

determined by the number of localized bonds in a Kekulé structure.

Appendix 2. Ab Initio Determination of QMRE

This method was developed by Kollmar.⁴⁸ Using benzene as an example, one first performs a standard SCF calculation on benzene to obtain the SCF energy of the delocalized C₆H₆ species. In a second calculation, the pure Kekulé form is generated by replacing the delocalized π -MOs by three completely localized π -MOs extracted from a calculation of ethylene with the same C-C bond length as in benzene. The σ -MOs remain those of benzene. The three localized π -MOs are then orthonormalized by a unitary transformation which leaves the complete wave function unchanged. The SCF energy of this Kekulé form cor-

responds to a set of three localized π -bonds that interact by electron-electron and overlap repulsions. The SCF energy difference between the localized and delocalized C₆H₆ is then the requested QMRE as shown in **21** in the text.

Determination of Overlap Repulsion. The overlap repulsion can be estimated from the energy difference between two guess functions, one in which the localized ethylene π -bond orbitals are orthonormalized and one in which they are not. The energies of these two guess functions are obtained at the first cycle of the SCF calculation.

Registry No. C₃H₅^{*}, 1981-80-2; C₄H₄, 1120-53-2; **2**, 71-43-2; N₆, 7616-35-5.

Mechanistics Studies on the Cobalt(II) Schiff Base Catalyzed Oxidation of Olefins by O₂

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Abstract: The cobalt complex [bis(salicylidene- γ -iminopropyl)methylamine]cobalt(II), CoSMDPT, has been shown to catalytically oxidize olefins in the presence of dioxygen or hydrogen peroxide. When terminal olefins are oxidized, the methyl ketone and corresponding secondary alcohol are produced selectively. Internal as well as terminal olefins are oxidized. The most common pathway for the oxidation of olefins catalyzed by first-row transition metals—autoxidation—has been ruled out in this system. A Wacker-type mechanism, oxidation by peracids, and mechanisms involving the formation of peroxymetalloxy species have also been ruled out. A new mechanism for O₂ oxidations is proposed which involves oxidation of the primary alcohol solvent by CoSMDPT to produce the corresponding aldehyde and hydrogen peroxide. Reaction of hydrogen peroxide with CoSMDPT occurs to form a cobalt hydroperoxide, which can be viewed as a stabilized hydroperoxy radical which has spin paired with the d_{z²} electron of CoSMDPT. The cobalt hydroperoxide then adds to the olefin double bond, leading to formation of an alkyl hydroperoxide. Haber-Weiss decomposition of this alkyl hydroperoxide by CoSMDPT produces the observed ketone and alcohol products. Deactivation of the catalyst is due to oxidation of the ligand system of the cobalt complex as well as formation of a μ -peroxo-dicobalt complex.

In almost all cases where selective catalytic oxidation of olefins is achieved, second- or third-row transition-metal complexes are involved, whereas first-row transition-metal complexes tend to be involved in autoxidation.¹⁻²⁰ Autoxidation of olefins has been

studied extensively over the past 40 years and is now generally recognized as a free-radical chain reaction. This chain reaction is often initiated by radical impurities or trace peroxides, which react with the olefins and generally form allylic radicals. The allylic hydroperoxide is formed and is decomposed to give products such as allylic ketones, allylic alcohols, epoxides, aldehydes, acids, and oligomers. Catalysts in autoxidation reactions are generally involved in either initiation of the chain reaction or in decomposition of the hydroperoxide intermediate. Because radical chain processes are involved, a mixture of products is often obtained.

Other reactions have been reported where oxidation of olefins occurs with remarkable selectivity, but second- or third-row transition-metal complexes are involved. These include Wacker-type processes, in which water is activated to transfer oxygen to the substrate,⁷⁻¹¹ and the oxidation of olefins by metal-nitro complexes,¹²⁻¹⁶ which involves oxygen atom transfer from bound NO₂. Mimoun and others have also reported the selective oxidation of terminal olefins by rhodium complexes to form methyl

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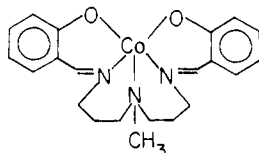


Figure 1. The structure of CoSMDPT.

ketones.¹⁷⁻¹⁹ The RhCl₃-catalyzed oxidation of terminal olefins has been proposed to proceed via addition of a rhodium hydroperoxide to the terminal olefin.²⁰

We have found that olefins are catalytically oxidized in the presence of dioxygen and [bis(salicylidene- γ -iminopropyl)-methylamine]cobalt(II), abbreviated CoSMDPT (Figure 1), when a primary alcohol solvent is employed. When terminal olefins are used, the methyl ketone and corresponding secondary alcohol are selectively produced. The reaction is unique in that the olefinic carbon is oxygenated, and none of the products from the auto-oxidation of the allylic carbon are detected. We report here results from the investigation of the catalytic oxidation of olefins by CoSMDPT.

Experimental Section

CoSMDPT was prepared as previously described.²¹ The yield obtained was 50–60%. Absolute ethanol was stored over 3Å molecular sieves and used without further purification. Anhydrous isopropanol, methanol, 1-propanol, *n*-butyl alcohol, *tert*-butyl alcohol, and benzyl alcohol were stored over 4Å molecular sieves and used without further purification. 1-Hexene (97%, Aldrich) was refluxed over calcium hydride under nitrogen or argon prior to fractional distillation. Distilled 1-hexene was stored over 4Å molecular sieves. Immediately prior to use it was passed through an alumina column to remove trace peroxides. 1-Hexene (99%, Aldrich) was passed through alumina before using. Other substrates (2-methyl-1-hexene, 3-methyl-1-hexene, 2-hexene, *trans*-3-hexene, 2-methyl-2-butene, and 3,3-dimethyl-1-butene) were obtained from Aldrich and used without further purification. Butadiene was purchased from Matheson. Hydrogen peroxide (30%, Fisher), *tert*-butylhydroperoxide (70%, Aldrich), and peracetic acid (40%, FMC Corp.) were used as received. Rhodium(III) chloride trihydrate and dichlorobis(benzonitrile)palladium(II) were purchased from Alfa, silver nitrate (ACS) was purchased from Anachemia, *N*-phenyl-1-naphthylamine was obtained from Matheson, Coleman, and Bell, and AIBN was obtained from Eastman.

Authentic samples of alcohols, ketones, and aldehydes were purchased when available for comparison to oxidation products. Following the reported procedure,²² 2-methyl-1-hexanol was obtained by hydroboration of 2-methyl-1-hexene. Dichromate oxidation of 3-methyl-1-hexene was used to synthesize 3-methyl-2-hexanone.²³

Elemental analyses were performed by the microanalytical lab at the University of Illinois, by the microanalysis service of the University of Florida, or by Galbraith. Typical analysis of CoSMDPT showed the following: % C = 61.58 (61.46), % H = 6.12 (6.14), % N = 10.34 (10.24), and % Co = 14.34 (14.36). Analysis of the spent catalyst showed the following: % C = 56.49, % H = 6.41, % N = 7.29, % Co = 10.44, and % O = 19.22.

GC spectra were recorded on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector, by using a stainless steel column (8 ft, 1/8 in.) packed with 5% diethylene glycol adipate on Chromosorb P or on a Varian Model 940 gas chromatograph with flame ionization detector, by using a copper column (1 m, 1/16 in. i.d.) packed with diethylene glycol adipate supported on Chromosorb P.

Oxidations were carried out in 250-mL Parr pressure bottles (Thomas Scientific) equipped with brass or stainless steel Swagelok pressure heads and placed inside a steel mesh explosion shield. *Mixtures of O₂ and organic vapors are potentially explosive, and care should be taken to protect personnel.* Samples were removed by using a 2.5-mL gas tight syringe connected to a syringe stopcock (available from Aldrich or Becton, Dickinson and Co.) and a 12-in., 20 gauge needle. For a typical oxidation 50 mL of solvent, 5 mL of substrate, 0.28 mL of 2-octanone (internal GC standard), and a plastic cap containing 0.3 g of the catalyst CoSMDPT were added to a 250-mL pressure bottle containing a mag-

netic stir bar. The bottle was attached to the pressure head and placed in a constant temperature oil bath at 60 °C. The system was then purged several times with oxygen before charging to the desired pressure. Stirring was begun to capsize the catalyst-containing cap and initiate the oxidation. The progress of the reaction was monitored by withdrawing samples (~0.2 mL) of the oxidation solution via the silicone septum and injecting an aliquot (0.4–0.5 μ L) into the GC for analysis. The amounts of products present were calculated from calibration curves, by using 2-octanone as the standard.

For the oxidations with hydrogen peroxide, peracetic acid, or KO₂/18-crown-6, the catalyst was weighed into a round-bottom flask which was then purged with argon via a sleeve stopper. Argon-purged solvent was added, the solution was purged with argon, 2-octanone was added, and the solution was purged again. The flask was heated to the desired temperature in a constant temperature oil bath, and excess pressure was vented. 1-Hexene, which had been passed through a column of alumina and purged with argon, was added, followed by addition of the oxidant. Samples were removed and injected into the GC for analysis.

A Bruker ER 200D-SRC spectrometer or a Varian Model E-9 spectrometer equipped with a Hewlett-Packard frequency counter was used to obtain EPR spectra. UV-vis-near IR spectra were obtained from a Perkin-Elmer 330 or Cary 14 spectrophotometer. NMR spectra were obtained on a Varian EM-390 (90 MHz) or EM-360L (60 MHz) spectrometer. IR spectra were obtained from a Perkin-Elmer 283B infrared spectrometer or a Nicolet 7000 series Fourier Transform IR.

Results and Discussion

Scope of the Reaction. When 1-hexene is oxidized by O₂ (up to 90 psi) in the presence of CoSMDPT, 2-hexanone and 2-hexanol are formed. Products arising from cleavage of the double bond (e.g., valeraldehyde), other ketones (e.g., 3-hexanone), other alcohols (e.g., 1-hexanol), and the epoxide were not detected. Up to 19 turnovers (based on CoSMDPT) have been observed, but no attempt to optimize this was made.

Styrene is also oxidized by this catalyst. Acetophenone is the major product, but some 2-phenylethanol as well as a small amount of benzaldehyde was formed. Neither styrene oxide nor benzyl alcohol was detected. Oxidation of other terminal olefins such as 3,3-dimethyl-1-butene, 3-methyl-1-hexene, and 2-methyl-1-hexene also led to formation of the methyl ketone and the corresponding alcohol. Oxidation of butadiene led to formation of 3-buten-2-ol, methyl vinyl ketone, acetylmethylcarbinol, and 2,3-butanedione but not 2,3-butanediol. However, when 3-buten-2-ol was oxidized, both acetylmethylcarbinol and 2,3-butanediol were produced.

Internal as well as terminal olefins are oxidized by this catalyst. Both 2-hexene and 3-hexene are oxidized to form 2- and 3-hexanone and 2- and 3-hexanol. In both cases formation of the 3-products were favored (only slightly in the case of 2-hexene), but for 3-hexene the ratio of 3-hexanone to 2-hexanone was almost 3:1. Oxidation of 2-methyl-2-butene led to formation of *tert*-amylalcohol. These results are summarized in Table I.

Most of the products observed from the CoSMDPT-catalyzed oxidation of olefins can be explained by the addition of hydrogen peroxide across the double bond and subsequent decomposition of the intermediate. Markovnikoff addition takes place, so terminal alcohols and aldehydes are not produced. Even in the oxidation of 2-methyl-2-butene neither of the anti-Markovnikoff products, 3-methyl-2-butanone and 3-methyl-2-butanol, are observed.

Catalyst Deactivation. Organic acids strongly inhibit decomposition of hydroperoxides by homogeneous catalysts, and low molecular weight acids have the strongest effect.²⁴ In our system, peracetic acid formed from solvent oxidation was considered responsible for deactivation of the catalyst. It was found that addition of peracetic acid to a standard reaction mixture (CoSMDPT, 1-hexene in ethanol under O₂) prevents catalysis. Addition of sodium carbonate (50 equiv) to the oxidation mixture at the beginning of the reaction extends the lifetime of the catalyst without significantly changing the rate (19 turnovers compared to 12 without Na₂CO₃ are observed). The lifetime of the catalyst is also extended when the oxygen pressure is reduced. For O₂

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Table I. Summary of the Results of the CoSMDPT-Catalyzed Oxidation of Alkenes by O₂ in Ethanol

substrate	product(s)		

Table II

% ethanol ^a	turnovers, 24 h	2-hexanone/2-hexanol
100	12.1	1.1
90	10.2	1.1
70	8.6	1.1
50	6.8	1.2
30	5.1	1.5
16	3.3	1.9
10	2.7	2.0
8	2.8	2.2
4	1.3	2.6
2	0.94	2.7

^a Remainder is isopropyl alcohol.

pressures of 80, 30, and 20 psi the number of turnovers found are 12, 14, and 17, respectively. Since the rate of formation of peracetic acid from solvent oxidation would depend on the pressure of O₂, the pressure dependence and the above observations implicate peracetic acid as a possible contributor to catalyst deactivation.

The spent catalyst was recovered by removing the solvent from solutions of the reaction mixture after oxidation had ceased. Elemental analysis of this spent catalyst indicated a slight decrease in the carbon and nitrogen content and a large increase in the oxygen content with respect to the starting CoSMDPT. EPR and magnetic susceptibility measurements indicate that the spent catalyst is diamagnetic.

IR spectra (KBr pellets) indicate that the peaks due to the phenolic group of CoSMDPT are absent in the spectrum of the spent catalyst. The imine C=N stretch (1630 cm⁻¹) and amine C-N stretch (1050 cm⁻¹) are not significantly changed. New peaks appear at 800 cm⁻¹, 620 cm⁻¹, between 1540 and 1590 cm⁻¹, and 3100–3300 cm⁻¹ (br). Loss of the phenyl rings is supported by the NMR spectrum of the spent catalyst, since no peaks are seen between 6 and 8 ppm. The IR spectrum also suggests that carboxylic acid groups may be present in the spent catalyst.

In addition to deactivation by destruction of the ligand system, irreversible formation of a μ -peroxy dicobalt complex may occur to halt the oxidation. Typically, μ -peroxy complexes of this type have absorption bands between 950 and 800 cm⁻¹, which are assigned to the O-O stretching vibration.²⁷ The IR spectrum

of the spent catalyst has a band at 800 cm⁻¹.

Mechanistic Considerations. Since first-row transition-metal complexes commonly catalyze autoxidation reactions, this mechanism is first considered for the CoSMDPT-catalyzed oxidation of olefins. Abstraction of the allylic proton of an olefin generally takes place in autoxidation since this leads to the most stable free-radical intermediate. Radical pairing with oxygen then takes place at this site, and the products observed are those that result from subsequent reaction of the resulting alkyl hydroperoxide intermediate. The allylic alcohol, ketone, and/or hydroperoxide are obtained instead of products where a carbon involved in the double bond has been oxygenated. The CoSMDPT-catalyzed oxidation is unusual because allylic products are not formed. Instead, only ketones and alcohols from oxygenation of the olefinic carbon² are produced. Both the products and the specificity suggest that a free radical chain reaction is not operating in this system. The observation that cyclohexene (a commonly used substrate in autoxidation studies) is not oxidized by CoSMDPT, but styrene and CH₂=CH(*t*-Bu), which have no allylic hydrogens, are, is also inconsistent with an autoxidation pathway. Furthermore, Co(acac)₃, which is a good autoxidation catalyst, does not catalyze the oxidation of 1-hexene under the conditions employed. The 1-hexene oxidation is found to be first order in 1-hexene and CoSMDPT and zero order in O₂ between 1–6 atm of O₂.

If the role of the catalyst is merely to initiate the chain reaction by forming radicals from the solvent or substrate, then replacement of the catalyst with an initiator should lead to the same product formation. In the system under study, when azobis(isobutyronitrile) (AIBN) was added instead of CoSMDPT, oxidation of 1-hexene did not occur. Addition of AIBN in addition to CoSMDPT led to essentially the same product distribution. The induction period was eliminated, but the maximum rate of the reaction was not increased, and the system did not remain active as long as in the absence of AIBN. Although addition of AIBN with the catalyst did effect the reaction, the changes are not those predicted to occur for a free-radical chain reaction.

Addition of a free-radical trap to the system should lead to complete inhibition of the reaction or lengthening of the induction period if a free radical chain process is occurring. Since the more common phenol traps were oxidized by CoSMDPT, *N*-phenyl-1-naphthylamine was chosen as a radical trap. Addition of 1 or 5 equiv of this trap did lead to nearly complete inhibition of oxidation. However, when ³/₁₀ of an equiv of trap was added, the rate of the reaction was reduced by 60%. Oxidation of 1-hexene did take place, with only a small reduction in the total number of turnovers (10.2 in 24 h, as compared to 12.1 without the trap). Since *N*-phenyl-1-naphthylamine can react with two radicals per trap, this result indicates that a radical chain process is not taking place, although the involvement of radicals is not excluded.

A Wacker-type mechanism in which water is the actual oxygen-containing reagent, although the net reaction involves O₂ as the oxidant, will be considered next. A first-order dependence on [H₂O] is found for Wacker processes. Addition of up to 8 equiv of water to the CoSMDPT-catalyzed oxidation of 1-hexene has little effect on the reaction rate. Addition of 76 equiv of water slows down the reaction and decreases the number of turnovers slightly (to 10.5). When water is added to a reaction which is carried out under argon instead of oxygen, only trace amounts of products are obtained, probably due to a small amount of O₂ in the system. Finally, when a water scavenger, 2,2-dimethoxypropane, is added to an oxidation carried out under oxygen, there is little effect on the rate or final turnover number. These results rule out a Wacker-type mechanism.

One of the unusual aspects of this system is the solvent requirement. In ethanol, under 80 psi of oxygen and at 60 °C, 12

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turnovers are obtained for the oxidation of 1-hexene after 24 h. In methanol, 1-propanol, or *n*-butyl alcohol as solvents fewer than three turnovers are seen in 24 h, while in benzyl alcohol ten turnovers are seen. Oxidation of 1-hexene does not occur with this catalyst in isopropanol, *tert*-butyl alcohol, THF, benzene, or in the neat substrate.

The requirement of a primary alcohol as the solvent led us to consider a mechanism involving a peracid.^{28,29} To test this possibility peracetic acid was employed as the oxidant in an attempted 1-hexene oxidation. The olefin was not oxidized in either the presence or absence of CoSMDPT. Acetaldehyde (5 equiv) was added to the reaction solution at the beginning of an oxidation with O₂ to test the effect of in situ generated peracetic acid. The induction period was decreased, the maximum rate attained was decreased, and the reaction began to slow down earlier. Therefore, participation of peracids in the oxidation may be ruled out, although these observations support our contention that they may be involved in deactivation of the catalyst.

In several studies involving the oxidation of olefins, formation of a peroxymetallocycle has been proposed,³⁰⁻³⁴ and this possibility will be considered next. For such an intermediate to form, two coordination sites on the metal must be vacant to bind the olefin and dioxygen to the catalyst and to form bonds to carbon and oxygen in the metalocycle. Since CoSMDPT has only one vacant coordination site (which is subsequently occupied by O₂), and this site is a poor Lewis acid, coordination of the olefin (and surely the internal and hindered olefins studied) will not occur, and a peroxymetallocycle is considered unlikely.

In 1979 it was reported that peroxide could be formed from a cobalt-O₂ complex in the presence of acids.³⁵ Much earlier it was observed that hydrogen peroxide arises from the oxidation of alcohols.³⁶ The possibility that H₂O₂ is formed in the CoSMDPT system by either of these processes led to our replacement of O₂ by H₂O₂ in this system. In the presence of CoSMDPT, 1-hexene oxidation did occur, with H₂O₂ to produce 2-hexanone and 2-hexanol although the relative amounts are not the same as in the O₂ case. When 12 mol-equiv of H₂O₂ per cobalt were added to an oxidation mixture in ethanol, and the reaction was carried out under argon, only 0.5 turnovers were observed, and 80% of this occurred in the first 130 min.³⁷ Decreasing the H₂O₂/CoSMDPT ratio to 6 led to 0.9 turnovers (to 0.9), and further reduction to ~1 resulted in 2.3 turnovers. Since the steady-state amount of H₂O₂ in a O₂ oxidation would be quite low, we decided to add hydrogen peroxide slowly as the reaction proceeded. Adding 50 equiv of hydrogen peroxide over a 6¹/₂-h period resulted in 3.1 turnovers.

Although oxidation of 1-hexene with hydrogen peroxide in the presence of CoSMDPT leads to the same products as oxidation under oxygen, the induction period seen with oxygen is nearly eliminated with H₂O₂ (Figure 2). This suggests that during the induction period hydrogen peroxide or a cobalt hydroperoxide intermediate is formed which is subsequently involved in the oxidation. The similarity of the maximum oxidation rates in the H₂O₂ and O₂ systems indicates that the rate-determining step in the olefin oxidation occurs after formation of hydrogen peroxide or the hydroperoxide in the O₂ system.

The addition of acid to the CoSMDPT system led to complete inhibition of the oxidation. Therefore, it is unlikely that hydrogen

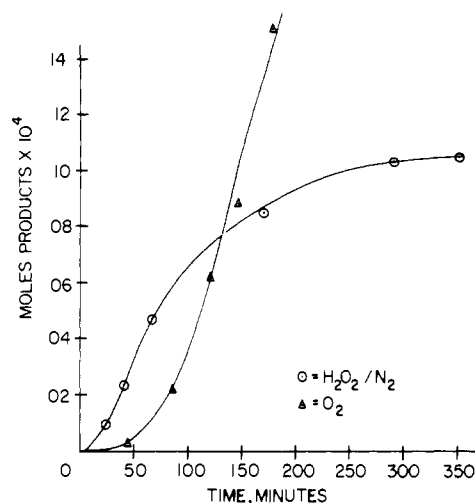
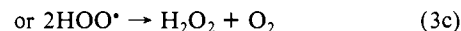
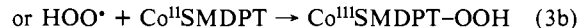
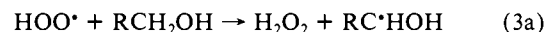


Figure 2. Oxidation of 1-hexene by CoSMDPT in ethanol. Δ indicates the reaction was carried out under 80 psi O₂, \circ indicates that the reaction was carried out under a nitrogen atmosphere with 1 mL (0.005 mol) of hydrogen peroxide solution added over 350 min in 8 additions to 10 mL of ethanol containing 0.0606 g (1.45×10^{-4} mol) of CoSMDPT and 1 mL (0.008 mol) of 1-hexene. Temperature = 60 °C. The 1-hexene and CoSMDPT concentrations were the same for both reactions.

peroxide is produced by addition of H⁺ to [CoSMDPT]₂O₂, as in the reaction described by Pignatello and Jensen.³⁵ Instead, hydrogen peroxide probably arises from autooxidation of the primary alcohol solvent. The mechanism proposed for this and shown below is analogous to that previously reported for the oxidation of isopropanol.³⁶



Alternatively, the radical product in step 2 can abstract a hydrogen atom to form RCHOH(O₂H) which is the perhemiacetal of H₂O₂ and the aldehyde.

We observe acetaldehyde formation during the CoSMDPT-catalyzed oxidation of olefins in ethanol, and other aldehydes are formed when the reaction is conducted in other primary alcohols (e.g., benzaldehyde from benzyl alcohol). Aldehyde production begins during the induction period of the oxidation, and even in the absence of an olefin these aldehydes are still produced. In the absence of both olefin and CoSMDPT, aldehyde production is not observed, indicating that the cobalt catalyst is involved in the alcohol oxidation. Its role may be to initiate the oxidation via step 1 above where In* would be CoSMDPT-O₂. The resulting HO₂ complex can participate in subsequent olefin oxidation, vide infra, or would decompose to form HO₂* and CoSMDPT. The HO₂* would disproportionate into H₂O₂ and O₂ at diffusion-controlled rates. If superoxide (as KO₂) is used in place of O₂ or H₂O₂, oxidation of 1-hexene does not take place. Olefin oxidation does not occur in alcohols whose oxidation is not catalyzed by CoSMDPT; for example, this complex does not catalyze the oxidation of isopropanol to acetone, and CoSMDPT-catalyzed olefin oxidation does not occur in this solvent. Quantification of acetaldehyde formed in ethanol solvent is difficult. However, the oxidation can be carried out in benzyl alcohol, and benzaldehyde production can be monitored. Its rate of formation is seen to parallel the formation of the olefin oxidation product (see Figure 3). We conclude that the coproduct of solvent oxidation, hydrogen peroxide, is involved in the olefin oxidation, and solvent oxidation is an integral part of the reaction.

The proposal that hydrogen peroxide is attaining a steady-state concentration during the induction period is consistent with the

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(37) These reactions involving hydrogen peroxide were carried out at 55 °C.

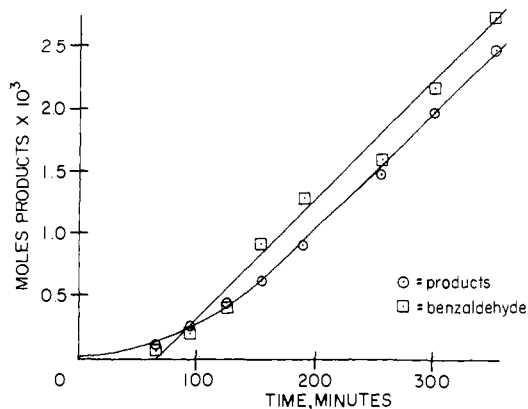


Figure 3. Moles of benzaldehyde and 2-hexanone plus 2-hexanol (formed during the oxidation of 1-hexene (0.040 mol) with CoSMDPT (7.32×10^{-4} mole) in 25 mL of benzyl alcohol and 25 mL isopropanol) vs. time. Temperature = 60 °C, initial pressure = 80 psi O_2 .

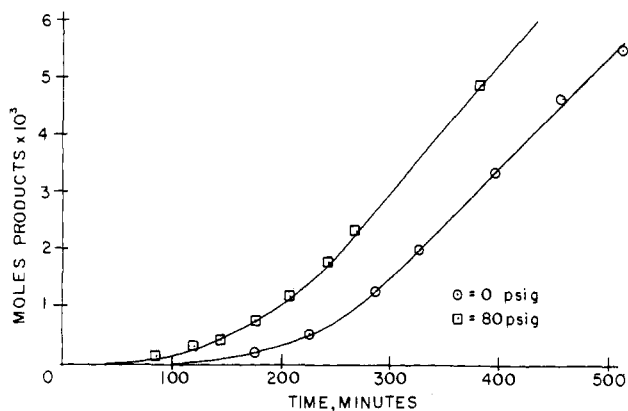


Figure 4. Oxidation of 1-hexene (0.040 mol) by CoSMDPT (7.31×10^{-4} mol) in 50 mL of ethanol at 60 °C as a function of O_2 pressure. \square indicates an oxygen pressure of 80 psig; \circ indicates an oxygen pressure of 0 psig (1 atm) above the reaction mixture.

observation that the length of the induction period is decreased as the oxygen pressure is increased, although the maximum rate of the reaction is independent of the pressure (see Figure 4). High pressure enhances the rate of step 2. The absence of an induction period when AIBN is added is attributed to its function as an initiator in step 1, increasing the rate of hydrogen peroxide formation. Addition of acetaldehyde to the reaction mixture also leads to a shorter induction period, because it is readily oxidized to form radicals which can initiate step 1.

In the absence of CoSMDPT reaction of the olefin substrate with hydrogen peroxide does not take place. Therefore, either the substrate or H_2O_2 is activated by the catalyst. Addition of dichlorobis(benzonitrile)palladium(II) leads to a drastic reduction in the amount of products formed, to less than $1/2$ a turnover. Since this compound is known to activate olefins,³⁸ this result coupled with the poor Lewis acidity of CoSMDPT and the bulky olefins oxidized by this system suggests that the role of CoSMDPT is not to activate the olefins.

Spectral studies indicate that CoSMDPT is altered during the induction period. EPR spectra recorded during this period show that the intensity of the signal (which arises from the O_2 adduct of CoSMDPT) decreases slightly, and there is a pronounced change in the visible absorption spectrum, as seen in Figure 5a. Similar changes in the visible spectrum also take place when hydrogen peroxide is added to a reaction solution under argon, as shown in Figure 5b. The EPR and visible spectral changes indicate that CoSMDPT reacts with hydrogen peroxide to produce the catalyst for double bond oxidation. A one-electron oxidation

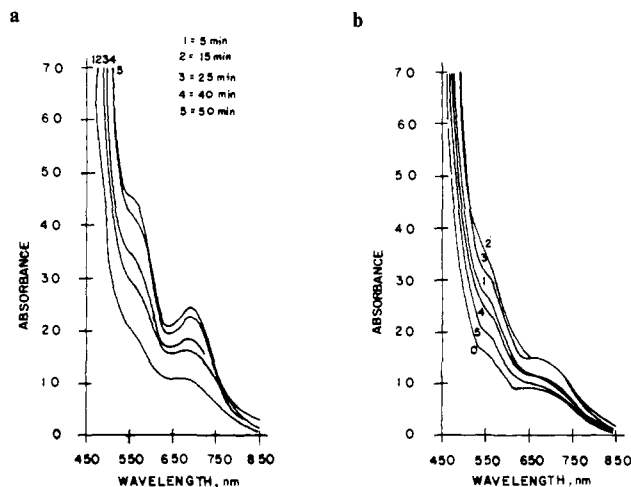


Figure 5. (a) Visible spectra recorded during the induction period of 1-hexene (0.040 mol) oxidation with CoSMDPT (7.31×10^{-4} mol) in 50 mL of ethanol. Temperature = 60 °C, pressure = 80 psi O_2 . Aliquots of 1 mL were diluted to 5 mL with ethanol before recording the spectra. (b) Visible spectra recorded during the oxidation of 1-hexene (0.040 mol) with CoSMDPT (7.31×10^{-4} mol) and H_2O_2 in 50 mL of ethanol. Temperature = 60 °C. Aliquots of 1 mL were diluted to 5 mL with ethanol before recording the spectra. Spectrum 1 was recorded just after addition of 0.1 mL (5×10^{-4} mol) of H_2O_2 ; spectra 2, 3, 4, and 5 were recorded 17, 40, 55, and 75 min after this addition.

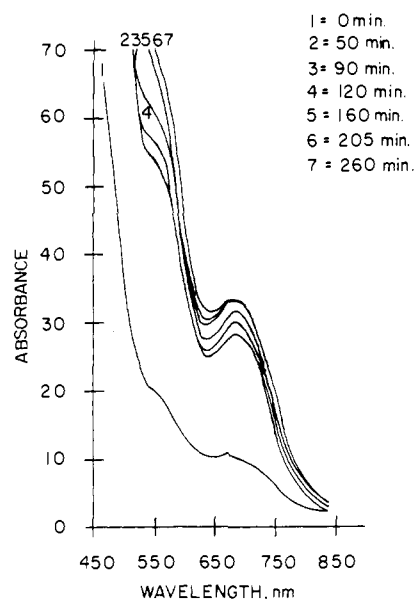
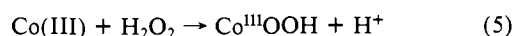
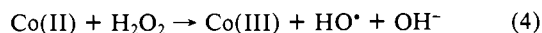


Figure 6. Visible spectra recorded during the oxidation of 1-hexene (0.040 mol) with CoSMDPT (7.32×10^{-4} mol) in 50 mL of ethanol. Temperature = 60 °C, pressure = 80 psi O_2 . Aliquots of 1 mL were diluted to 5 mL with ethanol before recording the spectra. Spectra 2, 3, and 4 were recorded during the induction period, while spectra 5, 6, and 7 were recorded with the reaction in progress at its maximum rate.

of cobalt(II) by an alkyl hydroperoxide has been reported,³⁹ and we write by analogy for H_2O_2



The hydroxyl radical can act as In^{\cdot} in eq 1. Formation of a cobalt hydroperoxide is consistent with the EPR signal diminishing during the induction period and as the reaction proceeds since this complex is not paramagnetic. A Co-OOH intermediate was postulated in the oxidation of triphenylphosphine catalyzed by

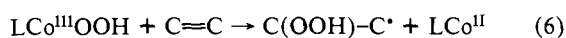
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CoSalen in ethanol.⁴⁰ As in the CoSMDPT system, the CoSalen-catalyzed oxidation of substrate (triphenylphosphine) did not occur in isopropanol.

A steady-state concentration of the cobalt hydroperoxide builds up during the induction period, and we attribute the initial change in the visible spectra during an oxidation (Figure 6) to this. After the induction period there is little change in the visible spectrum (spectra 5, 6, and 7) as long as olefin oxidation continues. In the hydrogen peroxide system, once olefin oxidation ceases, the visible spectrum again changes to nearly that of the starting CoSMDPT (Figure 5b). However, addition of hydrogen peroxide will lead to restored catalytic activity and a return of the visible spectrum to that of the active catalytic species. This cycle can be repeated for several additions of hydrogen peroxide. The reaction to form CoSMDPT-OOH occurs more quickly than production of H₂O₂ since use of hydrogen peroxide in place of O₂ drastically reduces the induction period. Systems with AIBN or aldehyde added, in which hydrogen peroxide is produced more efficiently, would therefore be expected to have shorter induction periods. Addition of metal ions, such as Ag⁺, Cu⁺², and Rh⁺³ which can catalyze the reduction of O₂ to H₂O₂ by alcohols, leads to elimination of the induction period, although the maximum rate of the reaction is not altered. Unfortunately, these metals may also catalyze the autoxidation of acetaldehyde to form peracetic acid and lead to the demise of the catalyst.

The unique aspect of this reaction involves the formation of alcohols and ketones that arise from a Haber-Weiss decomposition of a hydroperoxide substituted at the alkene carbon. At this point we can only speculate about how such a hydroperoxide could form. Following a suggestion by Kochi⁴¹ for the addition of Co-OO-(*t*-Bu) to an alkene, we write



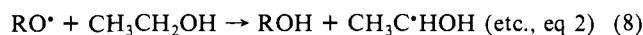
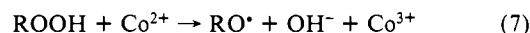
The resulting radical abstracts a hydrogen atom from the solvent to form the alkyl hydroperoxide (and initiates oxidation of the solvent). Since HO₂[·] disproportionates into H₂O₂ and O₂ very quickly, one can view LCo^{III}OOH as a stabilized hydroperoxy radical which has undergone a spin pairing²¹ interaction with the d_{z²} electron of Co^{II}SMDPT. The hydroperoxyl radical is transferred to the alkene carbon and cobalt(II) reforms as shown in eq 6.

Mimoun has proposed⁴² an alternate mechanism for our reaction. A hydrido-cobalt species forms from the reaction of CoSMDPT with alcohol, which adds across a double bond to form a cobalt alkyl. Insertion of O₂ into the cobalt-carbon bond forms a cobalt alkyl peroxide. A similar mechanism has been proposed⁴³ for the cobalt-catalyzed oxidation of styrene employing borohydride. In our system the reaction occurs not only with O₂ but also with H₂O₂. In the latter case, this hydrido species would have to form when H₂O₂ is added to CoSMDPT, and the O₂ from H₂O₂ decomposition would have to insert. These reactions are without precedent and cause us to favor CoOOH addition to the double bond.

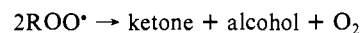
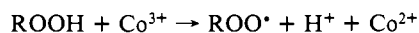
The next step in the catalytic reaction involves the well-known Haber-Weiss process for the conversion of alkyl hydroperoxides into ketone and alcohol.⁴⁴ To support the proposal that CoSMDPT behaves like other cobalt complexes^{39,46,47} and can

catalyze this decomposition, we have shown that 2-hydroperoxyhexane is decomposed by a solution of CoSMDPT in ethanol, to form 2-hexanol and 2-hexanone.⁴⁵ Thus, hydroperoxides formed as intermediates in the oxidation of olefins with CoSMDPT probably are converted by CoSMDPT to ketone and alcohol products. The CoSMDPT-catalyzed decomposition of 2-hydroperoxyhexane occurs faster than catalyzed oxidation of olefins suggesting that the rate-determining step of the reaction occurs before decomposition of the alkyl hydroperoxide.

The mechanism of decomposition of the hydroperoxide intermediate is not well understood but, according to the Haber-Weiss proposal, involves the metal catalyst cycling between two different oxidation states.⁴⁴ Cobalt(II) would be involved in formation of the alcohol via



while cobalt(III) would be involved in ketone formation via



Cobalt(III) could also be reconverted to cobalt(II) via



This alkylperoxy complex in step 9 has been shown to decompose³⁹ into ketone and alcohol, regenerating cobalt(II).

In summary, the mechanism proposed involves (1) binding of O₂ to CoSMDPT,⁴⁸ (2) cobalt-catalyzed oxidation of the primary alcohol solvent to produce the corresponding aldehyde and hydrogen peroxide, (3) formation of a cobalt-hydroperoxy species by reaction of hydrogen peroxide produced in situ with Co(III)SMDPT, followed by (4) addition of this hydroperoxide to the olefin to yield an alkylhydroperoxide, and (5) decomposition of the alkylhydroperoxide to ketone and alcohol by CoSMDPT via the Haber-Weiss mechanism. Steps 1, 2, and 3 occur during the induction period of the reaction, until a steady-state concentration of the cobalt hydroperoxide has built up. Step 4 leads to formation of the Markovnikoff products which are detected as ketone and alcohol following step 5. One of the novel features of this reaction is the ability of the solvent to inhibit the formation of autoxidation products. This probably occurs because allylic radicals, if formed, act as initiators in eq 1 and regenerate the alkene via solvent oxidation.

Acknowledgment. We acknowledge the National Science Foundation for their generous support of this research through Grant no. 8408149.

Registry No. CoSMDPT, 15391-24-9; O₂, 7782-44-7; H₂O₂, 7722-84-1; H₂C=CH(CH₂)₃CH₃, 592-41-6; C₆H₅CH=CH₂, 100-42-5; (H₃C)₃CCH=CH₂, 558-37-2; H₂C=CHCH=CH₂, 106-99-0; H₃CCH(OH)CH=CH₂, 598-32-3; H₂C=CHCH(CH₃)(CH₂)₂CH₃, 3404-61-3; H₂C=C(CH₃)(CH₂)₃CH₃, 6094-02-6; H₃CCH=CH(CH₂)₂CH₃, 592-43-8; H₃CCH₂CH=CHCH₂CH₃, 592-47-2; H₃CCH=C(CH₃)₂, 513-35-9.

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(48) Although the equilibrium constant for the binding of O₂ to CoSMDPT in toluene is not large, it has been shown that addition of a small amount of trifluoroethanol shifts the equilibrium in favor of the oxygen adduct by hydrogen bonding to the bound O₂. (See: Drago, R. S.; Cannady, J. P.; Leslie, K. A. *J. Am. Chem. Soc.* **1980**, *102*, 6014.) The solvent ethanol should similarly shift the equilibrium so that under high pressure of oxygen virtually all the CoSMDPT binds O₂.

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