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Oxygen−Oxygen Bond Homolysis in a Novel Titanium(IV) Alkylperoxide Complex, $Cp_2Ti(OO^tBu)Cl$

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Metal-catalyzed oxidations by peroxides are of importance from industrial to biological chemistry.[1] Metal ions can bind peroxides, can activate them toward oxidation of substrates, and can catalytically decompose them. Examples include the large-scale epoxidation of propylene by alkyl hydroperoxides, the metal-mediated autoxidation of cyclohexane,[1a−c,2] and the Sharpless titanium-tartrate chiral epoxidation.[3] Metal-peroxide species are key intermediates in the reactions of a variety of oxidizing metalloenzymes,[1d−f] and a variety of biomimetic metal catalysts have been developed.[1,4] In many cases, the metal-peroxide complex is thought to undergo O−O bond cleavage to give a metal-oxo species that is the reactive oxidant.[5] This O−O bond cleavage, whether homolytic or heterolytic, is thought to be facilitated by oxidation of the metal center (eq 1).[6]

$$L_nM^{n+}OOR \rightleftharpoons L_nM^{(n+1)}O + {\bullet}OR \quad L_nM^{(n+2)}O^+ + {}^-OR \qquad (1)$$

We report here a new d^0 titanocene *tert*-butylperoxide complex and mechanistic studies of its decomposition that implicate O−O bond homolysis *without* metal oxidation.

Cp_2TiCl_2 (Cp = η^5-C_5H_5) reacts with $NaOO^tBu$ in THF at −20 °C to give $Cp_2Ti(OO^tBu)Cl$ (**1**) which is extracted into hexane and isolated in 84% yield (eq 2).[7,8] This synthesis follows the briefly

$$Cp_2TiCl_2 + NaOO^tBu \rightarrow Cp_2Ti(OO^tBu)Cl\ (\mathbf{1}) + NaCl \qquad (2)$$

reported in situ generation of $Cp_2Zr(OO^tBu)Cl$.[9] Related $Cp^*_2Hf(OO^tBu)R$ complexes have been prepared by protolytic reactions.[10] Complex **1** has been characterized by ^1H and ^{13}C NMR, IR, high-resolution mass spectrometry, elemental analysis, and X-ray diffraction (Figure 1).[7,8,11] The complex has a typical bent-metallocene geometry and is similar to the structures of $Cp_2Ti(OEt)Cl$[12] and $Cp^*_2Hf(OO^tBu)Et$.[10] The Ti−O distance in **1** of 1.9090(14) Å is close to the Ti−ethoxide distance of 1.855(2) Å.[12] The peroxide distances of 1.4668(19) in **1** and 1.489(12) Å in the hafnium derivative[10] are typical of peroxides.[13] The *tert*-butylperoxo ligand in **1** is bound through only one oxygen, as indicated by the long Ti···O(2) distance (2.952(2) Å) and the open Ti(1)−O(1)−O(2) angle (121.5(1)°). This contrasts with the one other structurally characterized titanium alkylperoxide, which has an η^2-^{t}BuOO ligand.[14]

Complex **1** decomposes in CD_2Cl_2 at 300 K to give *tert*-butyl alcohol and a number of Cp-containing products in small yield, including Cp_2TiCl_2 (Table 1). Decay of **1** follows first-order kinetics (by ^1H NMR), proceeding more slowly in cyclohexane ($t_{1/2}$ = 2.1 h) and benzene (1.0 h) than in CD_2Cl_2 (0.5 h). An Eyring plot of rate constants for decomposition from 273 to 313 K in CD_2Cl_2 gives $\Delta H^{\ddagger}$ = 27 ± 2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 15 ± 5 eu. Preliminary

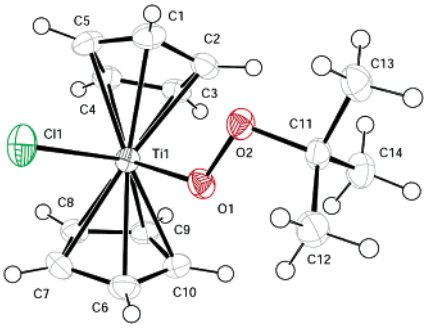

Figure 1. ORTEP diagram of **1**, with thermal ellipsoids drawn at 30% probability. Selected data not included in the text: Ti(1)−Cl(1), 2.3956(6) Å; O(1)−Ti(1)−Cl(1), 97.31(4)°; C(11)−O(2)−O(1), 107.65(13)°; Cl(1)−Ti(1)−O(1)−O(2), −79.7(1)°.

Table 1. Products and Rate Constants for Reactions of $Cp_2Ti(OO^tBu)Cl$ with PR_3 in CD_2Cl_2[a]

reaction	R_3PO	R_2PO^tBu	^{t}BuOH[b]	Me_2CCH_2	^{t}BuCl	Cp_2TiCl_2	k_{obs} (×10^{-4} s^{-1})
1			96%	n/o	n/o	5%	4.1(2)
1 + 1PPh_3	98%	n/o	24%	59%	12%	50%	5.9(3)
1 + 5PPh_3	96%	n/o	29%	56%	11%	48%	7.2(6)
1 + 20PPh_3	97%	n/o	26%	57%	11%	44%	6.9(5)
1 + 20^nBu_3SnH			98%	n/o	n/d	4%	2.8(8)
1 + 1PPh_3 + 20^nBu_3SnH	23%	n/o	72%	n/o	n/d	4%	5.2(6)
1 + 1PEt_3	n/o	∼95%[c]	3%	tr	tr	27%	1.6(7)
1 + 1$P(OPh)_3$	n/o	50%	28%	8%	3%	28%	3.2(7)
1 + CBr_4			95%	tr	tr	34%	3.5(5)

[a] n/d = not determined; n/o = not observed by ^1H or $^{31}P\{^1H\}$ NMR; tr = detected in trace amount (<1%). [b] Hydroxyl resonance not observed in ^1H or ^2H NMR. [c] Et_2PO^tBu grows in to a maximum of 70% yield but is concurrently consumed; the yield of Et_2PO^tBu and its apparent decay products is ∼95%.

results indicate that cyclohexene and norbornene do not react directly with **1** because the rate of decomposition is unchanged and epoxide products are not observed.

Complex **1** reacts with 1 equiv of PPh_3 in CD_2Cl_2 to quantitatively form Ph_3PO (98%), as expected for a peroxide complex.[1] Cp_2TiCl_2 (50%) and a number of other Cp-containing species are formed, with the total integrated Cp intensity being roughly constant. The ^{t}Bu groups in **1** are converted to *tert*-butyl alcohol (23%), isobutylene (59%), and ^{t}BuCl (12%). In contrast, solutions of **1** with 1 equiv of PEt_3 do not form any Et_3PO (by $^{31}P\{^1H\}$ NMR). Instead, this reaction yields the phosphinite Et_2PO^tBu, which was identified by ^{31}P NMR, mass spectrometry, and independent synthesis.[15]

The only reasonable pathway to form Et_2PO^tBu from PEt_3 is by addition of ^{t}BuO• (eq 3). This reaction is very rapid (k_3 = 1.2 × 10^9 M^{-1} s^{-1}) and quantitatively forms Et_2PO^tBu.[16] P^nBu_3 traps ^{t}BuO• to give 20% ^{n}Bu_3PO and 80% ^{n}Bu_2PO^tBu (eq 4).[17]

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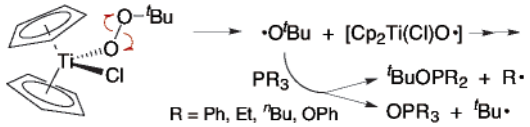
Scheme 1



Decomposition of **1** in the presence of 1 equiv of P^nBu_3 in CD_2Cl_2 yields this same ratio of phosphine oxide to phosphinite by ^{31}P NMR integration, confirming the intermediacy of $^tBuO\bullet$ in the decay of **1**.[8] Reaction of **1** with $P(OPh)_3$ gives the phosphite $^tBuOP(OPh)_2$ without any phosphate $(PhO)_3PO$. Given the known reactivity of $P(OPh)_3$ with oxyl radicals (eq 5),[18] this shows that peroxyl radicals are not present.

$$PEt_3 + {}^tBuO\bullet \rightarrow [Et_3{}^{\bullet}PO{}^tBu] \rightarrow Et_2PO{}^tBu + Et\bullet \quad (3)$$

$$P{}^nBu_3 + {}^tBuO\bullet \rightarrow \rightarrow 0.8\{{}^nBu_2PO{}^tBu + {}^nBu\bullet\} + 0.2\{{}^nBu_3PO + {}^tBu\bullet\} \quad (4)$$

$$OP(OPh)_3 \xleftarrow{{}^tBuOO\bullet} P(OPh)_3 \xrightarrow{{}^tBuO\bullet} {}^tBuOP(OPh)_2 \quad (5)$$

The reaction of **1** with PPh_3 is also consistent with the involvement of $^tBuO\bullet$, as $PPh_3 + {}^tBuO\bullet$ gives exclusively Ph_3PO and $^tBu\bullet$.[19] The formation of isobutylene and ^{t}BuCl supports the intermediacy of $^tBu\bullet$. As additional confirmation of this pathway, $^nBu_3SnH$ was used as a competitive trap for $^tBuO\bullet$. The yield of Ph_3PO is reduced from 98 to 23% when 20 equiv of $^nBu_3SnH$ is added to an equimolar solution of **1** and PPh_3. This is consistent with $^nBu_3SnH + {}^tBuO\bullet \rightarrow {}^nBu_3Sn\bullet + {}^tBuOH$ being 9 times slower than $PPh_3 + {}^tBuO\bullet \rightarrow Ph_3PO + {}^tBu\bullet$ (2.2×10^8 vs 1.9×10^9 M^{-1} s^{-1}).[19,20] The lower yield of PPh_3 is not due to direct reaction of **1** and $^nBu_3SnH$, as the decay of **1** is not accelerated by $^nBu_3SnH$ (Table 1).

The rate constant for decay of **1** is only slightly affected by the presence of additives (Table 1). Increasing the concentration of PPh_3 causes small increases in *k*, but not linearly, and the presence of PEt_3 or $^nBu_3SnH$ actually slows the decomposition of **1**. The small changes in *k* are most likely a result of the differing stoichiometry of the reactions, changing the amount of **1** that reacts with product radicals such as $^tBu\bullet$.

The above results clearly show that $^tBuO\bullet$ is an intermediate in the decomposition of **1**. This most likely occurs by rate-limiting O−O bond homolysis (Scheme 1). While a complete mechanistic description is hampered by the multiple titanium species formed, homolysis is supported by the positive $\Delta S^{\ddagger}$ for decomposition. Other routes to $^tBuO\bullet$ are difficult to reconcile with the data. Radical chain processes related to the Haber−Weiss mechanism[1a] are unlikely because of the simple first-order kinetic behavior and because decomposition is only marginally slowed by reductive ($^nBu_3SnH$) or oxidative (CBr_4) traps. Ti−O bond homolysis[21] to give $^tBuOO\bullet$ is ruled out by the lack of formation of $(PhO)_3PO$ or Et_3PO.[22] Intramolecular induced homolysis, such as attack of a Cp ligand on the peroxide, is unlikely because of the positive $\Delta S^{\ddagger}$ and the apparent lack of consumption of Cp ligands.

Because titanium compounds are increasingly used as catalysts for peroxide oxidations,[23] the lack of oxygen atom transfer reactivity of **1** is unexpected. Most likely it is sterically difficult for **1** to adopt the reactive η^2-peroxide conformer. Surprisingly, the "$Cp_2Ti(O\bullet)Cl$" generated by homolysis does not rapidly oxidize PEt_3 to Et_3PO.

In summary, **1** undergoes O−O bond homolysis at 300 K. This is surprising because the Ti(IV) center is d^0 and cannot be oxidized. As noted above, all previous clear examples of homolytic cleavage of metal peroxide complexes are facilitated by oxidation of the metal center. It is not clear why decomposition of **1** is so much more facile than homolysis of $^tBuOO^tBu$: at 300 K, $\Delta G^{\ddagger} = 22$ kcal mol^{-1} for **1** versus 34 kcal mol^{-1} for $^tBuOO^tBu$.[24] Homolytic decomposition of d^0 peroxides may not be unique to **1**, as an isolated siloxide-ligated $TiOO^tBu$ complex decomposes to ^{t}BuOH, and a titanium silasesquioxane complex is reported to react with ^{t}BuOOH to give ^{t}BuOH and a trace of $^tBuOO^tBu$.[25] Work is continuing both on the chemistry of **1** and on generating more reactive peroxide compounds.

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Supporting Information Available: Synthetic, spectroscopic, kinetic, and X-ray crystallographic information for **1** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) *Caution*: Solid samples of **1** can be explosive. NMR: ^1H (499 MHz) (C_6D_6, 20 °C, δ), 5.98 (s, 10H, C_5H_5), 1.17 (s, 9H, $C(CH_3)_3$). HR-MS (EI^+): calculated 302.05530 *m/z*; measured 302.05544. Anal. Calcd: C, 55.62%; H, 6.34%. Found: C, 55.71%; H, 6.33%.
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