CATALYTIC CONVERSION OF CYCLOHEXYLHYDROPEROXIDE TO CYCLOHEXANONE AND CYCLOHEXANOL*

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Summary

The low-conversion air oxidation of cyclohexane yields a mixture of cyclohexylhydroperoxide, cyclohexanone and cyclohexanol. The cyclohexylhydroperoxide is converted to additional cyclohexanone and cyclohexanol before the mixture is concentrated. Cobalt octoate is an active but shortlived catalyst for this transformation. Using a combination of pulse calorimetry and chemical luminescence techniques, a new family of long-lived catalysts has been discovered. These catalysts, based upon the (bis(2-pyridylimino)isoindolinato) ligand, are very active and long-lived, allowing cyclohexylhydroperoxide to be converted in a selective, low temperature process. The structure of one of these active catalysts, bis[bis((3-methyl-2-pyridyl)imino)isoindolinato]cobalt(II), has been determined crystallographically. Under reaction conditions, it is likely that the active form of the catalyst has lost one ligand.

Introduction

The oxidation of hydrocarbons to polymer intermediates is the largest scale application of homogeneous catalysts [1]. These oxidation reactions are the least well understood reactions in homogeneous catalysis. This situation arises from a combination of two factors. The utility of NMR and X-ray crystallography is limited in these systems because the catalysts are often present in relatively low concentrations. Secondly, the high degree of complexity of the reactions daunts even the most experienced of mechanistic chemists; chemical models of small portions of the overall oxidation process are just beginning to emerge [2].

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A very simplified but useful model of the mechanism of cyclohexane oxidation to adipic acid precursors is shown in Scheme 1:



Scheme 1.

Cyclohexane is oxidized to cyclohexylhydroperoxide which can be decomposed to cyclohexanol and cyclohexanone. There is also an independent, direct oxidation to cyclohexanol and cyclohexanone involving cyclohexylperoxy radical intermediates [3] which does not pass through cyclohexylhydroperoxide. If a relatively high concentration of catalyst, typically cobalt octoate, is used for the oxidation, the cyclohexylhydroperoxide is decomposed during the oxidation process and is not observed in significant concentrations. In oxidations with low catalyst concentrations, cyclohexylhydroperoxide can account for as much as two-thirds of the oxidized material. It is imperative that it be converted in high yield to further cyclohexanol and cyclohexanone before the products are concentrated by distillation. The primary steps in this process occur by a modified Haber–Weiss [4] mechanism given by eqns. $(1) \cdot (5)$:

$$M^{II} + CyOOH \longrightarrow M^{III}OH + CyO^{*}$$
(1)

$$M^{III} + CyOOH \longrightarrow M^{II} + CyOO^{*} + H_2O$$
(2)

$$CyO^{*} + CyOOH \longrightarrow CyOH + CyOO^{*}$$
(3)

$$2 CyOO^{*} \longrightarrow CyOH + K + O_2$$
(4)

$$3 CyOOH \longrightarrow 2 CyOH + K + O_2 + H_2O$$
(5)

As might be expected for a process involving radical species, there are a myriad of other, secondary reactions. Our mechanistic investigation [5] indicated that the important ring-opening reaction:

 $CyO' \longrightarrow CH_2CH_2CH_2CH_2CH_2CH_2CH=O$

has an appreciable activation energy. The configuration of the industrial process [6] is such that ring-opened products, including adipic acid, complicate down-stream processing. Therefore, the simplest process is obtained with a lower temperature conversion of cyclohexylhydroperoxide which minimizes the ring opening reaction.

The commonly used catalyst, cobalt octoate, does not have sufficient activity at the reduced temperatures, so a program to discover new improved catalysts was initiated [7]. The results of that investigation are reported here.



Fig. 1. Schematic of the pulse reactor system.



Fig. 2. Diagram of the pulse reactor design.

Experimental

The catalytic investigation was carried out in the apparatus shown schematically in Fig. 1. It consisted of a 270 cm³ stainless steel reactor, depicted in detail in Fig. 2, equipped with a platinum resistance thermometer and a light pipe. The light pipe was connected by a $3/8 \times 18$ inch flexible light guide to a shuttered EMI-6255 photomultiplier supplied at 900 V with a Fluke power supply. The outputs of the resistance thermometer and the photomultiplier were recorded on a strip-chart recorder and stored at one point every two seconds on a data system of a PDP-10 computer. The stirrer was coupled magnetically to a variable speed motor. The injection port was similar to that on a gas chromatograph. Liquid volumes of 60 ml assured good contact with the light pipe.

A variety of metal complex catalysts were screened for low temperature activity by using 10 ppm by weight of metal for the decomposition of 1% by weight CHHP in cyclohexane. The reactor was first charged with the catalyst and 60 cm³ of cyclohexane, and a solution of 9,10-dibromoanthracene in chlorobenzene (0.1 M, 0.6 ml, giving 10^{-3} M) to enhance light output. The reactor was heated to 60 °C and stirred at 1300 rpm. When the reactor had come to temperature, data collection was begun, the shutter was opened and 0.6 ml of neat CHHP was injected.*

After 10 min, the reaction was quenched by injection of $P(OMe)_3$:

$P(OMe)_3 + CHHP \longrightarrow O = P(OMe)_3 + A$

The resulting exotherm (ΔT_q) indicated the amount of remaining CHHP. Typical traces are shown in Figs. 3 and 4. Table 2 presents the integrated values of the light and heat traces for a series of experiments involving various concentrations of Co(octoate)₂. To calculate the percent of the CHHP decomposed by any given catalytic run, it was necessary to determine (i) the temperature drop (ΔT_{endo}) of the reactor upon injection of the P(OMe)₃ if there is no CHHP, and (ii) the exotherm (ΔT_{uncat}) upon reaction with a full charge of CHHP in the absence of catalytic decomposition. This gives the empirical relationship for the percent of CHHP decomposed during the catalytic reaction:



Fig. 3. Traces from CHHP decomposition by Co(octoate)₂.

^{*}CAUTION! Great care should be exercised when handling neat or concentrated cyclohexylhydroperoxide. Mixing concentrated solutions of cyclohexylhydroperoxide with transition metal salts, especially those of Co and Mn, can cause vigorous heating and O_2 evolution, which can eject the solutions from the tubes in which they are mixed. Care must be taken to avoid skin contact because these compounds are powerful oxidizing agents.

TABLE 1

Decomposition of 14 C-labeled CHHP in cyclohexane and oxidation of 14 C-labeled cyclohexanol during CHHP decomposition

Metal	¹⁴ C-CHHP ^a	¹⁴ C-alcohol ^b	
	% Yield (*K + *A)/*CHHP	*K/*A	*K/*A
Mo	85.7(2)	1.1(1)	0.46
Cr	84.8(7)	4.0(5)	0.45
v	87.0(7)	1.1(2)	0.45
Со	87.5(8)	0.58(5)	0.08
none	76.3	0.34(5)	0.22

^a1.1 - 1.4% CHHP in cyane, 150 °C, 28 - 32 ppm metal.

^b0.11 M CHHP and 0.02 M *A in cyane, 150 °C, 2 h, 20 ppm metal.

TABLE 2

Cyclohexylhydroperoxide decomposition by Co(octoate)₂ ^a

[Co] (ppm)	Im (V)	Iq (mV)	ΔT_{c} (°C)	$\Delta T_{\rm q}$ (°C)	% CHHP decomp.	β	Cycles
0	0.0	0.0	0	8.4	(0)		
0.1	0.04	0.0	0.0	8.0	5	_	3300
0.4	0.52	3.5	0.07	7.7	10	0.8	1320
1.2	3.4	10.0	0.28	6.8	20	1.8	990
3	3.7	13.5	0.40	6.5	20	1.3	480
10	8.8	15.0	1.5	3.75	55	1.7	350
25	9.2	10.5	2.6	1.2	80	1.9	220
100	8.7	1.5	3.1	-0.5	100	1.5	65

^aSee text for definitions of $I_{\rm m}$, $I_{\rm q}$ and β .

% CHHP Decomp =
$$100 \left(\frac{\Delta T_{\text{uncat}} - \Delta T_{\text{q}}}{\Delta T_{\text{uncat}} - \Delta T_{\text{endo}}} \right)$$
 (6)

For the data in Table 2, this relationship became:

% CHHP Decomp = $100[(8.0 - \Delta T_q)/8.4]$

A slightly different reactor and procedure were used to screen a variety of transition metal catalysts for their efficacy in the decomposition of CHHP. The data from these reactions are presented in Table 3. The relationship which described the percent CHHP decomposed was found to be:

% CHHP Decomp =
$$100[(5.3 - \Delta T_q)/6.2]$$

The reported values of $t_{1/2}$ are the half-lives of the catalytic reactions as determined by the light output. For very active catalysts, this is a reflection of the concentration of available CHHP, but for catalysts of low activity, it is a reflection of the catalyst half-life under the reaction conditions.

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Screening results at 10 ppm catalyst

	T3: 1					~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~
Catalyst-	Final ppm	(\mathbf{V})	ΔT_{c} (°C)	$(s)^{t_{1/2}}$	$\Delta T_{\mathbf{q}}$ (°C)	% CHHP dec.
Fe(TPP)Cl	7.1	0.094	0.7	30	-0.9	100
Co(BPI) ₂	2.2	0.075	0.65	80	-0.7	100
Co(3MeBPI) ₂	2.9	0.098	0.8	100	-0.65	95
Fe(BPI) ₂	0.6	1.85	0.7	_	-0.65	95
Co(4MeBPI) ₂	3.0	0.057	0.6	110	-0.5	95
Co(TPP)	6.4	1.3	0.6	_	-0.5	9 5
Co(OEP)	1.1	1.55	0.9	—	0.65	75
Co(DBM) ₂ TMEDA	< 0.2	0.17	1.2	_	0.8	75
Cr(octoate) ₃	1.3	0.033	0.4		1.2	65
Co(acac) ₂ TMEDA	< 0.2	8.9	0.8	—	1.4	65
$Co(octoate)_2$	< 0.1	8.9	0.2	10	1.9	55
CoPc	0.1	0.14	0.5		2.6	45
[Co(salen)] ₂ O	3.8	0.076	0.7		2.8	40
$Co(acacF_6)TMEDA$	2.2	0.20	0.3	_	3.2	35
Fe(acacF ₆)TMEDA	0.9	2.2	0.7	_	3.5	30
$Co(CF_3CO_2)_2$ TMEDA	< 0.2	0.036	0.1	_	4.0	20
$Co[(C_8H_{17})_2PO_4]_2$	< 0.1	0.023	-0.8	—	5.5	0
Mg(TPP)	5.6	0.29	-1.0	500 ^b	5. 6	0
no catalyst	< 0.2	0.004	-0.4	-	5.3	0
Fe(TPP)Cl ^b	4.4	0.15	0.8		-0.8	100
Co(3MeBPI) ₂ ^b	5.4	0.065	0.7	100	0.4	80
$Co(octoate)_2$ ^b + HBPI	0.3	0.82	0.3	150	1.8	55
Fe(tBuPc) ^b	0.7	1.35	0.4	-	2.9	40
Co(tBuPc) ^b	1.0	0.10	0.6		3.7	25
Co(octoate) ₂ ^b	0.2	0.086	-1.6	<10	4.6	10

^aDBM = dibenzoylmethane, TMEDA = tetramethylethylenediamine, acac = acetylacetone, salen = bis(salicylaldehyde)ethylenediamine; other ligands defined in text. ^bMeasured at 100 °C in simulated plant stream.

X-ray structure determination of bis[bis((3-methyl-2-pyridyl)imino)isoindolinato]cobalt (benzene solvate)

Details of the crystal structure are given in Table 4. Data were collected on an Enraf-Nonius CAD4 diffractometer using the ω -scan method. The structure was solved using an automated Patterson analysis. Refinement was carried out by full-matrix least squares on F, using scattering factors from the International Tables [8] and included anomalous terms for cobalt. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were fixed. The largest residual density of 0.41 e Å⁻³ was found near the cobalt atom. Final fractional coordinates and thermal parameters of nonhydrogen atoms are presented in Table 5 and selected bond distances and angles are presented in Table 6. Full listings of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

TABLE 4

Crystal structure data for bis[bis((3-methyl-2-pyridyl)imino)isoindolinato]cobalt(II)

formula	CoNtoCarHan
fw	789 81
space group	monoclinic, $P2_1/c$ (No 14)
a, Å	10.900(4)
b, Å	39.683(9)
c, Å	8.994(3)
β , deg	93.49(3)
V, Å ³	3883.1
Z	4
$D(\text{calcd}), \text{g cm}^{-3}$	1.356
cryst dimen, mm	0.20 imes 0.30 imes 0.30
method of growth	benzene evap. from sealed vial over 4 yr.
temp, °C	-70
radiation	Mo K α (Graphite monochromated, $\lambda = 0.71069$ Å)
μ , cm ⁻¹	4.87
2θ limits, deg	1 - 53
max h, k, l	11, 49, 12 (+++,++)
data, $F_0^2 > 2\sigma(F_0^2)$	4273
final no. variables	514 (All non-H anisotropic; H fixed)
R	0.065
R _w	0.042
max. resid, $e \text{ Å}^{-3}$	0.41 near Co

Results⁺ and discussion

Initial studies of transition metal carboxylate-catalyzed decomposition of ¹⁴C-labeled CHHP in cyclohexane are shown in Table 1. The results indicate that while the combined yields of labeled *K and *A are not strongly dependent on the metal, the ratios of *K to *A are. The Haber–Weiss mechanism given in eqns. (1)-(5) would predict one labeled ketone for two labeled alcohol molecules. The higher ratios of *K to *A obtained for Group V and VI transition metals could be attributed to the reaction

$CHHP \longrightarrow K + H_2O$

These concurrent homolytic and heterolytic pathways have been suggested before [9]. The alternative explanation is that the excess ketone observed results at least in part from the subsequent oxidation of *A to *K. The latter possibility was tested by decomposing CHHP in the presence of ¹⁴C-labeled cyclohexanol using various metal catalysts. The reaction is indicated schematically by the equation

^{\dagger}Supplementary material available: Listings of anisotropic thermal parameters, hydrogen atom parameters and additional bond distances and angles are available from the indicated author. Tables of calculated and observed structure factors are also available. Full listings of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

 $CHHP + *A \longrightarrow K + A + *K$

The results in Table 1 indicate that Cr, Mo and V cause considerably more oxidation of the alcohol present than do Mn and Co. This greater tendency of earlier metals to use peroxide to oxidize alcohols to ketones could be related to the tendency of these metals to form oxo-species [10].

The laboratory scale pulse reactor shown in Figs. 1 and 2 was designed for studies of cyclohexylhydroperoxide (CHHP) decomposition at temperatures up to 105 °C under autogenous pressure. The pressure requirements result from the vapor pressures of the cyclohexane and other components in the reactor at temperatures that might be used in a plant. The course of the reaction was monitored by two rather unusual physical parameters — heat and light output. The decomposition of CHHP is an exothermic reaction, producing an easily measured rise in temperature. After completion of the catalytic reaction, the remaining hydroperoxide was consumed with excess trimethyl phosphite, resulting in a rapid exotherm which gave an assay of the extent of catalyzed decomposition. The ketone produced in the catalyzed free-radical reaction is in an excited state, and emits a photon of light which is detected with the photomultiplier.

$$2 \operatorname{CyOO}^{\bullet} \longrightarrow \mathrm{K}^* + \mathrm{O}_2 + \mathrm{A} \tag{7}$$

$$\mathbf{K}^* \longrightarrow \mathbf{K} + h\nu \tag{8}$$

The luminescent signal was enhanced by addition of 9,10-dibromoanthracene; this technique has been used by several researchers and has been demonstrated not to affect the rate of reactions [11]. The luminescence signal gives an immediate indication of what is actually occurring in the reactor, but was found to be far from quantitative (*vide infra*). The calorimetric measurements gave quantitative results after the reaction was over.

Catalysis by $Co(octoate)_2$

The first example, shown in Fig. 3, is CHHP decomposition catalyzed by $Co(octoate)_2$. Surprisingly, this article of commerce, based upon 2-ethylhexanoate, is an ill-defined mixture whose composition varies from manufacturer to manufacturer. It is, however, the catalyst of choice, or at least 'of practice', in the industry at present. The samples in this study were used as supplied in a medium weight hydrocarbon diluent. Upon injection of a solution of cyclohexylhydroperoxide, there was an exotherm and an intense pulse of light which decayed rapidly. After ten minutes, $P(OMe)_3$ was injected and the considerable exotherm caused by hydroperoxide oxidation of the phosphite to phosphate revealed an appreciable quantity of undecomposed CHHP. A follow-up experiment with multiple injections of CHHP, shown in Fig. 4, confirmed the rapid deactivation of catalytic activity. The strong light output decayed within the first few seconds of reaction, and the light pulses of subsequent injections were minimal. The heat trace shows an exotherm for the first injection, but subsequent injections of the room



Fig. 4. Traces from repeated injections of CHHP into Co(octoate)₂.

temperature cyclohexylhydroperoxide result in temperature drops. The exotherm upon addition of $P(OMe)_3$ accounts for about half of the cyclohexylhydroperoxide which had been added. It was rather evident from these experiments that $Co(octoate)_2$ is not an efficient catalyst for the desired transformation, in spite of its wide acceptance in the overall process of cyclohexane oxidation.

The effect of cobalt concentration was of interest, so a series of experiments was carried out in which the metal concentrations were varied from 0 to 100 ppm. The results of these experiments are presented in Table 2. Solutions of 1% CHHP in cyclohexane were heated to 60 °C and then the appropriate quantity of Co(octoate)₂ was injected. Ten minutes later the $P(OMe)_3$ was injected to quench the reaction. The maximum light intensity (I_m) was observed shortly after catalyst injection. As shown in Fig. 5, this I_m reached a rather flat maximum at 10 - 20 ppm cobalt. The second curve in Fig. 5 is the remaining light output (I_q) at 10 min, just before the $P(OMe)_3$ quench, and is about 10³ smaller than I_m .

The behavior of I_q as a function of [Co] can be explained by a model with the following features: (1) light intensity which is proportional to the rate of CHHP decomposition, (2) a decomposition rate which is first order in both CHHP and active cobalt, and (3) a decreasing cobalt catalyst activity as a result of poisoning by the CHHP decomposition products. This behavior is represented by eqn. (9):

$$I_{\rm q} = \beta [\rm Co] \, \frac{(1 - f_{\rm D})}{f_{\rm D}} \tag{9}$$



Fig. 5. Light intensities from decompositions with varying concentrations of Co(octoate)₂.

The fraction of CHHP decomposed is given by $f_{\rm D}$, [Co] is the total initial cobalt concentration, and β is a constant given by $I_{\rm q}f_{\rm D}/[{\rm Co}](1-f_{\rm D})$. Over a range of cobalt concentrations from 0.4 to 25 ppm, β has a mean value of 1.5 ± 0.4 (V ppm⁻¹). This value and an $I_{\rm q}$ of 1.5 mV in the case of the 100 ppm run is consistent with 99% decomposition of the cyclohexylhydroperoxide.

The poisining of the catalyst by decomposition products is consistent with the multiple injection experiment above and with another experiment in which the decrease in activity of successive injections of 2 ppm cobalt into CHHP was greater than could be accounted for by the decreased CHHP concentration.

Figure 6 shows that the percent CHHP decomposed in a 10 min period does not vary linearly with catalyst concentration. The number of cycles, defined as the moles of CHHP decomposed per mole of catalyst charged,



Fig. 6. Percent of CHHP decomposed by varying concentrations of Co(octoate)₂.



decreases from a high of 3300 at 0.1 ppm to only 65 at 100 ppm cobalt. The temperature change from the catalyzed decomposition of CHHP, ΔT_c , should be linearly and inversely related to the temperature change at quench by P(OMe)₃, ΔT_q . This relationship is demonstrated in Fig. 7, where ΔH_c is 0.35 times ΔH_q . This value can be compared with the values of ΔH calculated from data in the literature [12, 13].

 $3CyO_2H \longrightarrow K + 2A + H_2O + O_2 + 104 \text{ kcal}$ (10) $2CyO_2H + CyH \longrightarrow K + 2A + H_2O + 132 \text{ kcal}$ (11) $CyO_2H + P(OMe)_3 \longrightarrow A + OP(OMe)_3 + 110 \text{ kcal}$ (12)

Reaction (10) gives 35 kcal mol⁻¹ of CyO₂H decomposed, assuming that none of the O₂ liberated reacts, while reaction (11) gives 66 kcal mol⁻¹, the higher value resulting from complete consumption of the O₂ released to oxidize cyclohexane. The observed value of 0.35 is intermediate between the 0.32 expected for reaction (10) and the 0.60 exptected for reaction (11), consistent with consumption of about 12% of the O₂ released. (The degree of cyclohexane oxidation during hydroperoxide decomposition increases with temperature.)

Exploration of new catalysts

A number of cobalt complexes were synthesized for testing in a search for a new, superior catalyst system. Catalytic activity was expected to be based on having the proper redox potential to shuttle back and forth by one electron in a Haber-Weiss type cycle. The complex should also hold the metal tightly and should withstand the rigors of a high-temperature, free radical environment. The results of the catalytic investigations are presented in Table 3.

Two initial, obvious choices were cobalt phthalocyanines and porphyrins. These square planar tetraazamacrocycles are well established in oxidation chemistry [14].

Co(phthalocyanine), CoPc, was of little use, despite its considerable stability, because its solubility is so low that the required concentration of cata-



lyst could not be achieved. The tetra-t-butyl derivative of phthalocyanine, tBuPc, was prepared for testing by a rather laborious route [15]. Despite the ability to achieve intensely purple cyclohexane solutions of this complex, the activity, indicated in Table 3, was not as high as might have been expected; it is possible that the t-butyl groups were oxidized in the initial stages of the catalysis. The cobalt and iron complexes of tetraphenylporphyrin, TPP, and octaethylporphyrin, OEP, were more effective than the phthalocyanines, decomposing most or all of the CHHP used in the screening process. Unfortunately, these complexes were only of academic interest due to the high cost of preparing the ligands. As an interesting aside, the magnesium complex of tetraphenylporphyrin was almost totally ineffective as a catalyst, leaving more CHHP than an uncatalyzed decomposition. The exceptionally high light output from the small amount of decomposition suggests that the 0.3×10^{-3} M (10 ppm) MgTPP is much more efficient in enhancing light output than the 10^{-3} M DBA used in all of the experiments. Green plants use closely related magnesium complexes to convert light to energy in photosynthesis [16]; in our reaction stored chemical energy is efficiently turned into light.

A series of cobalt and iron β -diketonate complexes bearing bidentate diamine ligands were relatively effective and inexpensive, but a new class of compounds were found to be even more effective. The cobalt and iron complexes of the bis(2-pyridylimino)isoindolinato ligand, referred to as BPI, displayed many of the features desired. This paper will deal only with the parent structure and analogs bearing methyl substituents on the pyridyl ring; in the shorthand nomenclature used, <u>3MeBPI</u> refers to the <u>Bis((3-Me</u>thyl-2-<u>Pyridyl)imino)I</u>soindolinato ligand.

The structure of this compound does not have the square planar array of nitrogen donors usually observed for cobalt complexes involved in oxidation catalysis. A single ligand affords a planar, tridentate array of nitrogen donors similar to a fragment of a phthalocyanine complex.

The structure of the bis ligand complex, bis[bis((3-methyl-2-pyridyl)imino]isoindolinato)cobalt(II), has been determined crystallographically and is shown in Fig. 8. The structure is distorted octahedral and very similar to that found for a related manganese complex [17]. Details of the structure determination are presented in Table 4. Results of the structure determina-





Fig. 8. Perspective view of the structure of bis[bis((3-methyl-2-pyridyl)imino)isoindolinato]cobalt(II).

tion are presented in Table 5, with selected bond distances and angles in Table 6.

Catalysis by $Co(BPI)_2$ complexes

The reaction of $Co(BPI)_2$ in the cyclohexylhydroperoxide decomposition screen is shown in Fig. 9. In contrast to the $Co(octoate)_2$, light emission built up and continued over a period of minutes. The total heat output was considerably higher than that observed for the $Co(octoate)_2$, and there was no exotherm upon addition of phosphite after 10 min. Thus, most of the CHHP was decomposed over the course of 10 min. An experiment with repeated injections of CHHP, shown in Fig. 10, demonstrated that there

Atom	x	у	z	B_{iso}^{a} (Å ²)
Co(1)	1976.6(5)	-1412.5(1)	2353.2(7)	2.0(1)
N(1)	340(3)	-1500(1)	3178(4)	2.0(1)
N(2)	472(3)	-1155(1)	5414(4)	2.4(1)
N(3)	-614(3)	-1889(1)	1359(4)	2.3(1)
N(4)	2510(3)	-1199(1)	4559(4)	2.3(1)
N(5)	1154(3)	-1640(1)	309(4)	2.3(1)
N(6)	3616(3)	-1329(1)	1526(4)	2.0(1)
N(7)	3540(3)	-725(1)	1041(4)	2.3(1)
N(8)	4530(3)	-1890(1)	1586(4)	2.1(1)
N(9)	1512(3)	-894(1)	1646(4)	2.3(1)
N(10)	2730(3)	-1908(1)	3012(4)	2.1(1)
C(1)	-65(4)	-1363(1)	4470(5)	2.4(1)
C(2)	-1303(4)	-1499(1)	4718(5)	2.4(1)
Ciaí	-1582(4)	-1722(1)	3584(5)	2.2(1)
C(4)	-552(4)	-1718(1)	2586(5)	2.2(1)
$\hat{\mathbf{C}(5)}$	-2073(4)	-1441(1)	5853(5)	3.3(1)
C(6)	-3165(5)	-1617(1)	5797(6)	4.0(2)
C(7)	-3480(4)	-1840(1)	4637(6)	3.6(1)
C(8)	-2672(4)	-1900(1)	3519(5)	3.1(1)
C(9)	1694(4)	-1071(1)	5488(5)	2.4(1)
C(10)	2086(4)	-859(1)	6706(5)	2.9(1)
C(11)	3315(4)	-813(1)	6993(5)	3.5(1)
C(12)	4149(4)	-962(1)	6099(6)	3.6(1)
C(13)	3708(4)	-1146(1)	4892(5)	3.0(1)
C(14)	175(4)	-1853(1)	218(5)	2.1(1)
C(15)	-137(4)	-2041(1)	-1080(5)	2.7(1)
C(16)	530(4)	-1984(1)	-2314(5)	3.1(1)
$\hat{C}(17)$	1490(4)	-1760(1)	-2249(5)	2.9(1)
C(18)	1766(4)	-1594(1)	-925(5)	2.7(1)
C(19)	4033(4)	-1023(1)	1055(5)	2.1(1)
C(20)	5258(4)	-1067(1)	472(5)	2.4(1)
C(21)	5539(4)	-1408(1)	573(4)	2.2(1)
C(22)	4496(4)	-1571(1)	1284(5)	2.1(1)
C(23)	6065(4)	-839(1)	-94(5)	3.1(1)
C(24)	7181(4)	-962(1)	-527(6)	3.6(1)
C(25)	7472(4)	-1300(1)	-388(5)	3.4(1)
C(26)	6648(4)	-1530(1)	145(5)	3.1(1)
C(27)	2348(4)	653(1)	1378(4)	2.3(1)
C(28)	2026(4)	-308(1)	1311(5)	2.6(1)
C(29)	818(4)	-223(1)	1484(5)	3.3(1)
C(30)	-50(4)	-471(1)	1660(5)	3.3(1)
C(31)	337(4)	-798(1)	1752(5)	2.9(1)
C(32)	3726(4)	-2056(1)	2462(5)	2.2(1)
C(33)	4036(4)	-2396(1)	2829(5)	2.4(1)
C(34)	3348(4)	-2563(1)	3825(5)	2.9(1)

Fractional coordinates (10^4) and isotropic thermal parameters of non-hydrogen atoms for the structure of [bis((3-methyl-2-pyridyl)imino)isoindolinato]cobalt(II)

(continued)

TABLE 5

Atom	x	у	Z	B_{iso}^{a} (Å ²)
C(35)	2379(4)	-2403(1)	4439(5)	3.1(1)
C(36)	2093(4)	-2082(1)	3988(5)	2.6(1)
C(37)	1156(5)	-704(1)	7644(6)	4.3(2)
C(38)	-1179(4)	-2283(1)	-1141(6)	4.4(2)
C(39)	2959(5)	-46(1)	1031(6)	4.5(2)
C(40)	5101(4)	-2567(1)	2190(5)	3.4(1)
C(41)	6982(5)	-644(1)	3948(7)	5.3(2)
C(42)	8022(5)	-558(1)	4748(6)	4.6(2)
C(43)	8236(5)	-229(1)	5133(6)	4.8(2)
C(44)	7386(7)	13(1)	4735(7)	6.1(2)
C(45)	6328(6)	-75(2)	3933(8)	6.5(2)
C(46)	6141(5)	-404(2)	3513(7)	5.8(2)

TABLE 5 (continued)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.



Fig. 9. Traces from CHHP decomposition by $Co(BPI)_2$.

is considerable residual activity left in the catalyst. The additional injections of peroxide were decomposed completely by the original charge of catalyst.

There is considerable evidence that only one bis(2-pyridylimino)isoindolinato ligand per cobalt is required for long-lived catalysts. The reaction of $Co(3MeBPI)_2$ with CHHP was followed spectrophotometrically. In a

TABLE 6

Selected bond distances (Å) and angles (°) in the structure of bis[bis((3-methyl-2-pyridyl)-imino)isoindolinato]cobalt(II)

Distances	(Å)	Angles	(°)
Co(1)-N(1)	2.000 (3)	N(1)-Co(1)-N(4)	85.7 (1)
Co(1) - N(4)	2.200 (4)	N(1) - Co(1) - N(5)	84.9 (1)
Co(1) - N(5)	2.188 (4)	N(1)-Co(1)-N(6)	179.5 (5)
Co(1) - N(6)	2.001 (3)	N(1) - Co(1) - N(9)	94.3 (1)
Co(1) - N(9)	2.201 (3)	N(1)-Co(1)-N(10)	94.1 (1)
Co(1) - N(10)	2.195 (3)	N(4) - Co(1) - N(5)	170.6 (1)
N(1)-C(1)	1.378 (5)	N(4)-Co(1)-N(6)	94.5 (1)
N(1) - C(4)	1.382 (5)	N(4)-Co(1)-N(9)	86.9 (1)
N(2)-C(1)	1.296 (5)	N(4) - Co(1) - N(10)	91.5 (1)
N(2)-C(9)	1.368 (5)	N(5)-Co(1)-N(6)	94.9 (1)
N(3)-C(4)	1.291 (5)	N(5)-Co(1)-N(9)	93.8 (1)
N(3) - C(14)	1.384 (5)	N(5)-Co(1)-N(10)	89.2 (1)
N(4) - C(9)	1.354 (5)	N(6) - Co(1) - N(9)	86.2 (1)
N(4) - C(13)	1.336 (5)	N(6)-Co(1)-N(10)	85.5 (1)
N(5)-C(14)	1.359 (5)	N(9)-Co(1)-N(10)	171.3 (1)
N(5) - C(18)	1.340 (5)	Co(1) - N(1) - C(1)	125.5 (3)
N(6)-C(19)	1.373 (5)	Co(1) - N(1) - C(4)	125.9 (3)
N(6)-C(22)	1.379 (5)	Co(1) - N(4) - C(9)	123.6 (3)
N(7)-C(19)	1.296 (5)	Co(1) - N(4) - C(13)	117.6 (3)
N(7) - C(27)	1,379 (5)	Co(1) - N(5) - C(14)	125.9 (3)
N(8)-C(22)	1.294 (5)	Co(1) - N(5) - C(18)	116.2 (3)
N(8) - C(32)	1.381 (5)	Co(1) - N(6) - C(19)	125.4 (3)
N(9)-C(27)	1.351 (5)	Co(1)-N(6)-C(22)	125.9 (3)
N(9)-C(31)	1.343 (5)	Co(1) - N(9) - C(27)	124.6 (3)
N(10)-C(32)	1.353 (5)	Co(1) - N(9) - C(31)	116.6 (3)
N(10) - C(36)	1.342 (5)	Co(1) - N(10) - C(32)	125.9 (3)
		Co(1) - N(10) - C(36)	116.0 (3)
		C(1)-N(1)-C(4)	108.6 (3)
		C(1)-N(2)-C(9)	125.8 (4)
		C(4) - N(3) - C(14)	125.2 (4)
		C(9) - N(4) - C(13)	118.0 (4)
		C(14) - N(5) - C(18)	117.4 (4)
		C(19) - N(6) - C(22)	108.7 (3)
		C(19) - N(7) - C(27)	125.5 (3)
		C(22) - N(8) - C(32)	125.2 (4)
		C(27) - N(9) - C(31)	117.7 (4)
		C(32) - N(10) - C(36)	118.1 (3)

reaction which is first order in CHHP, the UV/Vis spectrum changes from that of $Co(3MeBPI)_2$ to one which appears to be a combination of free H-3MeBPI and a cobalt-BPI complex in the 3⁺ oxidation state. The complex $[Co(3MeBPI)_2][PF_6]$ was prepared independently [18] for comparison. The rate constant for this catalyst conversion is on the same order as the rate constant for the catalytic decomposition of CHHP, about 6×10^{-4} s⁻¹ at 62.5 °C. Thus, for most of the catalytic reaction the catalyst is in the Co(III) oxidation state and has lost one ligand.



Fig. 10. Traces from repeated injections of CHHP into CoBPI₂.

To get some idea of the stabilities of various species in the 3MeBPI/ Co(octoate)₂ system, a spectrophotometric titration was carried out in cyclohexane. Co(octoate)₂ was added to a solution of H3MeBPI to keep the concentration of chromophore constant. Since the extinction coefficient of H3MeBPI is $\approx 24\,000$ at $\lambda_{max} = 397$ nm, the light absorption by Co(octoate)₂ (ϵ_{max} is ≈ 200 at 688 nm) makes little contribution to the spectra. The titration is pictured in Fig. 11. The isosbestic points indicate a clean reaction up to the addition of one equivalent of cobalt. After that point, there is little further reaction. Thus the stable species in the system appears to have the



Fig. 11. Spectrophotometric titration of H3MeBPI with $Co(octoate)_2$. Traces 1 - 7 are mol % of $Co(oct)_2$ added to H3MeBPI ranging from 0 to 96 in increments of 16%.

stoichiometry Co(3MeBPI)(octoate). The complex was easily isolated, as its solubility was considerably less than that of Co(3MeBPI)₂. The lower solubility is at first surprising, but the observation of IR bands at 1545 and 1423 cm⁻¹ attributable to bridging carboxylate groups suggests a dimeric or oligomeric structure. A carboxylate-bridged dimer would be similar to the chlorobridged structure proposed for $[Ru(4MeBPI)Cl_2]_2$ [19]. Further spectrophotometric titrations with a variety of other acids gave no evidence for displacement of more than one BPI ligand.

Cyclohexylhydroperoxide is decomposed quite effectively with a mixture of $Co(octoate)_2$ and free BPI ligands if they are intimately mixed prior to the catalytic reaction. It is presumed that they react to form Co(BPI)-(octoate) species *in situ*. Effective catalysis is not achieved if the $Co(octoate)_2$ and BPI ligand are mixed under the high dilution conditions found in the catalytic reactor. Apparently, even though there is a relatively high formation constant for the active complex, the $Co(octoate)_2$ is evidently converted to an unreactive form by the peroxides and other species present before the BPI ligand can react.

Cyclohexylhydroperoxide is also decomposed quite effectively with a mono-BPI derivative [20], $C_6H_5CO_2$)(OO-t-Bu).



The complex was isolated by reaction of CoBPI(benzoate) with t-butyl hydroperoxide, and may be a good representation of the active form of the catalyst. In laboratory experiments, this complex has the added advantage of good solubility.

The distribution of products from the $Co(BPI)_2$ -catalyzed decompositions is very similar to that observed in $Co(octoate)_2$ -catalyzed reactions. The ratio of cyclohexanone to cyclohexanol remains in the range of 0.4 to 0.7, as is usually observed for cobalt-catalyzed reactions. The observed range and concentration of byproducts are similar to those observed using a large excess of $Co(octoate)_2$ at the same temperature. In either case, this array of byproducts is considerably diminished from that observed for decompositions carried out using comparable concentrations of $Co(octoate)_2$ at the much higher temperatures required to obtain complete reaction. When the pyridyl group of the BPI ligand is changed to a thiazolyl group, it is reported [21] that the ratio of cyclohexanone to cyclohexanol is increased.

Conclusions

For a catalyst to be effective for the decomposition of cyclohexylhydroperoxide under conditions compatible with a commercial cyclohexane oxidation plant, it must not only be effective for the desired transformation, but also must be able to withstand the rigors of a free-radical reaction. The commercially used catalyst, cobalt octoate, is a very effective catalyst for a short time, but its active lifetime is limited so that relatively few molecules of cyclohexylhydroperoxide are converted per cobalt. A class of complexes based upon the ligand bis(2-pyridylimino)isoindoline has been found to yield moderately active but long-lived catalysts, making them effective for the lower temperature conversion of CHHP to cyclohexanol and cyclohexanone in high yield.

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