

Co(III)—Alkylperoxo Complexes: Syntheses, Structure—Reactivity Correlations, and Use in the Oxidation of Hydrocarbons

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ABSTRACT

Crystalline $[\text{LCo}^{\text{III}}\text{—OOR}]$ complexes with strong-field ligands, L, afford ROO^\bullet and RO^\bullet radicals upon mild heating in solution. This fact allows oxidation of hydrocarbons by these complexes under mild conditions. The extent of hydrocarbon oxidation by discrete $[\text{LCo}^{\text{III}}\text{—OOR}]$ complexes depends on the nature of L, the solvent, the temperature, and the presence of other M(II) ions. Such systems are catalytic in the presence of excess ROOH.

Introduction

Hydrocarbons account for one of the largest sources of natural feedstock material which traditionally have been used as fuels, lubricants, and solvents. During the past few decades, there has been an increase in interest in the oxidation of inexpensive hydrocarbons by transition metal salts (or complexes) to more commercially valuable products related to pharmaceuticals, flavors, fragrances, plasticizers, and polymer precursors.¹ Development of metal-based catalysts which carry out these oxidation processes under mild conditions and with inexpensive and environmentally benign oxidants (such as O_2 , H_2O_2 , and ROOH) has for some time been a sought after goal for both industry and academia.² For hydrocarbons, catalytic oxidation is always the preferred method since use of traditional stoichiometric oxidants such as permanganate and dichromate results in production of large amounts of toxic inorganic effluents which are difficult to dispose of.²

Ferman A. Chavez received his B.A. in chemistry from California State University, Long Beach, in 1989. After a brief stint in medical school he worked for the Food and Drug Administration, Department of Health and Human Services, at the Los Angeles Pesticide Residue Laboratory as an analytical chemist. He joined the Department of Chemistry of the University of California at Santa Cruz and did research in the area of hydrocarbon oxidation under the supervision of Prof. Pradip Mascharak. He received his Ph.D. in 1999 and is currently a postdoctoral fellow in the group of Prof. Tolman at the University of Minnesota in Minneapolis.

Pradip K. Mascharak was born in Jaipur, India, in 1953. He received his Ph.D. from the Indian Institute of Technology, Kanpur, in 1979. In the same year, he joined the research group of Prof. Richard Holm at Stanford University and later moved to Harvard University. He also worked with Prof. Steve Lippard at the Massachusetts Institute of Technology for two years before joining the University of California at Santa Cruz (UCSC) in late 1984. He is currently a professor of chemistry and biochemistry at UCSC. Modeling of active sites of metalloenzymes and design of antitumor drugs and catalysts for hydrocarbon oxidation are the major focus of his research.

A few industrial processes that use catalytic oxidation on a large scale include the Mid-Century/Amoco process and the Du Pont adipic acid synthesis. In the Mid-Century/Amoco process, *p*-xylene is oxidized to terephthalic acid, an important precursor in the production of polyester fibers, films, and plasticizers. In the Du Pont process, cyclohexane is oxidized to cyclohexanol and cyclohexanone (K/A oil). The K/A oil is then further oxidized to adipic acid,³ which is a precursor in the synthesis of nylon 6,6 and other polymers. Both these methods employ a cobalt catalyst, and the conversions are performed under high pressure and temperature. The cobalt catalyst initiates the free radical autoxidation chains and decomposes alkyl hydroperoxides generated in the reaction mixture.

A key step in this decomposition process is believed to be the formation of Co(III)—alkylperoxo intermediates.^{1c,d,4} Coordination of the alkyl hydroperoxide to cobalt is presumed to weaken the O—O bond of the ROO^- group, resulting in homolytic scission of this bond and subsequent decomposition of the ROOH.

Although consensus regarding the existence of Co(III)—alkylperoxo ($[\text{Co}^{\text{III}}\text{—OOR}]$) intermediate(s) in the industrial oxidations existed before we began our work, no systematic studies on discrete complexes with $\text{Co}^{\text{III}}\text{—OOR}$ units were completed to assess their oxidizing capacities and establish the role (if any) of the proposed $[\text{Co}^{\text{III}}\text{—OOR}]$ moiety in hydrocarbon oxidations. The pertinent literature contained a few examples of complexes with $[\text{LCo}^{\text{III}}\text{—OOR}]$ formulation, where L's were strong-field ligands. These complexes were isolated from varied reaction mixtures and were mostly studied for other reasons. Nevertheless, their stability indicated that designed $[\text{LCo}^{\text{III}}\text{—OOR}]$ complexes with a kinetically inert low-spin d^6 Co(III) center can be isolated to study their reactivity in a systematic fashion. We were curious to find out whether such species indeed act as strong oxidants and can promote oxidation of hydrocarbons under mild conditions. In this Account we present the results of our work in this direction in two parts. The first part of the report includes (a) a survey of all $[\text{LCo}^{\text{III}}\text{—OOR}]$ complexes structurally characterized to date, (b) the general requirements for the formation and isolation of $[\text{LCo}^{\text{III}}\text{—OOR}]$ complexes, (c) the synthetic strategies to such complexes, and (d) the structural features of such complexes. The second part comprises discussion on (e) the capacity of these complexes to promote thermal and photochemical oxidation of hydrocarbons and (f) the mechanism(s) of the oxidation reactions. To date, several reviews that describe the properties and reactivities of $[\text{L}_n\text{M—OOR}]$ complexes, where M is an early transition metal ($\text{M} = \text{Ti}, \text{V}, \text{Mo}, \text{W}; \text{R} = \text{alkyl}$), have been published.⁵ However, no review with a focus on the properties and reactivities of $[\text{L}_n\text{Co}^{\text{III}}\text{—OOR}]$ complexes has appeared.

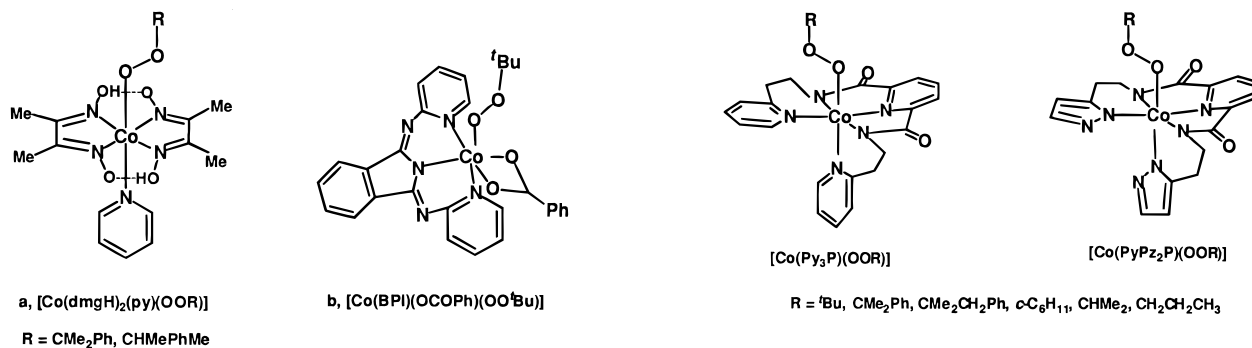


FIGURE 1. Structures of some well-characterized $[LCo^{III}-OOR]$ complexes.

Discussion: Part 1

[LCo^{III}–OOR] Complexes. When we embarked on our research, only a small number of discrete $[LCo^{III}-OOR]$ complexes were reported in the literature.^{6–14} They are $[Co(dmgH)_2(py)(OOR)]$ ($R = -CMe_2Ph, -CHMe-p-Tol$; $dmgH^-$ = monoanion of dimethylglyoxime)^{7,8} (structure a, Figure 1), $[Co(Salpr)(4-OO-(2,4,6-tBu-C_6H_2O))]$ ($Salpr^{2-}$ = dianion of salicylpropylenetriamine),¹⁰ $[Co(BPI)(OCOPh)(OOtBu)]$ ($BPI = 1,3-bis(2-pyridylimino)isoindoline$)¹¹ (structure b, Figure 1), $[Co(TPP)(py)(OO-CH_2CH=CH_2)]$,¹² and *trans*-(*t*-N,*O*(C))- $[Co\{OOCH(Me)COO-O,O\}(tren)]BF_4$.¹⁴

These known $[LCo^{III}-OOR]$ complexes comprise dissimilar ligands and entirely different OOR groups, a fact that makes it difficult to draw structure/reactivity correlations and estimate changes in oxidizing capacities of such complexes with varying coordination environments. In addition, most reports lacked mechanistic information on the mode of decomposition of these $[LCo^{III}-OOR]$ complexes. As a consequence, one could not draw conclusions regarding their role as intermediates in cobalt-catalyzed hydrocarbon oxidation. This was, however, not surprising since most of these complexes were studied for quite different reasons. For example, studies on $[Co(dmgH)_2(py)(OOR)]$ were related to the chemistry of vitamin B₁₂ while *trans*-(*t*-N,*O*(C))- $[Co\{OOCH(Me)COO-O,O\}(tren)]^+$ was obtained as a byproduct from the photolysis of *trans*-(*t*-N,*S*)- $[Co\{S(O)_2CH_2COO-S,O\}(tren)]^+$. The only exception was the work on $[Co(BPI)(OCOPh)(OOtBu)]$ by Mimoun and co-workers;¹¹ the focus of their study was on the importance of alkylperoxy complexes as intermediates in the decomposition of ROOH and generation of radical species by cobalt complexes in hydrocarbon oxidation reactions.

Since the primary goal of our work is to determine the effect(s) of the coordination environment on the overall stability and reactivity of the $[LCo^{III}-OOR]$ complexes, we have synthesized a series of such complexes utilizing different ligands L and alkyl groups R. The complexes that we have synthesized and studied so far are shown in Figure 2. These are denoted as $[Co(Py_3P)(OOR)]$ and $[Co(PyPz_2P)(OOR)]$ (where Py_3P^{2-} = dianion of *N,N*-bis[2-(2-pyridyl)ethyl]pyridine-2,6-dicarboxamide, $PyPz_2P^{2-}$ = *N,N*-bis[2-(1-pyrazolyl)ethyl]-pyridine-2,6-dicarboxamide, and $R = CMe_3$ (*t*Bu), CMe_2Ph (Cm), CMe_2CH_2Ph , *c*-C₆H₁₁ (Cy), $CHMe_2$ (*t*Pr), and $CH_2CH_2CH_3$ (*n*Pr))^{15,16} and

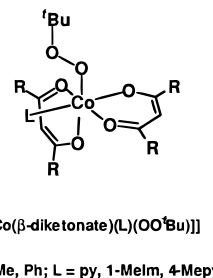


FIGURE 2. Structures of the new $[LCo^{III}-OOR]$ complexes.

$[Co(\beta\text{-diketonate})_2(L)(OOtBu)]$ (where $\beta\text{-diketonate} =$ monoanion of acetylacetonate ($acac^-$) or dibenzoylmethane (dbm^-) and $L =$ pyridine (py), 4-methylpyridine (4-Mepy), or 1-methylimidazole (1-MeIm)).¹⁷

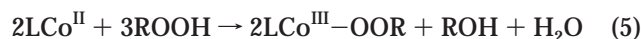
The structures of $[Co(Py_3P)(OOR)]$ ($R = tBu, Cm, CMe_2CH_2Ph, Cy, tPr, nPr$), $[Co(PyPz_2P)(OOCy)]$, $[Co(acac)_2(L)(OOtBu)]$ ($L = py, 1\text{-MeIm}$), and $[Co(dbm)_2(py)(OOtBu)]$ have been determined by X-ray crystallography.

Synthesis of $[LCo^{III}-OOR]$ Complexes: General Requirements. A close scrutiny of all $[LCo^{III}-OOR]$ complexes mentioned above reveals that all the well-characterized complexes except one are neutral. The only charged complex, *trans*-(*t*-N,*S*)- $[Co\{S(O)_2CH_2COO-S,O\}(tren)]^+$, contains a coordinated alkyl peroxide which is part of another coordinated ligand. It is also apparent that anionic ligands with hard donor centers such as deprotonated amido groups, carboxylates, phenolates, oximates, or $\beta\text{-diketonates}$ are required for the formation and isolation of $[LCo^{III}-OOR]$ complexes. In addition, it appears that the preferred geometry is octahedral to distorted octahedral.¹⁸ In one instance, a $[LCo^{III}-OOR]$ complex, namely, $[Co(salen)(OOtBu)]$, is assigned a square pyramidal geometry although no structural data exist for this complex.¹⁹

Synthetic Strategies. The synthetic procedures employed so far include (1) addition of excess ROOH to a $[LCo^{II}]$ precursor,^{11,13,15,17} (2) dioxygen insertion into the metal–alkyl bond ($LCo-R$),^{9,10,12} (3) dioxygen insertion into the metal–ligand bond promoted by irradiation,^{6–8,14} and (4) reaction of a hydroxo precursor complex ($[LCo(OH)]$) with ROOH.¹⁶

If one plans to synthesize a $[LCo^{III}-OOR]$ complex by the first method under ambient conditions, the $[LCo^{II}]$ precursor must be relatively stable in the presence of air. If the $[LCo^{II}]$ precursor is sensitive to oxygen, then the procedure requires anaerobic manipulations. For example, $[Co^{II}(BPI)(OOCR)]$ complexes are moderately stable, and

therefore the corresponding [Co(BPI)(OOCR')(OOR)] complexes are readily synthesized in the presence of air. In contrast, the synthesis of [Co(Py₃P)(OO^tBu)] requires that the initial synthesis of the [Co^{II}(Py₃P)] precursor must be performed under anaerobic conditions since the presence of air rapidly converts it to the superoxo complex [Co^{III}(Py₃P)(O₂⁻).¹⁵ In some cases, addition of an exogenous ligand is required to change the oxidation potential of the cobalt center and allow rapid oxidation under ambient conditions. We have successfully synthesized [Co(acac)₂(L)(OO^tBu)] (L = py, 1-Melm, 4-Mepy) and [Co(dbm)₂(py)(OO^tBu)] complexes utilizing the first approach.¹⁷ The utility of this method is however limited to [LCo^{III}–OOR] complexes with tertiary R groups. Attempts to synthesize [LCo^{III}–OOR] complexes in which R is secondary or primary have been unsuccessful in our hands. The proposed set of reactions that afford the [LCo^{III}–OOR] (R = tertiary) complexes by the first method are as follows:¹¹



The second and third methods in which dioxygen is inserted into a Co–R bond have primarily been used for the syntheses of the [(dmgH)₂(py)Co^{III}–OOR] complexes,^{6–8} although other types of examples do exist.¹² The exact mechanism of formation is still a matter of debate. It is however noteworthy that recemization of the α -carbon of the R group occurs during the Co–R \rightarrow Co–O–OR transformation.²⁰ When the R group is a primary or secondary alkyl, these reactions occur only upon irradiation of [(dmgH)₂(py)Co^{III}–R] species. In the case of benzylic or allylic R groups, the peroxy complexes form either thermally (in the dark) or photochemically. Finally, photolysis of [LCo^{III}–R'] (R' = secondary or primary alkyl, allylic or benzylic group) in the presence of excess ROOH with tertiary R yields [LCo^{III}–OOR] complexes with tertiary R groups. The last reaction is believed to proceed via initial homolysis of the Co–R bond in [LCo^{III}–R], a process that gives rise to [LCo^{II}].^{8,21} Presumably, the [LCo^{II}] complex then reacts with the tertiary ROOH according to reactions 1–5 shown above. Photochemical insertion of dioxygen into Co–R bonds of [(TPP)Co^{III}–R] (R = alkyl) has also been demonstrated.²²

The method our group utilized to synthesize [LCo^{III}–OOR] complexes is the reaction of the [LCo^{III}(OH)] precursor with ROOH in halocarbon solvents (method 4, see reaction 3). This reaction involves an anionic ligand exchange reaction with the concomitant formation of water. Since we use mostly halocarbon solvents, both deprotonation of ROOH ($pK_a \approx 12$ in water) and protonation of [LCo^{III}(OH)] ($pK_a([\text{LCo}^{\text{III}}(\text{H}_2\text{O})^+] \approx 7$ in water¹⁵)

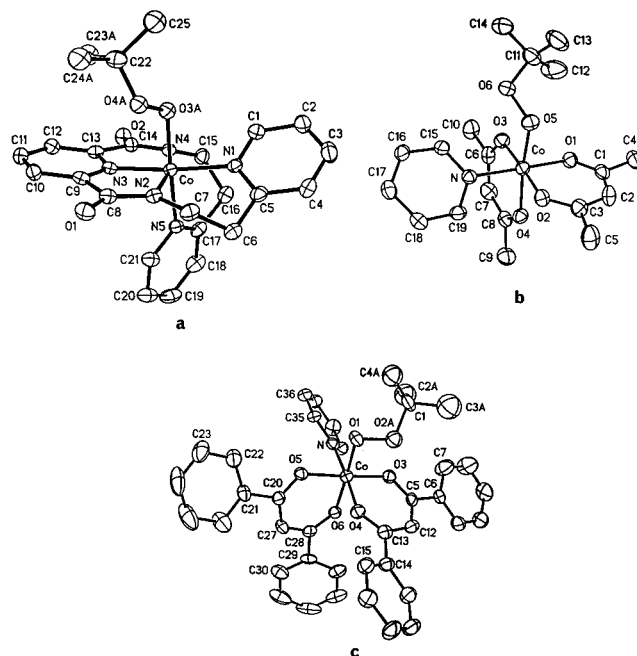
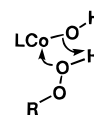


FIGURE 3. Structures of [Co(Py₃P)(OO^tBu)] (a), [Co(acac)₂(py)(OO^tBu)] (b), and [Co(dbm)₂(py)(OO^tBu)] (c).

are unlikely. Such a situation would result in formation of two charged species (ROO⁻ and [LCo^{III}(H₂O)]⁺) in an aprotic and relatively nonpolar solvent such as dichloromethane. A more likely mechanism is the concerted nucleophilic attack by the distal oxygen of the ROOH on Co(III) and deprotonation of the ROOH by the leaving OH ligand:



Unlike the first method for the synthesis of [LCo^{III}–OOR] complexes indicated above, the fourth method is suitable for the synthesis of [LCo^{III}–OOR] complexes with tertiary, secondary, and primary R groups. We have used this method to isolate [Co(Py₃P)(OOR)] and [Co(PyPz₂P)(OOR)] complexes with R = ^tBu, Cm, CMe₂CH₂Ph, Cy, ⁱPr, and ⁿPr. In addition, this method has several advantages over the methods previously used. They are as follows. There is no change in the oxidation state of the cobalt, and hence the [LCo^{III}–OH] \rightarrow [LCo^{III}–OOR] conversion can be monitored easily by NMR spectroscopy. The reactions are clean, and the only side product is water. There is no need to purify the final product by column chromatography or other means, and crystalline material is readily obtained in most cases. The synthesis is also versatile, and any ROOH can be employed.¹⁶

Important Structural Features of [LCo^{III}–OOR] Complexes. During the past three years, we have determined the structures of several [LCo^{III}–OOR] complexes. In Figure 3, the structures of selected examples are shown. Close scrutiny of the structural data for all [LCo^{III}–OOR] complexes reveals some general trends. For example, The O–O bond distances in [Co(Py₃P)(OO^tBu)] and [Co(BPI)–

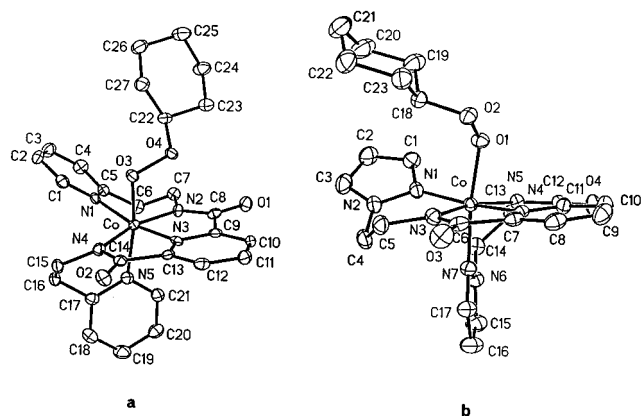


FIGURE 4. Structures of $[\text{Co}(\text{Py}_3\text{P})(\text{OOCy})]$ (a) and $[\text{Co}(\text{PyPz}_2\text{P})(\text{OOCy})]$ (b).

(OBz)(OO^tBu) are 1.49(5) and 1.444(6) Å, respectively. These values indicate that the O–O bond distance becomes somewhat weakened when an aromatic nitrogen is situated trans to the peroxide moiety. It is interesting to note that the Co–O distances in these two complexes also follow the same trend (1.905 (7) and 1.838 (5) Å, respectively). The structural data also indicate that the O–O bond distances in $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes are not very sensitive to changes in L and lie in the narrow range of 1.4–1.5 Å. The Co–O bond distances of the Co–OOR moiety also vary to a small extent and fall in the range of 1.85–1.92 Å. In the case of the O–R bond distances (range of 1.40–1.46 Å), the shorter distances mostly belong to primary R groups, while longer O–R distances are noted when the R group is tertiary.

The structures of $[\text{LCo}^{\text{III}}\text{–OOCy}]$ complexes synthesized in this laboratory are shown in Figure 4. $[\text{Co}(\text{Py}_3\text{P})(\text{OOCy})]$ (Figure 4a) and $[\text{Co}(\text{PyPz}_2\text{P})(\text{OOCy})]$ (Figure 4b) are the first two examples of structurally characterized complexes that possess the $[\text{Co}^{\text{III}}\text{–OOCy}]$ unit. Although $[\text{Co}^{\text{III}}\text{–OOCy}]$ has been proposed as one key intermediate in cobalt-catalyzed decomposition of cyclohexyl hydroperoxide,^{1c,e} these two complexes provide, for the first time, the opportunity to inspect the metric parameters of the coordinated –OOCy moiety. The structures of both complexes reveal that the cyclohexyl group of the –OOCy moiety is in the chair conformation. The ligand L (Py_3P^{2-} and $\text{PyPz}_2\text{P}^{2-}$) has a minor influence on the structural parameters of the –OOCy group, and the O–O bond distances differ only slightly (1.460 (4) Å vs 1.456 (3) Å).

Discussion: Part 2

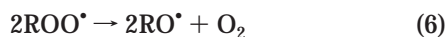
Hydrocarbon Oxidation Promoted by $[\text{LCo}^{\text{III}}\text{–OOR}]$ Complexes. It is important to note that $[\text{LCo}^{\text{III}}\text{–OOR}]$ species have been proposed in industrial oxidation processes only as fleeting intermediates in systems under very harsh conditions. Prior to our work,^{15–17} very few groups actually studied the oxidation of hydrocarbon substrates by discrete $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes at moderate temperatures.^{11,13} The initial results from Mimoun's laboratory demonstrated that $[\text{Co}(\text{BPI})(\text{OBz})(\text{OO}^t\text{Bu})]$ and its related derivatives promote oxidation of hydrocarbons upon warming. We initiated our oxidation work with a different

goal in mind. Since $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes are often crystalline solids which are stable in a dry atmosphere for long periods of time, one could use them as reagents to oxidize C–H bonds under mild conditions. Such a capacity would be highly desirable in the syntheses of fine chemicals that are susceptible to harsh conditions of conventional oxidation of C–H bonds. In our work, we have shown that the $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes can indeed be used for such a purpose. When solutions of $[\text{Co}(\text{Py}_3\text{P})(\text{OOR})]$ or $[\text{Co}(\text{PyPz}_2\text{P})(\text{OOR})]$ complexes in halocarbon solvents are warmed in the presence of a variety of hydrocarbon substrates, rapid oxidation of the hydrocarbons to the corresponding alcohols and ketones (or aldehydes) occurs at temperatures above 50 °C.¹⁶ The oxidation reaches an optimum rate at 80 °C. We have recently shown that solutions of $[\text{Co}(\beta\text{-diketonate})_2(\text{L})(\text{OO}^t\text{Bu})]$ complexes¹⁷ begin to oxidize hydrocarbons at temperatures as low as 2 °C and optimum reaction rates are attained at 50 °C.¹⁷ Clearly $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes have the potential for use in hydrocarbon oxidation under mild conditions. It seems likely that properly designed $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes will eventually find use in oxidation chemistry.

Studies on photoinduced oxidation of hydrocarbons in the presence of $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes at room temperature has also been explored in our laboratory.²³ In such studies, it is apparent that when $[\text{Co}(\text{BPI})(\text{OAc})(\text{OO}^t\text{Bu})]$, $[\text{Co}(\text{Me-BPI})(\text{OAc})(\text{OO}^t\text{Bu})]$, or $[\text{Co}(\text{Cl-BPI})(\text{OAc})(\text{OO}^t\text{Bu})]$ is irradiated in the presence of hydrocarbons, oxidation of hydrocarbons to alcohols and ketones occurs at room temperature. We anticipate that photoinduced oxidation of hydrocarbons in the presence of $[\text{LCo}^{\text{III}}\text{–OOR}]$ is a general phenomenon and many of these complexes will exhibit such activity.

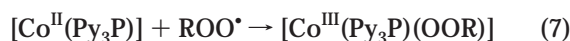
Mechanism(s) of Hydrocarbon Oxidation by $[\text{LCo}^{\text{III}}\text{–OOR}]$ Complexes. The process of oxidation of hydrocarbons by $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes is closely related to the modes of decomposition of these species. Results of NMR studies by us and others indicate that warming of the reaction mixtures results in overall loss of the “ROO group”, and in most cases, complexes of the type $[\text{CoL}_n]$ remain in the reaction mixtures at the end of oxidation.^{13,16} Mechanistic studies suggest that fragmentation of the Co–OOR moiety generates oxygen-based radicals that initiate radical-based autoxidation processes in these reaction mixtures much like the industrial processes.¹⁴ We have investigated the modes of fragmentation of the Co–OOR moiety and the nature of radicals formed in such processes in detail by carefully selecting the reaction conditions and the substrates and by analyzing the oxidation products.^{15–17} Two other groups have performed similar studies with few $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes.^{11,13} Close scrutiny of all these results has led us to realize that, in aprotic solvents, the $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes can undergo heat-induced homolytic scission of either the Co–O bond or the O–O bond depending on the ligands employed, and hence different sets of oxidation products are obtained with $[\text{LCo}^{\text{III}}\text{–OOR}]$ complexes with different ligands, L.

The evidence for either Co–O or O–O bond homolysis mostly lies in the oxidation products since homolysis of the Co–O bond affords ROO• radicals and [LCo^{III}] while O–O bond homolysis gives rise to RO• radicals and [LCo^{III}–O•] in the reaction mixture. In case of [Co(Py₃P)(OOR)] and [Co(PyPz₂P)(OOR)], we were able to demonstrate that these complexes decompose primarily via O–O bond homolysis so that the resultant oxidation is driven by RO• radicals.^{15,16} We also showed that [LCo^{III}–O•], the other product of decomposition, is not capable of promoting any oxidation by the use of 2-methyl-1-phenyl-2-propyl hydroperoxide (PhCH₂CMe₂OOH), which is a mechanistic probe designed to test whether metal-centered oxidations are present.²⁴ When one employs [Co(Py₃P)(OOCMe₂CH₂Ph)] to oxidize cyclohexane, very small amounts of oxidation products are obtained.¹⁶ Since O–O bond homolysis results in formation of [(Py₃P)Co–O•] and PhCH₂CMe₂OO• radical in this case and the PhCH₂CMe₂OO• radical undergoes rapid β-scission ($k = 2.2 \times 10^8 \text{ s}^{-1}$ at 25 °C) to produce PhCH₂• radical with poor H atom abstraction capability, very low yields of oxidation products clearly indicate that [LCo^{III}–O•], the other species in solution, is incapable of H abstraction from cyclohexane and promotion of radical-chain cascade leading to oxidation products. [Co(dmgH)₂(py)(OOR)] complexes have also been demonstrated to undergo O–O bond homolysis. Quite in contrast, [Co(BPI)(RCO₂)(OOR)] and [Co(Salen)(L₁)(OOR)] (L₁ = py, 4-Mepy) complexes decompose via both Co–O and O–O homolyses.^{16,19} The [Co(β-diketonate)₂(L)(OO^tBu)] complexes appear to decompose primarily via Co–O bond homolysis.¹⁷ The presence of significant amounts of ROO• radical in the reaction mixture is indicated by selective epoxidation of olefins by these [LCo^{III}–OOR] complexes when aldehydes are present. Since ROO• radicals can afford RO• radicals (reaction 6), it is often difficult to prove the exclusivity of Co–O bond homolysis.



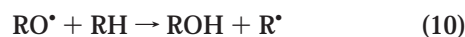
Nevertheless, it is quite evident that when relatively strong-field ligands are bonded to the cobalt center of [LCo^{III}–OOR] complexes, O–O homolysis is the primary mode of decomposition. This preference arises from the stability of the Co(III) center in such complexes. In contrast, when ligands bonded to cobalt are weak-field, Co–O bond homolysis with concomitant reduction of Co(III) to Co(II) (and formation of [LCo^{II}]) occurs in most cases. Of course, this fact does not preclude O–O bond homolysis. More [LCo^{III}–OOR] complexes with very weak ligands (L) are required to verify or refute this hypothesis.

We have recently discovered an NMR method to determine the extent of Co–O bond homolysis without the use of spin traps.¹⁷ The method involves mixing of [Co^{II}(Py₃P)] with the [LCo^{III}–OOR] complex of interest. If decomposition of the [LCo^{III}–OOR] complex generates ROO• radicals, these radicals²⁵ will be trapped by [Co^{II}(Py₃P)] to form [Co(Py₃P)(OOR)] by reaction 7. Since [Co(Py₃P)–



(OOR)] only begins to decompose significantly at temperatures above 60 °C, it is ideal for trapping experiments carried out at room temperature. The unique resonance of the R group of the ligated ROO moiety (usually located upfield relative to the free ROO or RO group) makes this method suitable for identification and quantitation.

What we have learned to date about hydrocarbon oxidation by [LCo^{III}–OOR] complexes at moderate temperatures is as follows. In all cases, oxidation of the hydrocarbon substrates (RH) results from H atom abstraction from RH by the O-centered radicals generated in the reaction mixtures to generate R• species. These species then enter into reaction pathways to produce ROOH (reactions 8 and 9). Thus, the chemistry can be explained in terms of what is known about radical-induced oxidation involving ROO• and RO•.²⁶ Propagation and termination steps in these autoxidation reactions provide the final oxidation products. Decomposition of the ROOH formed in the reaction mixtures by [LCo^{III}(OH)] or [LCo^{II}] via formation of [LCo^{III}–OOR] serves to sustain the production of radicals and formation of oxidation products. For example, with R = Cy, the abstraction of an H atom from cyclohexane substrate by CyO• radical (formed from homolysis of the O–O bond in [LCo^{III}–OOCy]) results in formation of CyOH and Cy• (reaction 10). In addition, oxidation of CyO• radical (reaction 11) or CyOH (reaction 12) by Cy• gives rise to the corresponding ketone (represented as R''O). A Russel termination reaction²⁷ (reaction 13) may also lead to formation of alcohol and ketone products.



Our initial studies have also shown that when [Co(BPI)(OCOPh)(OO^tBu)] and related complexes are irradiated in deoxygenated hydrocarbon solvents at room temperature, homolysis of the Co–O bond gives rise to ^tBuOO• radicals in solution.²³ As a consequence, one obtains *tert*-butylperoxy-1-adamantane and *exo*-2,3-epoxynorbornane with adamantane and norbornane as the substrates. In such oxidations, [(BPI)Co^{II}] is recovered as a precipitate at the end of irradiation. When oxygen is present in the reaction mixtures, alcohols and ketones are also obtained. The latter oxidation is carried out by both ^tBuOO• and ^tBuO• radicals. The presence of the BPI chromophore with a high extinction coefficient and the stability of the [(BPI)Co^{II}] types of complexes appear to favor the photoinduced homolysis of the Co–O bond in these complexes. We

anticipate that other [LCo^{III}–OOR] complexes with similar characteristics will promote light-induced hydrocarbon oxidation.

Catalytic Oxidation of Hydrocarbons by [LCo^{III}–OOR] Complexes. Oxidation reactions with [LCo^{III}–OOR] complexes are generally quite clean, and NMR studies on the reaction mixtures demonstrate that, with strong-field ligands such as Py₃P²⁻, one obtains [LCo^{III}(OH)] at the end of one turnover. This observation prompted us to design catalytic systems based on these complexes in conjunction with excess ROOH. Catalytic oxidation with turnovers as high as 200 has now been observed with both [LCo^{III}–OOR] and [LCo^{III}(OH)] complexes.¹⁶ In these radical-driven catalytic reactions, milligram quantities of the Co(III) complexes afford gram quantities of alcohols and ketones within 4 h at 60–80 °C. The reactions are noteworthy for the moderate conditions of the oxidation reactions. Our work clearly indicates that, in cobalt-catalyzed oxidation of hydrocarbons with ROOH, [LCo^{III}–OOR] complexes are viable intermediates; such species continue to form in the reaction mixtures and break down under mild conditions to provide RO• radicals to sustain the oxidation process. The notion that [LCo^{III}–OOR] complexes are “dead-end species” (the industrial processes employ acetic acid as the solvent to break up such intermediates) is therefore not correct. It now appears that one can design and then synthesize robust [LCo^{III}–OOR] complexes with strong-field ligands, L, and use them in stoichiometric and catalytic oxidation of hydrocarbons under mild conditions. Current research in our laboratory is directed toward this goal.

Summary and Conclusion

It is now quite apparent that discrete [LCo^{III}–OOR] complexes could be synthesized and isolated in crystalline forms. These complexes readily afford ROO• and RO• radicals upon mild heating and hence could be used as oxidizing agents. The mode of decomposition of such [LCo^{III}–OOR] species depends on L. The oxidation of hydrocarbons by the [LCo^{III}–OOR] complexes results from radical-driven autoxidation reactions initiated by the oxygen-based radicals. The yields of the oxidized products can be enhanced by (a) increasing the oxygen pressure, (b) sustaining the release of these oxygen-based radicals by introduction of M(II) salts, and (c) removal of water from the reaction mixtures.¹⁶ The temperature at which a certain [LCo^{III}–OOR] complex will initiate the radical-driven autoxidation process depends on the ligand L. Such systems are catalytic in the presence of excess ROOH.

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