemistry starting from O_2 and primary alcohol solvents [10].

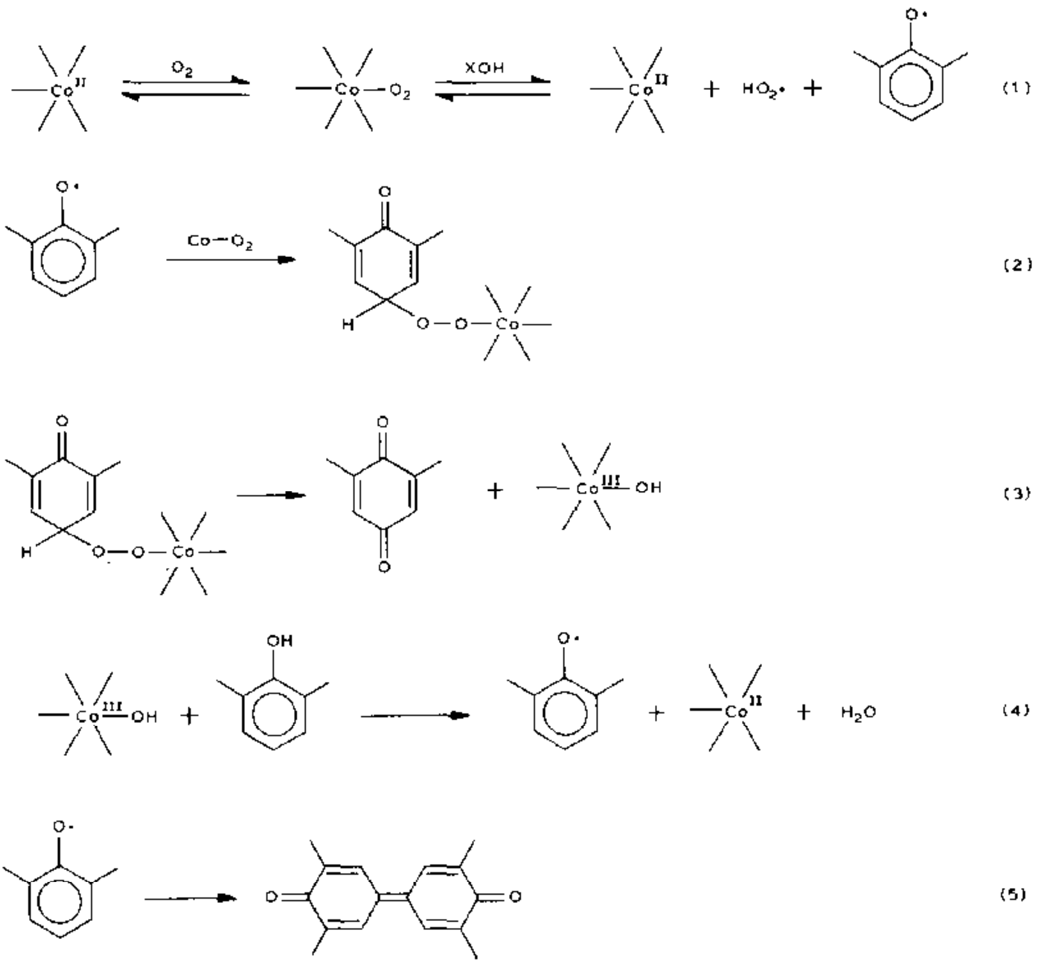
OXIDATION OF SUBSTITUTED PHENOLS

Reports on the use of cobalt Schiff-base complexes in the homogeneous oxidation of hindered phenols by O_2 were first published in 1967 [11]. Since that time, numerous studies involving both the homogeneous and heterogeneous oxidation of phenols have been carried out in order to determine what factors influence the oxidation reaction [9,12–14]. Depending upon the cobalt catalyst employed in the oxidation, a number of products may be obtained, including quinones, diphenoquinones, or polymers. We became interested in this system, since early work indicated that coordinated O_2 was involved in the reaction mechanism.

Study of the mechanistic pathway of phenol oxidations by cobalt-dioxygen complexes has been of interest for some time and part of the early work was reported by Nishinaga [12a,b]. We have expanded upon these studies using the pentadentate cobalt(II) Schiff-base–dioxygen complex [bis(salicylidene-γ-iminopropyl)methylamine]cobalt(II)–O_2, CoSMDPT–O_2. Reactions involving CoSMDPT and a series of substituted phenols were studied [15] and kinetic data, in addition to EPR results, indicated a mechanism in which an organic hydroperoxide was an intermediate. As shown in Scheme I, the mechanism involves firstly hydrogen bonding to the metal bound O_2 followed by hydrogen atom abstraction from the phenol by the cobalt(II)–dioxygen complex.

Step 2, which involves free radical addition of the phenoxy radical to the cobalt–dioxygen complex, has been designated as the rate-controlling step. Support for this step was based, in part, on EPR results which indicated that the cobalt–peroxyquinone intermediate reversibly dissociated to form the phenoxy radical and the cobalt–dioxygen complex. We also noted that at low cobalt concentrations, diphenoquinone formation increased via a competitive coupling of phenoxy radicals. Subsequent decomposition of the cobalt–peroxyquinone complex yields the corresponding quinone and cobalt(III)–OH complex, and the last step illustrates the regeneration of the catalytic species and formation of another phenoxy radical. The reaction can be stopped by the addition of competing hydrogen bonding compounds such as trifluoroethanol or benzoic acid. This supports our contention regarding the rate controlling step, because hydrogen bonding would inhibit the radical coupling reaction in step 2.

The mechanism of this reaction suggests two important changes in the reactivity of O_2 as a result of coordination to cobalt(II): (1) enhanced basicity so that hydrogen bonding with phenol occurs, and (2) enhanced radical reactivity of the unpaired electron localized on O_2. The latter change is reflected in the reactivity of cobalt–O_2 with the phenoxy radical. The phenoxy radical reacts with cobalt–O_2, but not with O_2 because at low



SCHEME I

cobalt–O_2 concentrations, the radical couples to form diphenoquinone rather than react with O_2.

Studies probing the hydrogen bonding interaction between the substrate and bound dioxygen were carried out [16]. Infrared studies using 2,2,2-trifluoroethanol and CoSMDPT–O_2 clearly demonstrated hydrogen bonding of the alcohol to bound O_2. The equilibrium constant and negative enthalpy for the formation of the dioxygen adduct were increased by this interaction. These findings regarding metal–O_2 basicity led to an investigation of the role of hydrogen bonding in the formation of dioxygen adducts of hemoproteins and model compounds.

The increase in dioxygen affinity of iron(II) and cobalt(II) picket fence porphyrins compared to other less hindered porphyrin systems has been of interest for some time. Based upon our work involving hydrogen bonding in the CoSMDPT–O_2 complex, hydrogen bonding interactions from the surrounding environment seemed a likely explanation. This was confirmed following re-examination of the X-ray crystal structure of picket fence porphyrins [17]. It was found that hydrogen bonding between the N–H protons of the pivalamide side chain and the terminal oxygen of bound dioxygen does exist. On this basis, similar analogies may be drawn in the case of hemoglobin, where hydrogen bonding of a distal imidazole to bound dioxygen could account for the enrichment in O_2 affinity observed for hemoglobins when compared to unhindered porphyrins. Subsequent studies by other workers have confirmed this hypothesis.

Enhanced radical reactivity of a cobalt bound O_2 was investigated next and demonstrated via spin-trapping experiments [18]. EPR studies of CoSMDPT–O_2 with the spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO) indicated the formation of a spin-paired adduct. In the absence of dioxygen, no EPR signal was observed at room temperature for CoSMDPT and addition of DMPO failed to produce such a signal. However, if DMPO was added to a solution of CoSMDPT–O_2, an EPR signal attributable to the spin-paired adduct was observed both at liquid nitrogen and room temperatures. These results further substantiate our previous claims concerning enhancement of the radical reactivity of coordinated dioxygen and support attack of the phenoxy radical on cobalt–O_2 in our mechanism.

TABLE I

Bond dissociation energies

Compound	ΔH_D (kcal mol^{-1})	Estimated errors (kcal mol^{-1})
O_2–H	47	
HOO–H	90	2
ROO–H	100–112 (R = C_4H_9 to CH_3)	4
CoOO–H	?	–
C_6H_5O–H	88	–
p-$CH_3C_6H_4O$–H	87	–
di(*o*-CH_3)C_6H_3O–H	87	–
C_2H_3–H	104	2
C_2H_5–H	98	1
$CH_3\overset{OH}{\underset{H}{C}}$–H	90	2
$C_6H_5CH_2$–H	85	1
CH_3CO–H	88	2
HCO–H	88	2

The influence of the extent of electron transfer on the catalytic properties of cobalt(II) Schiff-base complexes was investigated [14]. Increased electron transfer from cobalt to dioxygen can be induced by an increase in the ligand field strength of the ligand system. Systematic variations of the N–CH_3 portion of the ligand framework of CoSMDPT, eg. to O, S, and P–CH_3, had a more pronounced effect on catalytic activity than variation of substituents on the salicylaldehyde rings. Cobalt hyperfine coupling constants indicated electron transfer into bound dioxygen paralleled the activity of the derivatized CoSMDPT catalyst in the oxidation of hindered phenols.

Using thermodynamic arguments, we can set limits on the type of substrate which can be oxidized by a mechanism involving hydrogen atom abstraction. Some relevant bond dissociation energies [19,20] are summarized in Table I. We estimate that the CoOO–H bond dissociation energy is approximately 87 kcal mol^{-1} since CoO_2 will not oxidize phenol, but will oxidize methyl substituted phenols. Considering potential errors in these numbers, CoSMDPT–O_2 will not be able to abstract a hydrogen atom from any substrate which has a bond strength greater than approximately 88 kcal mol^{-1}. These considerations led us to search for mechanisms other than hydrogen atom abstraction for cobalt catalyzed oxidations.

OXIDATION OF OLEFINS

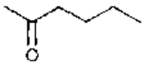
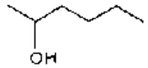
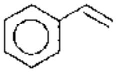
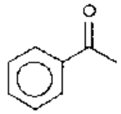
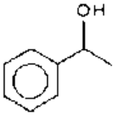
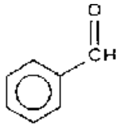
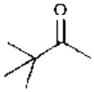
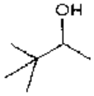
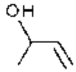
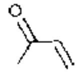
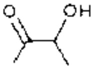
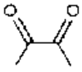
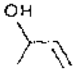
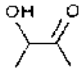
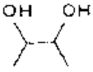
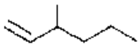
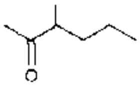
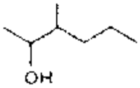
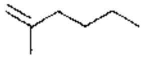
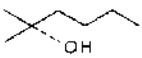
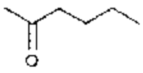
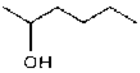
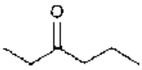
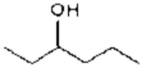
The selective, catalytic oxidation of olefins by transition metal complexes is of interest due to the desired products (glycols, dicarboxylic acids, etc.) that can be produced from these feedstocks. In general, first row transition metals give rise to autoxidation reactions, while the utilization of second and third row metals typically results in selective oxidation of the olefin [6,21–25]. In autoxidation reactions, a free radical chain mechanism is invoked which involves the formation of allylic hydroperoxides that typically decompose to several products. The metal's role is generally explained in terms of catalysis of the decomposition of the allylic hydroperoxy intermediate which initiates the free radical chain mechanism.

While there have been numerous reports on the selective catalytic oxidation of olefins by second and third row transition metals, including work on Rh(III)/Cu(II) catalysts [21,26] and on Pd(II)/Cu(II) systems [27], little work has been published concerning selective oxidation of olefins by cobalt complexes. Since enhanced radical reactivity was observed in phenol oxidations by CoSMDPT–dioxygen complexes, this system was investigated in terms of its utility in olefin oxidation catalysis.

Oxidation reactions in which CoSMDPT, a primary alcohol, and molecular oxygen were present resulted in selective oxidation of terminal olefins [10]. A series of terminal olefins was studied and in each case the only

TABLE II

Summary of the results of the CoSMDPT-catalyzed oxidation of alkenes by O_2 in ethanol

Substrate	Product(s)
	 
	   (minor)
	 
	   
	 
	 
	
	   
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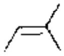
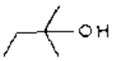
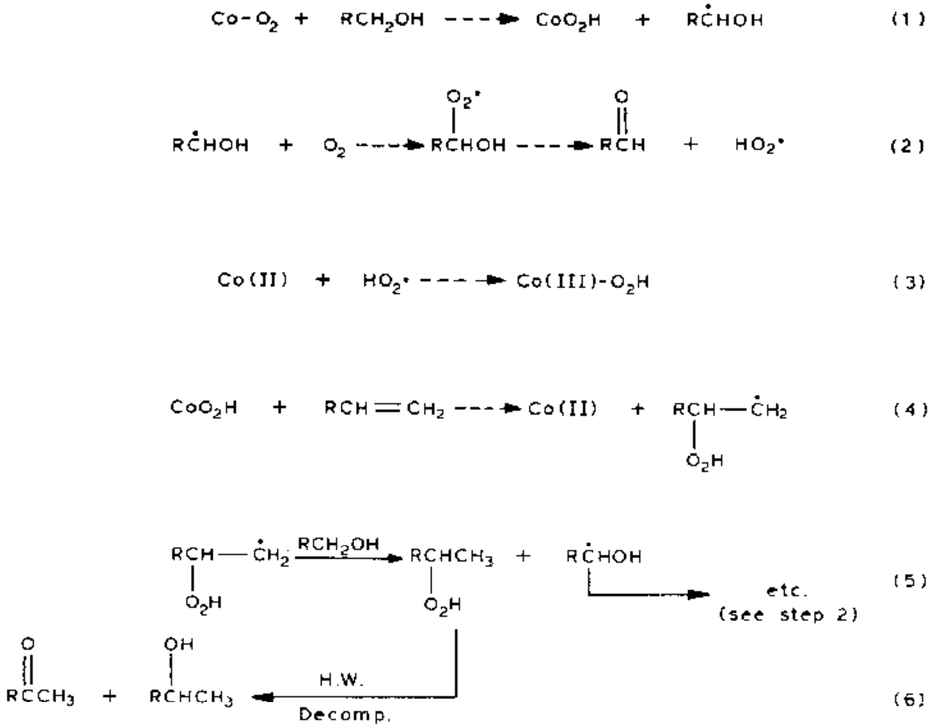
	

products observed were the corresponding 2-ketone and 2-alcohol as outlined in Table II. The studies indicated a solvent interaction in which the cobalt center converted molecular oxygen to CoOOH or H_2O_2 with concomitant oxidation of the alcohol solvent; these results were used to formulate the mechanism shown in Scheme II.

The products of the reaction are accounted for by Markovnikoff addition of CoOOH across the double bond, formation of an alkyl hydroperoxide by hydrogen atom abstraction from the solvent, and subsequent Haber–Weiss decomposition. It is significant that the alcohol solvent has inhibited the

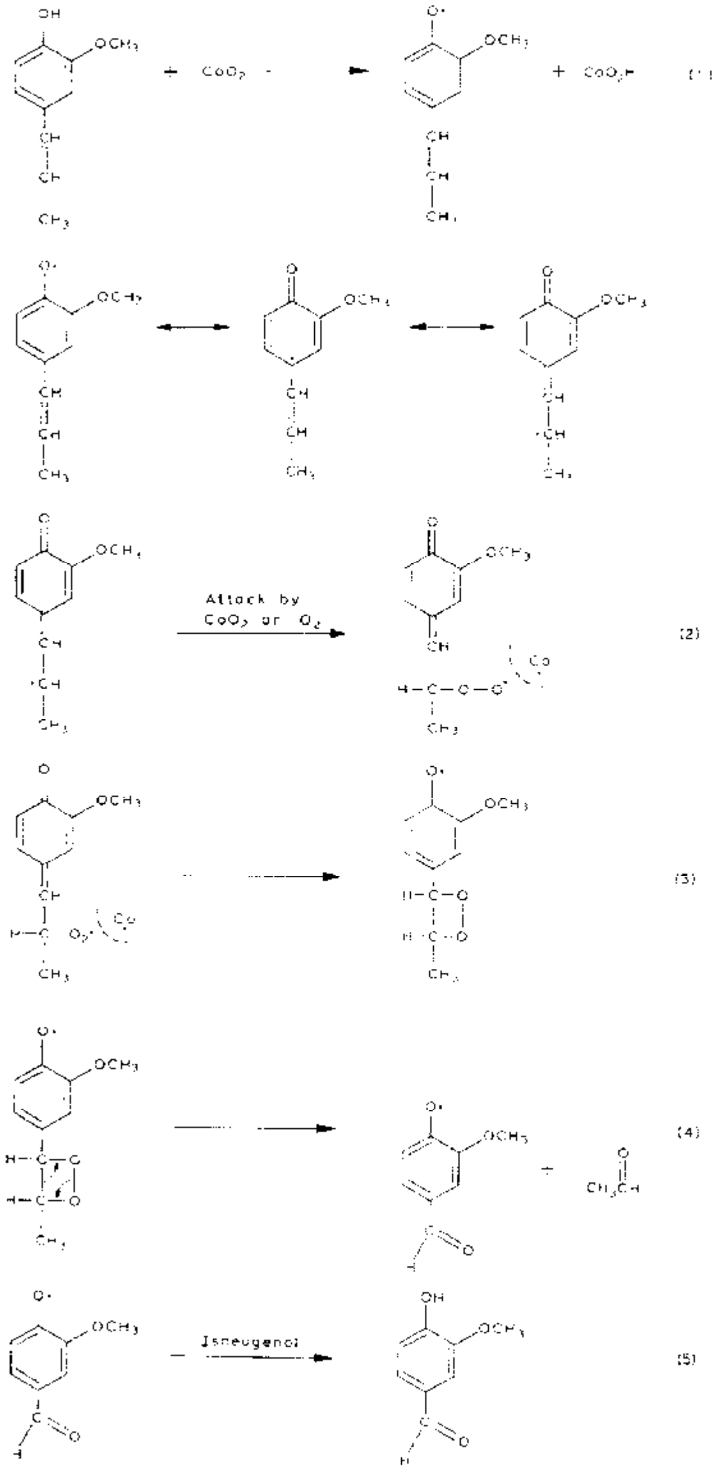


SCHEME II

autoxidation reaction as evidenced by the absence of products from an allylic hydroperoxide decomposition mechanism.

Co(II)-CATALYZED OXIDATION OF LIGNIN AND ISOEUGENOL

Additional studies [28] on CoSMDPT-catalyzed oxidations indicated the occurrence of catalytic conversion of lignin, a parasubstituted poly-phenolic polymer responsible for structural support in vegetation, to vanillin. The model compound, isoeugenol (2-methoxy-4-propenylphenol), was studied to gain insight into the basic reaction leading to formation of vanillin. Previous reports indicated isoeugenol could be oxidized to vanillin [29]; however, these were stoichiometric conversions. In the presence of CoSMDPT and molecular oxygen, catalytic oxidation of a C–C double bond resulted in bond cleavage of isoeugenol to form vanillin. The product mixture consisted of 50% vanillin and 20% of the dimerization product, dehydrodiisoeugenol. Overall, the reaction exhibited 75% selectivity; this could be varied by changes in the reaction conditions. Unlike previous olefin oxidations by CoSMDPT, solvent interactions did not play an integral role in the oxidation mechanism in this case. Initial results indicated that abstraction of a



OH
OCH₃
CoO₂
O·
CoO₂H
(1)
CH
CH
CH₃
O
Attack by
CoO₂ or O₂
Co
(2)
(3)
(4)
CH₃CH
(5)
Isoeugenol

SCHEME III

hydrogen atom from the phenolic framework to generate a reactive radical species occurred. A tentative mechanism (see Scheme III) can be offered to account for the products, in which CoO_2 reacts with the allyl substituent to form a dioxetane intermediate. Decomposition of this intermediate leads to the observed products, vanillin and acetaldehyde. The novel aspect of this chemistry involves the discovery of catalytic C–C double bond cleavage by molecular oxygen.

CONCLUSIONS

Activation of molecular oxygen by transition metal complexes for the selective catalytic oxidation of organic substrates is an area of intensive research. By employing the spin-pairing model for the binding of molecular oxygen to five-coordinate Co(II), we have attempted to explain some of the observations associated with the oxidation of substituted phenol and alkene substrates by Co(II) Schiff-base complexes. While different mechanisms are operating in these two systems, the underlying theme is the activation of molecular oxygen through coordination to the metal center to generate either the reactive intermediate or the precursor necessary for the generation of the reactive intermediate.

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