# Terminal and Internal Olefin Epoxidation with Cobalt(II) as the Catalyst: Evidence for an Active Oxidant Co(II)−Acylperoxo Species

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S Supporting Information

ABSTRACT: A simple catalytic system that uses commercially available cobalt(II) perchlorate as the catalyst and 3-chloroperoxybenzoic acid as the oxidant was found to be very effective in the epoxidation of a variety of olefins with high product selectivity under mild experimental conditions. More challenging targets such as terminal aliphatic olefins were also efficiently and selectively oxidized to the corresponding epoxides. This catalytic system features a nearly nonradical-type and highly stereospecific epoxidation of aliphatic olefin, fast conversion, and high yields. Olefin epoxidation by this catalytic system is proposed to involve a new reactive Co(II)−OOC(O)R species, based on evidence from $H_2^{18}O$-exchange experiments, the use of peroxyphenylacetic acid as a mechanistic probe, reactivity and Hammett studies, EPR, and ESI-mass spectrometric investigation. However, the O−O bond of a Co(II)−acylperoxo intermediate (Co(II)−OOC(O)R) was found to be cleaved both heterolytically and homolytically if there is no substrate.
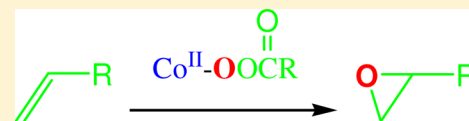
■ INTRODUCTION

Strong interest has been paid recently to catalytic oxidation of hydrocarbons by transition metal salts (or complexes) to produce commercially important products related to pharmaceuticals, flavors, fragrances, etc.[1] In particular, the epoxidation of terminal alkenes remains a challenge in organic synthesis, although the resulting 1,2-epoxides are versatile starting materials for the synthesis of more complicated molecules.[2] The epoxidation of terminal alkenes requires prolonged reaction times and shows a low conversion, because the low electron density of terminal olefins limits their reactivity for electrophilic oxygen transfer.[3] Therefore, the discovery of efficient and practical epoxidation methods under mild conditions and with inexpensive catalysts is an important goal in both academia and industry.

Much attention is currently being paid to the nature of reactive intermediates (M^{IV}=O, M^{V}=O, or M−OOR; M = Fe, Mn, Co) because they have been identified and/or implicated in the catalytic cycles of a number of heme and nonheme metal-containing enzymes that activate or evolve dioxygen.[4] Although their structures and reactivities have, to some extent, been well characterized and studied, the M−OOR species have been much less explored.[5] Recently, our and other groups suggested that, while the M^{IV}=O and M^{V}=O species are major reactive intermediates in the catalytic cycle, the species Mn−OOC(O)R is gradually involved in the oxidation reaction if the substrate is active or the concentration of the substrate is very high.[5] Moreover, we have, quite recently, suggested that (bpc)Co(III)−OOC(O)R shows partitioning between the heterolytic and homolytic cleavage of an O−O bond to afford Co(V)=O and Co(IV)=O intermediates, proposed to be responsible for stereospecific olefin epoxidation and radical-type oxidations, respectively. In contrast, under extreme

conditions, where the concentration of an active substrate is very high, Co(III)−OOC(O)R might be a possible reactive species for epoxidation.[6]

Iron and manganese porphyrins and related Schiff base complexes appear among the most successful oxidation catalysts for the epoxidation of a wide range of olefins and for the study of the reactive intermediates.[7] However, cost effectiveness and robustness are the major obstacles associated with the application of these metal complexes in industrial processes. Thus, there remains a need to develop an effective method based on inexpensive and nontoxic catalysts for the epoxidation of aliphatic internal and terminal alkenes under mild conditions.[2,3] In the search for efficient, less toxic, and low-cost oxidation catalysts, we have developed a simple catalytic system that shows efficient olefin epoxidation by 3-chloroperoxybenzoic acid (MCPBA).

Herein, we report a simple and highly efficient catalytic system that uses commercially available cobalt(II) perchlorate ($Co(ClO_4)_2$) (**1**) as the catalyst and MCPBA as the oxidant for the epoxidation of a wide range of olefins, especially including terminal olefins, with high yield and selectivity and fast conversion at ambient temperature. It is important to note that mechanistic studies of the olefin epoxidation reactions promoted by this catalyst provide evidence that a Co(II)−acylperoxo intermediate (Co(II)−OOC(O)R) shows partitioning between heterolytic and homolytic cleavage of the O−O bond to afford Co(III)=O and Co(IV)=O intermediates in the absence of substrate, whereas, in the presence of substrate, an adduct Co(II)−OOC(O)R might be a key intermediate for olefin epoxidation, proposed to be responsible for a nearly non-

Table 1. Olefin Epoxidations by MCPBA with Cobalt(II) Perchlorate (1) in CH$_3$CN at Room Temperature[a]

entry	substrate	product	conversion (%)[b]	yield (%)[b]
1	cyclopentene	epoxide	100	81.3 ± 1.4
2	cycloheptene	epoxide	100	∼100 (93)[c]
3	cyclooctene	epoxide	98.7 ± 1.1	97.9 ± 1.7 (92)[c]
4	cyclohexene	epoxide	95.3 ± 0.6	93.6 ± 2.7
		2-cyclohexen-1-ol		1.1 ± 0.1
		2-cyclohexenone		1.4 ± 0.1
5	1-hexene	epoxide	100	85.6 ± 2.7
6	1-octene	epoxide	93.6 ± 0.1	91.5 ± 0.2
7	cis-2-octene	cis-oxide	100	96.8 ± 1.6
		trans-oxide		2.9 ± 0.1
8	trans-2-octene	trans-oxide	100	∼100
9	cis-/trans-2-octene	cis-/trans-oxide		1.0
10	trans-1-phenyl-1-propene	1-phenylpropene oxide	100	99.8 ± 1.5
11	styrene	epoxide	98.2 ± 0.2	74.7 ± 1.4
		benzaldehyde		5.2 ± 0.4
		phenylacetaldehyde		2.7 ± 0.3
12	cis-stilbene	cis-oxide	100	49.0 ± 3.4
		trans-oxide		40.5 ± 2.5
		benzaldehyde		4.5 ± 0.7
13	trans-stilbene	trans-oxide	100	86.5 ± 2.2
		benzaldehyde		5.6 ± 0.5

[a]Reaction conditions: substrate (0.035 mmol), catalyst (1.0 × 10^{-3} mmol), MCPBA (0.05 mmol), solvent (1 mL, CH$_3$CN). [b]Based on substrate. [c]Isolated yields (see Experimental section for details).

radical-type and highly stereospecific epoxidation of aliphatic olefin. Evidence in support of this interpretation is based on reactivity and Hammett studies, EPR and ESI-mass spectrometric investigation, H$_2$^{18}O-exchange experiments, and the use of peroxyphenylacetic acid (PPAA) as a mechanistic probe.

RESULTS AND DISCUSSION

Catalytic epoxidation of various olefins using MCPBA as a terminal oxidant with cobalt(II) perchlorate as catalyst was performed in CH$_3$CN at room temperature (see the Experimental Section for details). CH$_3$CN was found to be the best solvent under the variety of conditions tested to establish the optimal reaction protocol. This mixture was stirred for 10 min at room temperature, although the epoxidation reactions were completed even within 1 min at room temperature (see the Supporting Information: Figure S1). Control experiments showed that the epoxide is stable and does not produce a diol under the conditions that were used in olefin epoxidation, and that direct substrate oxidation by MCPBA was negligible (Figure S1).[5m,n,8]

The epoxidation results are summarized in Table 1. Under the reaction conditions, the cyclic olefins cyclopentene, cycloheptene, and cyclooctene were oxidized to the corresponding epoxides in excellent yields (81−100%; entries 1−3), with conversions in the range of 99−100%. Interestingly, in contrast to the results obtained with alkyl hydroperoxides as the terminal oxidant in the presence of a variety of cobalt complexes,[9] the epoxidation reaction of cyclohexene produced predominantly the epoxidation product (93.6%; entry 4), along with trace amounts of cyclohexenone (1.4%) and cyclohexenol (1.1%), suggesting a nearly nonradical oxidation process.[10] Moreover, terminal alkenes, usually known as the least reactive olefins in metal-catalyzed epoxidations,[2,3] were readily oxidized to the corresponding epoxides with high yields (86% and 92%; entries 5 and 6).

cis-2-Octene was predominantly epoxidized to cis-2-octene oxide (96.8%), along with very small amounts of trans-2-octene oxide (2.9%), indicating that the catalytic epoxidation reaction occurs with high stereochemical retention (97%; entry 7).[11] trans-2-Octene was oxidized exclusively to trans-2-octene oxide and in high yield (∼100%). Competitive epoxidation of cis- and trans-2-octene gave a value of 1.0 for the ratio of cis- to trans-2-octene oxide (entry 9), indicating no preference for cis-olefin epoxidation to trans-olefin epoxidation by the intermediate generated in the reaction of cobalt(II) perchlorate (1) and MCPBA. This selectivity for aliphatic trans-olefin is unusual, because most of the metal-catalyzed systems described so far have shown a major reactivity for cis-olefins, and there are only two precedents to our knowledge for the reversal or the same of cis/trans selectivity upon epoxidizing aliphatic or aromatic olefins.[2b,5f] This value is nearly the same as for MCPBA epoxidation.[2b,8]

With styrene, the dominant reaction involved the formation of styrene oxide as the major product (74.7%) along with small amounts of phenylacetaldehyde (2.7%) and benzaldehyde (5.2%; entry 11). cis-Stilbene produced both cis-stilbene oxide (49.0%) and trans-stilbene oxide (40.5%) with minor amounts of benzaldehyde (4.5%; entry 12). trans-Stilbene was oxidized to trans-stilbene oxide (86.5%) and small amounts of benzaldehyde (5.6%; entry 13). It is of interest to note that only small amounts of benzaldehyde were produced in the aromatic olefin epoxidation reactions. The near-nonradical type of product distribution of these aromatic olefins implies to us that the peroxyl radical is minimally involved as the epoxidizing agent because these species would be expected to oxidize aromatic olefins to radical-induced rearranged products, based on previous reports.[5m,n,10] To the best of our knowledge, 1 is the most effective cobalt catalyst that affords high conversions and epoxide yields, minimal radical-type oxidation products, and a high stereospecificity of aliphatic olefin in the epoxidation of olefins by MCPBA.
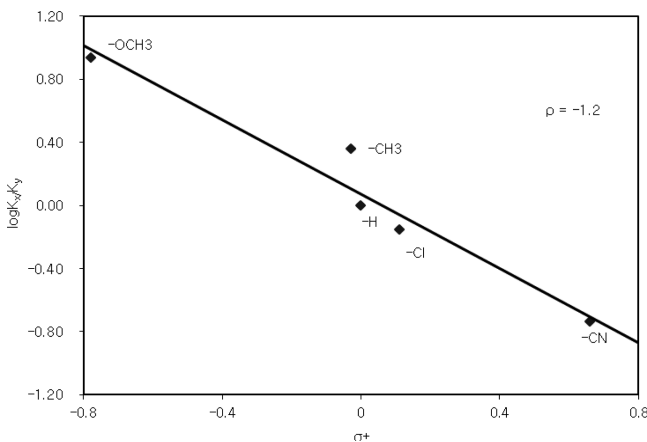
Next, we have carried out spectroscopic measurements by EPR to observe the possible reactive intermediates, Co^{II}–OOC(O)R and Co=O, and to determine the oxidation state of the cobalt ion during the catalytic reaction. As expected, the EPR spectrum of the frozen solution of $Co(ClO_4)_2$ indicated a typical high-spin cobalt(II) ($S = ^3/_2$). The reaction solution that was frozen 5 s and 1 min, respectively, after complex **1** was mixed with MCPBA at −40 °C or room temperature in MeCN was the same as the starting cobalt perchlorate (Figure S2). This suggests that the cobalt ion retained its +2 charge during the catalytic reaction and, moreover, that it is difficult to detect the possible reactive intermediates with this spectroscopic technique.

A further effort to detect the possible reactive species was carried out by electrospray ionization mass spectrometry experiments (ESI-MS) at low temperature (−40 °C). After 3 equiv of MCPBA were added to a solution of **1** (1 mM) in the absence of and in the presence of substrate cyclohexene, we tried to detect possible intermediates. However, we could not observe any of them, suggesting that the reactive intermediates might have very short lifetimes or be present in too low a concentration to be detected.

Therefore, a nearly minimal amount of free radical oxidation reaction, a high degree of stereospecificity of aliphatic olefin, and no change of the oxidation state of cobalt(II) ion during the catalytic reaction observed in our catalytic systems imply that the possible reactive species produced in these catalytic reactions might be two-electron oxidants Co^{IV}=O and Co^{II}–OOC(O)R.

Because an understanding of the nature and the mechanism of formation of the reactive intermediates is crucial in designing better catalysts, another investigation of the possible active species responsible for this epoxidation reaction was undertaken by examining the influence of substituent electronic effects on the rate of epoxidation using styrene and para-substituted styrenes. A Hammett plot analysis gave $\rho = -1.20$ which indicates that the active oxidant is electrophilic (Figure 1). The value is somewhat higher than those reported for the epoxidation of styrenes using MCPBA itself ($\rho = -0.76$; see Figure S3 of Supporting Information), Mn^{III} tetraphenylporphyrin ($\rho = -0.41$),[12] Mn(salen) ($\rho = -0.3$),[13] and $Mn(^{H,Me}PyTACN)(CF_3SO_3)_2$ ($\rho = -0.67$).[14]

Further mechanistic information arises from isotope labeling experiments, because ^{18}O-labeling experiments are commonly used in studies of reaction mechanism to address the origin of oxygen atoms found in oxidation products.[15] Epoxidation of cyclohexene by cobalt(II) perchlorate and MCPBA was conducted in the presence of a large excess of $H_2^{18}O$ in CH_3CN (~25−222 equiv; see Table S1 of Supporting Information and the Experimental Section for details). The product analysis by GC-MS showed no substantial ^{18}O-incorporation into cyclohexene oxide from $H_2^{18}O$, whereas cyclohexane hydroxylation showed 11% ^{18}O-incorporation of the cyclohexanol product in the previous study.[1e] These results could be explained by the relative rate difference of oxygen atom transfer and oxygen exchange, as previously reported,[15] or the direct epoxidation by Co^{II}–OOC(O)R species.

To distinguish homolytic vs heterolytic cleavage of the peracid O−O bond and to further examine the interplay between the O−O bond cleavage and substrate oxidation, PPAA as a mechanistic probe was used.[4r,5m,n,16] When the O−O bond of the coordinated anion (**2**) of PPAA undergoes heterolytic O−O bond cleavage (Scheme 1; pathway a) or

Scheme 1. Plausible Mechanism for the Formation of the Reactive Species from the Reaction of Peracids with Cobalt Complex
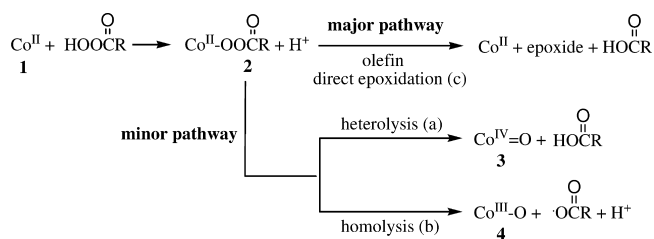
directly oxidizes substrate (pathway c), phenylacetic acid (PAA, **5**) is formed. In contrast, the homolytic cleavage of the O−O bond of **2** gives benzaldehyde (**6**), benzyl alcohol (**7**), and toluene (**8**) by a rapid β-scission of an acyloxyl radical generated from its homolytic cleavage (pathway b). First, a control experiment with PPAA as an oxidant under the same reaction conditions as MCPBA was carried out in the absence of substrate (Table 2; entry 1).

The heterolytic cleavage product, PAA (58% based on PPAA), and the homolytic cleavage products, benzaldehyde (15%) and benzyl alcohol (2.2%), were formed in a ratio of 77:23. These results suggest that heterolytic (77%) and homolytic (23%) O−O bond cleavage of **2** occur simultaneously to produce Co^{IV}=O (**3**) and Co^{III}=O (**4**) species. Next, we investigated the concentration effect of substrate, as previously shown by us and other groups.[5m,n,16] If the Co−OOR species was involved in the epoxidation reaction, then the ratio of **5** to (**6** + **7** + **8**) would vary according to the concentration of substrate employed.[16] We increased the concentration of substrate cyclohexene from 0 mM to 140 mM in the presence of cobalt(II) perchlorate. Importantly, the ratio of **5** to (**6** + **7** + **8**) varied from 3.4 (77:23) for 0 mM to 5.5 (85:15) for 20 mM to 7.5 (88:12) for 35 mM to 8.9 (90:10) for 70 mM to 11.4 (92:8) for 140 mM, as shown in Table 2 (entries 1−5). The fact that the ratio of **5** to (**6** + **7** + **8**) varies with substrate implies that there is an interaction between O−O bond cleavage and substrate oxidation, that is, the initially formed Co^{II}–acylperoxo intermediate contributes to the oxidation reaction, at least to some extent, as shown in Scheme 1 (pathway c).

Figure 1. Hammett plot for relative reactivities of styrene to para-substituted styrenes with cobalt(II) perchlorate.

Table 2. Yield (%) of Products Derived from Peroxyphenylacetic Acid (PPAA) Mediated by the Catalyst 1 in the Presence of Cyclohexene[a]

| entry | cyclohexene (mM) | heterolysis,[b] 5 | homolysis[b] | | | hetero (5)/homo (6 + 7 + 8) | oxidation products[c] | | |
			6	7	8		oxide	ol	one
1	0	58 ± 1	15 ± 1	2.2 ± 0.2	–	77/23 (3.4)	–	–	–
2	20	66 ± 8	9.5 ± 1.0	2.6 ± 0.2	–	85/15 (5.5)	88 ± 3[d]	1.2 ± 1.2[d]	0[d]
3	35	69 ± 2	7.0 ± 0.1	2.2 ± 0.1	–	88/12 (7.5)	78 ± 6[d]	1.8 ± 0.4[d]	2.3 ± 0.2[d]
4	70	74 ± 2	5.9 ± 0.1	2.4 ± 0.2	–	90/10 (8.9)	55 ± 1[b]	1.3 ± 0.1[b]	1.6 ± 0.1[b]
5	140	79 ± 2	4.8 ± 0.1	2.1 ± 0.6	–	92/8 (11.4)	61 ± 3[b]	2.0 ± 0.1[b]	2.0 ± 0.1[b]

[a]Reaction conditions: substrate (0−0.14 mmol), catalyst (1.0 × 10^{-3} mmol), PPAA (0.05 mmol), solvent (1 mL, CH$_3$CN). [b]Based on PPAA. 5, 6, 7, and 8 indicate phenylacetic acid, benzaldehyde, benzyl alcohol, and toluene, respectively. [c]ol, one, and oxide indicate cyclohexenol, cyclohexenone, and the cyclohexene oxide, respectively. [d]Based on cyclohexene.

Table 3. Yield (%) of Products Derived from Peroxyphenylacetic Acid (PPAA) Mediated by Cobalt(II) Perchlorate (1) in the Presence of 1-Hexene[a]

| entry | 1-hexene (mM) | heterolysis,[b] 5 | homolysis[b] | | | hetero (5)/homo (6+7+8) | oxidation product:[b] 1-hexene oxide |
			6	7	8		
1	0	58 ± 1	15 ± 1	2.2 ± 0.2	–	77/23 (3.4)	0
2	20	69 ± 8	12 ± 1	2.0 ± 0.2	–	83/17 (4.9)	96 ± 1[c]
3	35	74 ± 2	9.5 ± 0.2	1.6 ± 0.1	–	87/13 (6.7)	76 ± 4[c]
4	70	74 ± 1	8.3 ± 0.5	1.4 ± 0.2	–	88/12 (7.6)	60 ± 1[b]
5	140	78 ± 2	7.3 ± 0.1	1.1 ± 0.1	–	90/10 (9.3)	69 ± 1[b]

[a]Reaction conditions: substrate (0−0.14 mmol), catalyst (1.0 × 10^{-3} mmol), PPAA (0.05 mmol), solvent (1 mL, CH$_3$CN). [b]Based on PPAA. 5, 6, 7, and 8 indicate phenylacetic acid, benzaldehyde, benzyl alcohol, and toluene, respectively. [c]Based on 1-hexene.

Table 4. Terminal Olefin Epoxidations by MCPBA with Cobalt(II) Perchlorate (1) in CH$_3$CN at Room Temperature[a]

| entry | substrate | product | with 1 | | without 1 | |
			conversion (%)[b]	yield (%)[b]	conversion (%)[b]	yield (%)[b]
1	1-nonene	1,2-epoxynonane	73.7 ± 2.1	72.6 ± 2.4	5.6 ± 1.1	5.7 ± 1.0
2	1-decene	1,2-epoxydecane	88.6 ± 1.2	78.7 ± 1.1	10.0 ± 0.7	4.9 ± 0.2
3	1-undecene	1,2-epoxyundecane	90.7 ± 1.5	81.9 ± 1.7	14.9 ± 1.5	10.1 ± 0.1
4	1-dodecene	1,2-epoxydodecane	88.6 ± 2.2	77.5 ± 0.9	17.3 ± 2.0	12.4 ± 0.3
5	1-tridecene	1,2-epoxytridecane	88.7 ± 1.1	77.9 ± 1.7	27.1 ± 0.6	19.1 ± 1.3
6	1-tetradecene	1,2-epoxytetradecane	85.9 ± 3.6	73.6 ± 2.7	31.0 ± 1.7	17.1 ± 2.1
7	1-pentadecene	1,2-epoxypentadecane	90.6 ± 1.1	84.1 ± 1.0	31.1 ± 0.5	30.2 ± 1.0
8	vinylcyclohexane	vinylcyclohexane oxide	91.4 ± 4.0	80.5 ± 3.1	7.8 ± 1.3	7.7 ± 1.2

[a]Reaction conditions: substrate (0.035 mmol), catalyst (1.0 × 10^{-3} mmol), MCPBA (0.05 mmol), solvent (1 mL, CH$_3$CN). [b]Based on substrate.

These results suggest that the Co^{II}−OOC(O)R (2) might be a potent reactive species for epoxidation, as previously proposed for Mn(salen)-, Fe(porph)-, Re$_4$ cluster-supported Mn(saloph)-, Co(bpc)-, and Mn(bpc)-catalyzed epoxidation with MCPBA as oxygen donor.[5] In addition, this provides the first indirect evidence for the existence of the active Co^{II}−OOC(O)R (2) species, analogous to the active species ([(TMG$_3$tren)Co^{II}−OIPh]) proposed in the reaction of the cobalt(II) complex [Co^{II}(TMG$_3$tren)(OTf)](OTf) with PhIO.[17−19]

Next, we changed the substrate to one that is more difficult to oxidize (1-hexene), because it is proposed that, only when the substrate is active or the concentration of the substrate is high, the species M−OOC(O)R (2′) might be gradually involved in the epoxidation reaction.[5m,n,16] Surprisingly, a similar concentration dependence was also observed for 1-hexene (Table 3). That the difficult-to-oxidize substrate showed the same concentration dependence is the first case of such an observation, to the best of our knowledge, and again strongly suggests that Co^{II}−OOC(O)R (2) might be a major reactive species for epoxidation and have potential enough to oxidize the difficult-to-oxidize substrate.

Scheme 1 shows the most plausible mechanism for the formation of the reactive species responsible for olefin epoxidation that may well explain our present epoxidation reactions. Peracid reacts with a cobalt complex to form an initial cobalt(II)−acylperoxo intermediate (Co^{II}−OOC(O)R (2)), which then undergoes either a heterolytic (pathway a) or homolytic (pathway b) O−O bond cleavage to afford Co^{IV}=O (3), or Co^{III}=O (4) species if there is no substrate. However, when the substrate is present, the species Co−OOC(O)R (2) might be a major oxidant responsible for the epoxidation reaction (pathway c). More detailed mechanistic studies on the factors that influence heterolysis vs homolysis and the lifetime of Co^{II}−OOC(O)R (2) are in progress in our laboratory.

Terminal olefins are a particularly challenging class of substrate to epoxidize because of their relatively electron-deficient nature,[2,3] although the resulting 1,2-epoxides are versatile starting materials for the synthesis of more complicated molecules. Therefore, few simple catalytic systems for terminal olefin epoxidation exist that provide rapid conversion with high selectivity.[2,3] Because our catalytic system was proved to be very effective for terminal olefins (entries 5 and 6; Table 1), the present catalytic oxidation was applied to a

variety of terminal olefins. Representative results are shown in Table 4. They were rapidly epoxidized in good to excellent conversions (74−91%) and yields (73−84%), confirming that our catalytic system is also very effective for a variety of terminal olefins. For a comparison, in the absence of cobalt(II) perchlorate, the yields of epoxide (5−30%) were very low compared with those of epoxide in its presence within the same time interval (sixth and seventh columns in Table 4). Moreover, this catalytic system is a very rare case that shows very efficient terminal olefin epoxidations among a variety of cobalt catalysts.

CONCLUSION

In conclusion, the present work described a new method for the fast epoxidation of a wide range of olefins using MCPBA as terminal oxidant and using a commercially available $Co(ClO_4)_2$ as a catalyst. The selectivity for the formation of epoxides was generally excellent enough to afford epoxides in high yields almost irrespective of electronic and/or steric variation of the substrates. Moreover, this catalytic system features a minimally allylic oxidation reaction. In particular, terminal olefins, which are normally least reactive to electrophilic oxidants and typically require long reaction times, were found to undergo fast conversion and high yields. These results suggest that the system $Co(ClO_4)_2$/MCPBA in CH_3CN is particularly suitable to achieve high yields in alkene epoxidations under simple and mild conditions and that high activity and stability can be achieved without resorting to more extreme strategies such as very electron-deficient or complicated ligands.[3e]

Reactivity and Hammett studies, EPR and ESI-mass spectrometric investigation, $H_2{}^{18}O$ exchange experiments, and the use of PPAA as a mechanistic probe suggest that Co^{II}−OOC(O)R might be a key active intermediate in the epoxidation reaction. In contrast, the cobalt(II)−acylperoxo intermediate (Co^{II}−OOC(O)R) undergoes both a heterolytic and homolytic O−O bond cleavage to afford Co^{IV}=O and Co^{III}=O species, respectively, if there is no substrate. Future studies will focus on attempts to understand the exact nature of the reactive intermediate.

EXPERIMENTAL SECTION

General. Olefins, epoxides, cyclohexenol, cyclohexenone, acetonitrile, $Co(ClO_4)_2·6H_2O$, MCPBA (65%), and $H_2{}^{18}O$ (95% [18]O enrichment) were purchased and used without further purification. Peroxyphenylacetic acid (PPAA) was synthesized according to the literature method.[4r] Product analyses for olefin epoxidation, partition reaction of PPAA, and ^{18}O-incorporation reactions of cyclohexene oxide were performed on a mass spectrometer or a gas chromatograph equipped with a FID detector using a 30-m capillary column (DB-5 or HP-FFAP). EPR spectra were recorded on a spectrometer using 100-kHz field modulation. Electrospray ionization mass spectra (ESI-MS) were collected by infusing samples directly into the source using a manual method. The spray voltage was set at 4.2 kV and the capillary temperature at 80 °C.

Catalytic Olefin Epoxidations by Cobalt Catalyst with MCPBA. To a mixture of substrate (0.035 mmol), cobalt catalyst (0.001 mmol), and solvent (CH_3CN, 1 mL) was added MCPBA (0.05 mmol). The mixture was stirred for 10 min at room temperature, even though the reaction was complete within 1 min at room temperature (Figure S1). Reaction was monitored by GC/mass analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times, and the average product yields are presented. Product yields were based on substrate. In a competitive reaction of cis-2-octene and trans-2-octene, the concentration of the substrate was 0.20 mmol, respectively.

Isolated Yields. Cyclooctene oxide: Cyclooctene (244 μL, 1.75 mmol) and cobalt catalyst (0.05 mmol) were dissolved in 50 mL of CH_3CN. MCPBA (0.56 g, 2.5 mmol) wea added to the reaction solution. After 10 min, the reaction mixture was filtered through silica gel. Cyclooctene oxide was isolated from the filtrate through evaporation, yielding 0.20 g of product (92%). Cycloheptene oxide: The same method was used for the isolation of cycloheptene oxide. Cycloheptene oxide was isolated from the filtrate through evaporation, yielding 0.16 g of product (93%).

[18]O-Labeled $H_2{}^{18}O$ experiments. To a mixture of cyclohexene (0.01−0.02 mmol), cobalt catalyst (0.001 mmol), and $H_2{}^{18}O$ (10−40 μL, 0.556−2.22 mmol; 95% [18]O enriched, Aldrich Chemical Co.) in a dried solvent CH_3CN (1 mL) was added MCPBA (0.01 mmol). The reaction mixture was stirred for 3 min at room temperature and then directly analyzed by GC/mass spectrometry. The [16]O and [18]O composition in cyclohexene oxide were determined by the relative abundance of mass peaks at m/z = 99 for [16]O and m/z = 101 for [18]O. All reactions were run at least three times, and the average values are presented.

Analysis of the O−O Bond Cleavage Products by Cobalt Catalyst with PPAA. To a mixture of substrate (0−0.14 mmol), cobalt catalyst (0.001 mmol), and solvent (CH_3CN, 1 mL) was added PPAA (0.05 mmol). The mixture was stirred for 10 min at room temperature. Reaction was monitored by GC/mass analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times, and the average product yields are presented. Product yields were based on PPAA.

Competitive Reactions of Styrene and Para-Substituted Styrenes for Hammett plot. To a mixture of styrene (0.03 mmol) and para(X)-substituted styrene (0.03 mmol, X = OCH_3, CH_3, Cl, and CN), cobalt catalyst (0.001 mmol), and solvent (CH_3CN, 1 mL) was added MCPBA (0.05 mmol). The mixture was stirred for 10 min at room temperature. The amounts of styrenes before and after reactions were determined by GC. The relative reactivities were determined using the following equation: $k_x/k_y = \log(X_f/X_i)/\log(Y_f/Y_i)$ where X_i and X_f are the initial and final concentrations of substituted styrenes and Y_i and Y_f are the initial and final concentrations of styrene.[15b]

ASSOCIATED CONTENT

Ⓢ Supporting Information

[18]O-Labeled $H_2{}^{18}O$ experiments, control experiments with and without cobalt catalyst, X-band EPR spectra of $Co(ClO_4)_2$ and the reaction solution frozen after $Co(ClO_4)_2$ was mixed with MCPBA, and Hammett plot for relative reactivities of styrene to para-substituted styrenes by MCPBA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) (a) Lane, B. S.; Burgess, K. J. Am. Chem. Soc. 2001, 123, 2933−2934. (b) Ho, K.-P.; Wong, W.-L.; Lam, K.-M.; Lai, C.-P.; Chan, T. H.;

Wong, K.-Y. *Chem.—Eur. J.* **2008**, *14*, 7988−7996. (c) VanAtta, R. B.; Franklin, C. C.; Valentine, J. S. *Inorg. Chem.* **1984**, *23*, 4123−4125. (d) Komiya, N.; Noji, S.; Murahashi, S.-I. *Chem. Commun.* **2001**, 65−66. (e) Nam, W.; Ryu, J. Y.; Kim, I.; Kim, C. *Tetrahedron Lett.* **2002**, *43*, 5487−5490.

(2) (a) Dubois, G.; Murphy, A.; Stack, T. D. P. *Org. Lett.* **2003**, *5*, 2469−2472. (b) Garcia-Bosch, I.; Ribas, X.; Costas, M. *Adv. Synth. Catal.* **2009**, *351*, 348−352. (c) Duncan, D. C.; Chambers, R. C.; Hecht, E.; Hill, C. L. *J. Am. Chem. Soc.* **1995**, *117*, 681−691. (d) Collman, J. P.; Wang, Z.; Straumanis, A.; Quelquejeu, M. *J. Am. Chem. Soc.* **1999**, *121*, 460−461. (e) Tian, H.; She, X.; Xu, J.; Shi, Y. *Org. Lett.* **2001**, *3*, 1929−2931. (f) White, M. C.; Doyle, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 7194−7195. (g) Zuwei, X.; Ning, Z.; Yu, S.; Kunlan, L. *Science* **2001**, *292*, 1139−1141.

(3) (a) De Vos, D. E.; Sels, B. F.; Reynaers, M.; Subba Rao, Y. V.; P. Jacobs, A. *Tetrahedron Lett.* **1998**, *39*, 3221−3224. (b) Murphy, A.; Dubois, G.; Stack, T. D. P. *J. Am. Chem. Soc.* **2003**, *125*, 5250−5251. (c) Coperet, C.; Adolfsson, H.; Sharpless, K. B. *Chem. Commun.* **1997**, 1565−1566. (d) Sato, K; Aoki, M.; Ogawa, M.; Hashimoto, T.; Noyori, R. *J. Org. Chem.* **1996**, *61*, 8310−8311. (e) Murphy, A.; Pace, A.; Stack, T. D. P. *Org. Lett.* **2004**, *6*, 3119−3122. (f) Murphy, A.; Stack, T. D. P. *J. Mol. Catal. A: Chem.* **2006**, *251*, 78−88. (g) Taktak, S.; Ye, W.; Herrera, A. M.; Rybak-Akimova, E. V. *Inorg. Chem.* **2007**, *46*, 2929−2942. (h) Hao, E.; Wang, Z.; Jiao, L.; Wang, S. *Dalton Trans.* **2010**, *39*, 2660−2666.

(4) (a) Gunay, A.; Theopold, K. H. *Chem. Rev.* **2010**, *110*, 1060−1081. (b) Surendranath, Y.; Kanan, M. W.; Nocera, G. G. *J. Am. Chem. Soc.* **2010**, *132*, 16501−16509. (c) McEvoy, J. P.; Brudvig, G. W. *Chem. Rev.* **2006**, *106*, 4455−4483. (d) Mukhopadhyay, S.; Mandal, S. K.; Bhaduri, S.; Armstrong, W. H. *Chem. Rev.* **2004**, *104*, 981−4026. (e) Ray, K.; Lee, S. M.; Que, L., Jr. *Inorg. Chim. Acta* **2008**, *361*, 1066−1069. (f) Cho, J.; Jeon, S.; Wilson, S. A.; Liu, L. V.; E. Kang, A.; Braymer, J. J.; Lim, M. H.; Hedman, B.; Hodgson, K. O.; Valentine, J. S.; Solomon, E. I.; Nam, W. *Nature* **2011**, *478*, 502−505. (g) Bill, E.; Bothe, E.; Chaudhuri, P.; Chlopek, K.; Herebian, D.; Kokatam, S.; Ray, K.; Weyhermuller, T.; Neese, F.; Wieghardt, K. *Chem.—Eur. J.* **2005**, *11*, 204−224. (h) Comba, P.; Wunderlich, S. *Chem.—Eur. J.* **2010**, *16*, 7293−7299. (i) Company, A.; Prat, I.; Frisch, J. R.; Mas-Balleste, R.; Guell, M.; Juhasz, G.; Ribas, X.; Munck, E.; Luis, J. M.; Que, L., Jr.; Costas, M. *Chem.—Eur. J.* **2011**, *17*, 1622−1634. (j) De Visser, S. P.; Kumar, D.; Shaik, S. *J. Inorg. Biochem.* **2004**, *98*, 1183−1193. (k) Kurahashi, T.; Fujii, H. *J. Am. Chem. Soc.* **2011**, *133*, 8307−8316. (l) Sawant, S. C.; Wu, X.; Cho, J.; Cho, K.-B.; Kim, S. H.; Seo, M. S.; Lee, Y.-M.; Kubo, M.; Ogura, T.; Shaik, S.; Nam, W. *Angew. Chem.* **2010**, *44*, 8366−8370; *Angew. Chem., Int. Ed.* **2010**, *49*, 8190−8194. (m) Makhlynets, O. V.; Rybak-Akimova, E. V. *Chem.—Eur. J.* **2010**, *16*, 13995−14006. (n) Pan, Z.; Harischandra, D. N.; Newcomb, M. *J. Inorg. Biochem.* **2009**, *103*, 174−1818. (o) Lyakin, O. Y.; Bryliakov, K. P.; Talsi, E. P. *Inorg. Chem.* **2011**, *50*, 5526−5538. (p) Kumar, D.; Karamzadeh, B.; Sastry, G. N.; de Visser, S. P. *J. Am. Chem. Soc.* **2010**, *132*, 7656−7667. (q) Das, P.; Que, L., Jr. *Inorg. Chem.* **2010**, *49*, 9479−9485. (r) Lee, S. H.; Han, J. H.; Kwak, H.; Lee, S. J.; Lee, E. Y.; Kim, H. J.; Lee, J. H.; Bae, C.; Lee, S. N.; Kim, Y.; Kim, C. *Chem.—Eur. J.* **2007**, *13*, 9393−9398. (s) Shin, J. W.; Rowthu, S. R.; Hyun, M. Y.; Song, Y. J.; Kim, C.; Kim, B. G.; Min, K. S. *Dalton Trans.* **2011**, *40*, 5762−5773.

(5) (a) Franke, A.; Fertinger, C.; van Eldik, R. *Angew. Chem.* **2008**, *28*, 5316−5320; *Angew. Chem., Int. Ed.* **2008**, *47*, 5238−5242. (b) Nam, W.; Ho, R.; Valentine, J. S. *J. Am. Chem. Soc.* **1991**, *117*, 7052−7054. (c) Machii, K.; Watanabe, Y.; Morishima, I. *J. Am. Chem. Soc.* **1991**, *113*, 6691−6697. (d) Watanabe, Y.; Yamaguchi, K.; Morishima, I.; Takehiro, K.; Shimizu, M.; Hayakawa, T.; Orita, H. *Inorg. Chem.* **1991**, *30*, 2581−2582. (e) Adam, W.; Roschmann, K. J.; Saha-Moller, C. R.; Seebach, D. *J. Am. Chem. Soc.* **2002**, *124*, 5068−5073. (f) Nam, W.; Lim, M. H.; Lee, H. J.; Kim, C. *J. Am. Chem. Soc.* **2000**, *122*, 6641−6647. (g) Collman, J. P.; Zeng, L.; Brauman, J. I. *Inorg. Chem.* **2004**, *43*, 2672−2679. (h) Collman, J. P.; Zeng, L.; Decreau, R. A. *Chem. Commun.* **2003**, 2974−2975. (i) Bryliakov, K. P. D.; Babushkin, E.; Talsi, E. P. *J. Mol. Catal. A: Chem.* **2000**, *158*, 19−

35. (j) Mahammed, A.; Gross, Z. *J. Am. Chem. Soc.* **2005**, *127*, 2883−2887. (k) Ottenbacher, R. V.; Bryliakov, K. P.; Talsi, E. P. *Inorg. Chem.* **2010**, *49*, 8620−8628. (l) Kumar, A.; Goldberg, I.; Botoshansky, M.; Buchman, Y.; Gross, Z. *J. Am. Chem. Soc.* **2010**, *132*, 15233−15245. (m) Lee, S. H.; Xu, L.; Park, B. K.; Mironov, Y. V.; Kim, S. H.; Song, Y. J.; Kim, C.; Kim, Y.; Kim, S. J. *Chem.—Eur. J.* **2010**, *16*, 4678−4685. (n) Song, Y. J.; Lee, S. H.; Park, H. M.; Kim, S. H.; Goo, H. G.; Eom, G. H.; Lee, J. H.; Lah, M. S.; Kim, Y.; Kim, S.-J.; Lee, J. E.; Lee, H.-I.; Kim, C. *Chem.—Eur. J.* **2011**, *17*, 7336−7344.

(6) Song, Y. J.; Hyun, M. Y.; Lee, J. H.; Lee, H. G.; Kim, J. H.; Jang, S. P.; Noh, J. Y.; Kim, Y.; Kim, S.-J.; Lee, S. J.; Kim, C. *Chem.—Eur. J.* **2012**, *18*, 6094−6101.

(7) (a) Lane, B. S.; Burgess, K. *Chem. Rev.* **2003**, *103*, 2457−2473. (b) McGarrigle, E. M.; Gilheany, D. G. *Chem. Rev.* **2005**, *105*, 1563−1602. (c) Kryatov, S. V.; Rybak-Akimova, E. V. *Chem. Rev.* **2005**, *105*, 2175−2226. (d) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Jr. *Chem. Rev.* **2004**, *104*, 939−986. (e) Nam, W. *Acc. Chem. Res.* **2007**, *40*, 522−531. (f) Dolphin, D.; Traylor, T. G.; Xie, L. Y. *Acc. Chem. Res.* **1997**, *30*, 251−259. (g) Kim, C.; Watanabe, Y. *Encyclopedia of Catalysis* **2002**, 593−643. (h) Jin, N.; Ibrahim, M.; Spiro, T. G.; Groves, J. T. *J. Am. Chem. Soc.* **2007**, *129*, 12416−12417. (i) Lansky, D. E.; Goldberg, D. P. *Inorg. Chem.* **2006**, *45*, 5119−5125. (j) Yin, G.; McCoemick, J. M.; Buchalova, M.; Danby, A. M.; Rodgers, K.; Day, V. W.; Smith, K.; Perkins, C. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *Inorg. Chem.* **2006**, *45*, 8052−8061. (k) Zhang, R.; Newcomb, M. *Acc. Chem. Res.* **2008**, *41*, 468−477. (l) Nam, W.; Kim, I.; Kim, Y.; Kim, C. *Chem. Commun.* **2001**, 1262−1263.

(8) Kim, C.; Traylor, T. G.; Perrin, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 9513−9516.

(9) (a) Chavez, F. A.; Mascharak, P. K. *Acc. Chem. Res.* **2000**, *33*, 539−545. (b) Chavez, F. A.; Briones, J. A.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1999**, *38*, 1603−1608. (c) Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005**, *105*, 2329−2363.

(10) (a) Shing, T. K. M.; Yeung, Y. Y.; Su, P. L. *Org. Lett.* **2006**, *8*, 3149−3151. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapter 2.

(11) We have examined the stability of *cis*-epoxide in the presence of catalyst **1**. *cis*-Epoxide was not converted to *trans*-epoxide over 40 min under the reaction conditions.

(12) Bortolini, O.; Meunier, B. *Perkin Trans. 2* **1984**, 1967−1970.

(13) Adam, W.; Mock-Knoblauch, C.; Saha-Moller, C. R.; Herderich, M. *J. Am. Chem. Soc.* **2000**, *122*, 9685−9691.

(14) Garcia-Bosch, I.; Company, A.; Fontrodona, X.; Ribas, X.; Costas, M. *Org. Lett.* **2008**, *11*, 2095−2098.

(15) (a) Groves, J. T.; Lee, J.; Marla, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 6269−6273. (b) Han, J. H.; Yoo, S.-K.; Seo, J. S.; Hong, S. J.; Kim, S. K.; Kim, C. *Dalton Trans.* **2005**, 402−406. (c) Bernadou, J.; Meunier, B. *Chem. Commun.* **1998**, 2167−2173. (d) Nam, W.; Lim, M. H.; Moon, S. K.; Kim, C. *J. Am. Chem. Soc.* **2000**, *122*, 10805−10809. (e) Yin, G.; Buchalova, M.; Danby, A. M.; Perkins, C. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *Inorg. Chem.* **2006**, *45*, 3467−3474. (f) Nam, W.; Valentine, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 1772−1778.

(16) (a) Suzuki, N.; Higuchi, T.; Nagano, T. *J. Am. Chem. Soc.* **2002**, *124*, 9622−9628. (b) Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1986**, *25*, 4808−4810.

(17) Pfaff, F. F.; Kundu, S.; Risch, M.; Pandian, S.; Heims, F.; Pryjomska-Ray, I.; Haack, P.; Metzinger, R.; Bill, E.; Dau, H.; Comba, P.; Ray, K. *Angew. Chem.* **2011**, *123*, 1749−1753; *Angew. Chem., Int. Ed.* **2011**, *50*, 1711−1715.

(18) TMG$_3$tren = tris[2-(*N*-tetramethylguanidyl)ethyl]amine.

(19) Quite recently, a Mn^{II}−OOC(O)R species was also proposed as a reactive species in the olefin epoxidation reaction by a manganese-based hybrid mesoporous material with MCPBA: Tang, J.; Zu, Y.; Huo, W.; Wang, L; Wang, J.; Jia, M.; Zhang, W.; Thiel, W. R. *J. Mol. Catal. A: Chem.* **2012**, *355*, 201−209.