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Nonredox Metal-Ions-Enhanced Dioxygen Activation by Oxidovanadium(IV) Complexes toward Hydrogen Atom Abstraction

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S Supporting Information

ABSTRACT: Dioxygen activation toward efficient catalysis at ambient temperature is still a big challenge for industrial oxidations, while it proceeds smoothly in nature. This work presents an example of that adding nonredox metal ions as Lewis acid can enhance dioxygen activation by oxidovanadium(IV) complex, [V^{IV}(O)Cl(TPA)]PF₆ (where TPA is tris-[(2-pyridy)methyl]amine), which leads to efficient hydrogen abstraction at ambient temperature, whereas, in the absence of a Lewis acid, the catalytic hydrogen abstraction of the oxidovanadium(IV) complex is very sluggish. Ultraviolet-visible light (UV-vis), electron paramagnetic resonance (EPR), mass, and nuclear magnetic resonance (NMR) studies have provided informative clues to indicate the interaction between the Lewis acid and vanadium complexes, including assisting the dissociation of the chloride from the oxidovanadium(IV) complex, interacting with the vanadium oxido group, and stabilizing the vanadium(V) superoxo species. These interactions enhanced the dioxgyen activation efficiency of oxidovanadium(IV)



complex, and improved the hydrogen abstraction ability of vanadium(V) oxido species, which leads to efficient hydrogen abstraction in a catalytic process. A brief mechanism has also been proposed for dioxygen activation toward hydrogen abstraction by an oxidovanadium(IV) complex.

INTRODUCTION

Although the activation of dioxygen at ambient temperature and its application in industrial oxidations are greatly attractive, until now, most industrially aerobic oxidations are performed at elevated temperature, which generally proceeds via a radical chain process and leads to non- or low-selective products. In contrast, utilization of dioxygen in nature proceeds smoothly and is highly selectively at ambient temperature.¹⁻³ To unveil the mechanism of dioxygen activation by redox enzymes, many synthetic models having metal oxido,^{4–10} hydroxo,^{11–18} hydroperoxide,^{19–24} peroxo,^{25–28} or superoxo^{29–32} functional groups were extensively developed, and direct synthesis of these complexes from dioxygen had also been achieved.³³⁻³⁷ Generally, the formation of the redox metal superoxo species is the first step in dioxygen activation. Delivering one electron to this superoxo species can generate the peroxo species, and its next protonation results in the hydroperoxide species which can further go through the O-O bond cleavage to generate the active metal oxido species. This is a typical haem enzymatic mechanism.^{38,39} Alternatively, abstracting one H atom (concerted proton and electron transfer) from the substrate by the metal superoxo species can also lead to the hydroperoxide product directly, and this is the pathway of many non-haem enzymes.^{40,41} However, the hydrogen abstract ability of those iron(III)-superoxo moieties in non-haem enzymes and related synthetic models is relatively weak, which can only abstract hydrogen from an activated C-H bond.⁴¹⁻

$$V(IV) + O_2 \rightleftharpoons V(V) - O_2^{\bullet-}$$
(1)

In the literature, vanadium(V) superoxo species was generally proposed to be the first step in many vanadiumbased chemical transformations, such as aerobic oxidation. For examples, in vanadium-dependent oxidation of NADP(H), it was proposed that vanadium(IV) was autoxidized to vanadium-(V) with superoxide radical formation, which next initiated the free-radical chain oxidation of NAD(P)H,^{44,45} and in Cp₂V-(acac)₂ initiated lipid peroxidation, oxidovanadium(IV) was also first oxidized by dioxygen to the vanadium(V) superoxo species via an inner sphere electron transfer.⁴⁶ In particular, Krüger and Mayer independently reported that the vanadium-(V) superoxo species are capable of hydrogen abstraction from robust THF having a bond dissociation energy (BDE_{CH}) of 92 kcal/mol, in which Krüger's vanadium(V) superoxo species was prepared by electrochemical oxidation of the corresponding vanadium(V)-oxido-peroxo complex,³¹ whereas, in Mayer's studies, the vanadium(V) superoxo species was proposed to occur in direct reduction of dioxygen via an oxidovanadium(IV) complex.²⁵ However, the hydrogen abstraction from THF by a vanadium(V) superoxo species is very sluggish, and the induction period could be long, on the order of days. In addition to the relatively weak hydrogen abstraction ability, the sluggish hydrogen abstraction rate of the vanadium(V)

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Figure 1. Structures of (i) $[V^{IV}(O)Cl(TPA)]^+$, (ii) $[V^{IV}(O)(OTf)(TPA)]^+$, (iii) $[V^{V}(O)_2(TPA)]^+$, (iv) $[V^{V}(O)(O_2)(TPA)]^+$, and (v) $[\{V^{IV}(O)(TPA)\}_2(\mu-O)]^{2+}$.

superoxo species is also possibly related to its low concentration in solution, because of the unfavorable equilibrium in the initial binding of O₂ to the oxidovanadium-(IV) complex (eq 1). Accordingly, driving the chemical equilibrium from oxidovanadium(IV) and dioxygen to the vanadium(V) superoxo complex at ambient temperature may have opportunities to offer efficient dioxygen activation, which can be applied in a catalytic process. In the literature, Fukuzumi even reported that the binding of a Lewis acid to the superoxide, $O_2^{\bullet-}$, could make electron transfer from (TPP) Co to O₂ become possible, that is, driving dioxygen activation through stabilizing the $O_2^{\bullet-}$ product; Borovik also reported Ca²⁺ promoted dioxygen activation by their manganese(II) and iron(II) complex to generate heterobimetallic complexes with μ -O bridge.⁴⁷⁻⁴⁹ Together with our understanding on Lewisacid-promoted catalytic oxidations by redox catalysts, 50-57 here, we present a Lewis-acid-enhanced dioxygen activation via an oxidovanadium(IV) complex, which leads to efficient hydrogen atom abstraction, whereas, in the absence of Lewis acid, the hydrogen abstraction efficiency is very low.

EXPERIMENTAL SECTION

Materials. All chemical reagents are commercially available and used without further purification, except for acetonitrile, which was dried by molecular sieves prior to use. 1,4-Cyclohexadiene (CHD), cyclooctene, methyl phenyl sulfide, methyl phenyl sulfoxide, benzyl phenyl sulfide, and triphenylphosphine were purchased from Alfa Aesar. Sodium trifluoromethanesulfonate (NaOTf), magnesium trifluoromethanesulfonate (Mg(OTf)₂), and scandium trifluoromethanesulfonate (Sc(OTf)₃) came from Aldrich. Other trifluoromethanesulfonates, including Zn(OTf)₂, Ca(OTf)₂, Al(OTf)₃, Y(OTf)₃, and Yb(OTf)₃, came from local chemical companies. Tris-[(2-pyridy)-methyl]amine (TPA) with corresponding vanadium complexes [V^{IV}(O)Cl(TPA)]PF₆, and [V^V(O)(C2)(TPA)]PF₆ were synthesized according to the literature.^{58–61} [V^{IV}(O)(OTf)(TPA)]PF₆ was obtained by replacing the Cl⁻ ion of [V^{IV}(O)Cl(TPA)]PF₆ with AgOTf in acetone solution (Figure 1).

Instrumentation. UV-vis spectra were collected on Analytikjena specord 205 UV–vis spectrometer. Mass spectra were determined by a Bruker SolariX 7.0T spectrometer. Gas chromatography–mass spectroscopy (GC-MS) analysis was performed on an Agilent, Model 7890A/5975C spectrometer, and NMR spectra were obtained on a Bruker AV400 spectrometer. Electron paramagnetic resonance (EPR) experiments were conducted at 298 K on a Bruker A200 spectrometer. Quantitative analysis of H_2O_2 was performed using a high-performance liquid chromatography (HPLC) (Model FL-2200) system that was equipped with a UV detector and $C_{\rm 18}$ column (250 mm \times 4.6 mm).

General Procedure for Hydrogen Abstraction through Dioxygen Activation by $[V^{IV}(O)Cl(TPA)]PF_6$ in the Presence of Al(OTf)₃. In a typical experiment, $[V^{IV}(O)Cl(TPA)]PF_6$ (1.67 mg, 0.003 mmol), Al(OTf)₃ (2.85 mg, 0.006 mmol), and 1,4-cyclohexadiene (24.0 mg, 0.3 mmol) were dissolved in 3 mL of acetonitrile in a glass tube, and then the reaction solution was magnetically stirred at 303 K in a water bath with a dioxygen balloon for 5 h. After the reaction, the quantitative analysis was performed by GC with the internal standard method. Control experiments using $[V^{IV}(O)Cl-(TPA)]PF_6$ or Al(OTf)₃ alone were carried out in parallel, and similar control experiments using commercial acetonitrile in place of dry acetonitrile or using freshly distilled CHD. Reactions were performed at least in duplicate, and average data were used in discussions.

General Procedure for the Hydrogen Abstraction Kinetics through Dioxygen Activation by $[V^{IV}(O)Cl(TPA)]PF_6$ in the Presence of Al(OTf)₃. In a typical experiment, $[V^{IV}(O)Cl(TPA)]PF_6$ (1.67 mg, 0.003 mmol), Al(OTf)₃ (2.85 mg, 0.006 mmol) and 1,4-cyclohexadiene (24.0 mg, 0.3 mmol) were dissolved in 3 mL of acetonitrile in a glass tube. The reaction solution then was magnetically stirred at 303 K in water bath with dioxygen balloon. The product analysis was performed by GC using the internal standard method at set intervals. Control experiments using $[V^{IV}(O)Cl(TPA)]$ -PF₆ or Al(OTf)₃ alone were carried out in parallel. Similar kinetics were also conducted using $[V^{V}(O)cl(TPA)]$ PF₆. In addition, the hydrogen abstraction kinetics was also recorded using a UV-vis spectrometer at set intervals.

General Procedure for Stoichiometric Hydrogen Abstraction by $[V^{V}(O)(O_{2})(TPA)]PF_{6}$ with Al(OTf)₃. In a typical experiment, $[V^{V}(O)(O_{2})(TPA)]PF_{6}$ (10.68 mg, 0.02 mmol), Al(OTf)₃ (18.96 mg, 0.04 mmol) and 1,4-cyclohexadiene (1.6 mg, 0.02 mmol) were dissolved in 1 mL of deaerated acetonitrile in a glass tube. The reaction solution then was magnetically stirred at 303 K in water bath under an argon atmosphere. The product analysis was performed by GC using the internal standard method.

General Procedures for Sulfoxidation and Epoxidation Reactions by $[V^{IV}(O)Cl(TPA)]PF_6$ in the Presence of Al(OTf)₃. In a typical experiment, $[V^{IV}(O)Cl(TPA)]PF_6$ (1.67 mg, 0.003 mmol), Al(OTf)₃ (2.85 mg, 0.006 mmol), thioanisole, or cyclooctene (0.075 mmol) were dissolved in 3 mL of acetonitrile in a glass tube. The reaction solution then was magnetically stirred at 303 K in a water bath with a dioxygen balloon. The product analysis was performed by GC using the internal standard method. The similar experiments by adding 1,4-cyclohexadiene (24.0 mg, 0.3 mmol) to the above reaction solution were also conducted.

RESULTS AND DISCUSSION

Lewis-Acid-Promoted Dioxygen Activation toward Hydrogen Abstraction by the Oxidovanadium(IV) **Complex.** As shown in eq 1, because of the instability of the metal superoxo species, the low efficiency of dioxygen activation by redox metal ions at ambient temperature (for example, oxidovanadium(IV)) is plausibly related to the unfavorable equilibrium between the metal complex and dioxygen (eq 1). Therefore, driving the equilibrium from the left to right may facilitate dioxygen activation. Fukuzumi even found that the presence of the Lewis acid may stabilize the superoxide species, thus promoting the dioxygen activation by Co(TPP).^{47,48} In present studies, using CHD as a substrate, catalytic dioxygen activation toward hydrogen abstraction by $[V^{IV}(O)Cl(TPA)]PF_6$ complex was tested in dry acetonitrile, a list of nonredox metal ions were scanned as Lewis acid to promote dioxygen activation, and the results were summarized in Table 1. It can be seen that, in the absence of Lewis acids, the

Table 1. Lewis-Acids-Promoted Hydrogen Abstraction from 1,4-Cyclohexadiene by $[V^{IV}(O)Cl(TPA)]PF_6$ under Dioxygen^a

entry	Lewis acid	temperature (K)	time (h)	conversion (%)	yield (%)
1		313	24	30.3	10.4
2	NaOTf	313	24	32.2 (20.3)	14.5 (3.2)
3	$Mg(OTf)_2$	313	24	62.2 (21.3)	44.8 (3.1)
4	$Ca(OTf)_2$	313	24	70.1 (19.1)	52 (3.3)
5	$Ba(OTf)_2$	313	16	71.3 (17.4)	59.2 (3.0)
6	$Zn(OTf)_2$	313	16	99.2 (16.5)	75.2 (2.9)
7	$Y(OTf)_3$	313	8	99.3(12.1)	86.3(3.2)
8	Yb(OTf) ₃	313	8	99.5(13.2)	82.3(2.8)
9	$Al(OTf)_3$	313	8	99.6(11.1)	83.3 (3.2)
10	$Sc(OTf)_3$	313	8	99.4 (11.2)	85.3 (2.8)
11		303	24	12.3	2.9
12	$Y(OTf)_3$	303	8	6.5	2.9
13	Yb(OTf) ₃	303	8	6.7	2.8
14	$Al(OTf)_3$	303	5	92.8 (6.2)	82.5 (2.9)
15	$Sc(OTf)_3$	303	5	93.2 (5.9)	86.2 (3.0)

^{*a*}Conditions: CH₃CN, 3 mL; 1,4-cyclohexadiene, 100 mM; [V^{IV}(O)-Cl(TPA)]PF₆, 1 mM; Lewis acid, 2 mM; under dioxygen balloon. The yields were based on 1,4-cyclohexadiene conversion, and the data shown in parentheses represent oxidations using Lewis acid alone in control experiments.

 $[V^{IV}(O)Cl(TPA)]PF_6$ complex alone is very sluggish in dioxygen activation, leading to only 30.3% conversion of CHD with a 10.4% yield of benzene after 24 h at 313 K. Adding Lewis acids can sharply improve the hydrogen abstraction, leading to a high yield of benzene. For example, adding 2 equiv of Y(OTf)₃ leads to 99.3% conversion with 86.3% yield after 8 h at 313 K, and 2 equiv of Zn(OTf)₂ lead to 99.2% conversion with 75.2% yield after 16 h at 313 K. In particular, adding Al(OTf)₃ or Sc(OTf)₃ can provide 92.8% or 93.2% conversion with 82.5% or 86.2% yield of benzene, respectively, within 5 h at 303 K. In control experiments, Lewis acid alone has no catalytic activity, and the minor benzene detected in the reaction mixture is due to the impurity of the commercial CHD, which naturally contains $\sim 3\%$ benzene. Sometimes, commercial CHD may contain a trace amount of peroxide, which may affect the oxidation reaction; here, the use of freshly distilled CHD as the substrate was also tested, which provided

similar results (conversion, 91.6%; yield, 83.6%; in control experiments: conversion = 6.1% and yield = 3.0%) as those using commercial CHD as substrate (Table 1, entries 1 and 14), indicating the potential trace peroxide in CHD does not affect the reaction in this system. In another control experiment using commercial acetonitrile in place of dry acetonitrile, it also provided results similar to those from dry acetonitrile, that is, a conversion of 90.6% vs 92.8%, and a yield of 80.2% vs 82.5%, indicating that the trace water does not affect the reaction seriously if it were there in dry acetonitrile. Apparently, adding Lewis acid to [V^{IV}(O)Cl(TPA)]PF₆ can sharply improve its dioxygen activation ability, leading to efficient hydrogen abstraction from CHD, and the promotional effect is highly dependent on the Lewis acidity, that is, a stronger Lewis acid provided a higher efficiency.

Hydrogen abstract kinetics further confirmed the promotional effect of Lewis acid to the oxidovanadium(IV) catalyst. As shown in Figure 2, in the absence of $Al(OTf)_3$, the



Figure 2. Kinetics of hydrogen abstraction from 1,4-cyclohexadiene by $[V^{IV}(O)Cl(TPA)]PF_6$ in the absence (red line) or presence (black line) of Al(OTf)₃. Conditions: CH₃CN, 3 mL; 1,4-cyclohexadiene, 100 mM; $[V^{IV}(O)Cl(TPA)]PF_6$, 1 mM; Al(OTf)₃, 2 mM, under dioxygen balloon, 303 K. (Legend: (\blacksquare) conversion of 1,4-cyclohexadiene; (\bigcirc) yield of benzene.)

oxidovanadium(IV) complex is very sluggish for hydrogen abstraction from CHD, while in the presence of Al(OTf)₃, it greatly accelerated the hydrogen abstraction rate, even though it still demonstrated an induction period of ~ 2 h. Figure 3 displayed the influence of Al(III)/V(IV) ratio on hydrogen abstraction from CHD. One may see that, increasing the ratio from 0 to 1 sharply improves the catalytic efficiency, and further increasing the ratio to 4 just slightly improves the efficiency, implicating an 1:1 ratio of interaction between Al(III) and V(IV) in catalysis. Similar promotional effects were also observed with other vanadium complexes including $[V^{IV}(O)]$ - $(OTf)(TPA)]PF_{6}$, $[V^{V}(O)_{2}TPA]PF_{6}$, $[V^{V}(O)(O_{2})TPA]PF_{6}$ and $[{V^{IV}(O)(TPA)}_2(\mu-O)](PF_6)_2$ (Table 2), in which $[V^{V}(O)_{2}(TPA)]PF_{6}$ demonstrated a very similar induction period to that of $[V^{IV}(O)Cl(TPA)]PF_{6}$, while $[V^{V}(O)(O_{2})-$ TPA]PF₆ has an induction period as long as 10 h (Figure S1(b)) in the Supporting Information). However, in the absence of Al(OTf)₃, all of these vanadium complexes demonstrated a very sluggish catalytic efficiency in hydrogen abstraction with dioxygen. Importantly, a comparable long induction period of $[V^{V}(O)_{2}TPA]PF_{6}$ and $[V^{IV}(O)Cl(TPA)]PF_{6}$ complexes with



Figure 3. Influence of Al(III)/V(IV) ratio on hydrogen abstraction from 1,4-cyclohexadiene. Conditions: CH₃CN, 3 mL; CHD, 100 mM; $[V^{IV}(O)Cl(TPA)]PF_{6}$, 1 mM; under dioxygen balloon, 303 K, 5 h.

 Table 2. Al(OTf)₃-Promoted Hydrogen Abstraction from

 1,4-Cyclohexadiene by Other Vanadium Complexes^a

entry	vanadium source	conversion (%)	yield (%)
1	[V ^{IV} O(OTf)(TPA)]PF ₆	95.2 (7.2)	85.1 (2.9)
2	$[V^{V}(O)_{2}(TPA)]PF_{6}$	95.0 (6.5)	88.1 (2.8)
3 ^b	$[V^{V}(O)(O_{2})(TPA)]PF_{6}$	94.6 (12.5)	83.5 (2.9)
4 ^{<i>c</i>}	$[{V^{IV}(O)(TPA)}_2(\mu-O)](PF_6)_2$	92.2 (6.4)	84.1 (2.9)
^a Condi	tions, CH CN 2 mL, 14 gralak	avadiana 100 mM	1. wanadium

"Conditions: CH₃CN, 3 mL; 1,4-cyclohexadiene, 100 mM; vanadium complex, 1 mM; Al(OTf)₃, 2 mM; under dioxygen balloon, 303 K, 5 h. The data given in parentheses represent the use of vanadium complexes alone as control experiments. ^bThe reaction time is 24 h. $c[{V^{IV}(O)(TPA)}_2(\mu-O)](PF_6)_2$, 0.5 mM.

much longer induction period of $[V^V(O)(O_2)TPA]PF_6$ clearly supports that the formation of the vanadium(V) oxido, $V^V = O$, or vanadium(V) peroxo, $V^V - (O_2)$ functional group is not the origin of the induction period in oxidovanadium(IV)-catalyzed hydrogen abstraction.

Interaction between Al^{3+} and Vanadium Complexes. The interaction of Al^{3+} with the $[V^{IV}(O)Cl(TPA)]PF_6$ complex was first evidenced by mass spectra studies. As shown in Figure 4a, $[V^{IV}(O)Cl(TPA)]PF_6$ in acetonitrile revealed one major mass peak at 392.05912, corresponding to the $[V^{IV}(O)Cl-(TPA)]^+$ species. Adding $Al(OTf)_3$ to this solution disclosed



Figure 4. Mass spectra of (a) $[V^{IV}(O)Cl(TPA)]PF_6$ (1 mM) and (b) $[V^{IV}(O)Cl(TPA)]PF_6$ (1 mM) and $Al(OTf)_3$ (2 mM) in acetonitrile.

one new peak at 506.04231, corresponding to the $[V^{IV}(O)$ -(OTf)(TPA)]⁺ species (Figure 4b), indicating the dissociation of the chloride from the coordination sphere of oxidovanadium-(IV) complex. In UV-vis studies, adding Al(OTf)₃ also caused the absorbance change of $[V^{IV}(O)Cl(TPA)]PF_6$ in acetonitrile. As the Al(OTf)₃/ $[V^{IV}(O)Cl(TPA)]^+$ ratio increased from 0 to 2, the absorbance at \sim 731 nm decreased and shifted to 690 nm gradually; meanwhile, the absorbance at ~574 and 363 nm also decreased (Figure 5a). However, the spectrum generated in situ by adding Al^{3+} to $[V^{IV}(O)Cl(TPA)]PF_6$ is still different from that of authentic $[V^{IV}(O)(OTf)(TPA)]PF_6$, whose absorption also changed in the presence of Al³⁺ (Figure 5b), implicating that Al³⁺ not only assists the removal of chloride from $[V^{IV}(O)Cl(TPA)]^+$ species, but also has interaction with the resulting $[V^{IV}(O)(OTf)(TPA)]^+$ species. The final absorbance at ca. 350 nm is very different in Figures 5a and 5b; this is possibly, but not conclusively, related to their different ion components in the solution. For example, in Figure 5a, there exists Al(III)-bound chloride, which may interact with the vanadium(IV) species, whereas in Figure 5b, no chloride exists.

For the C_{4v} symmetric oxidovanadium(IV) complexes, it is generally regarded that the unpaired electron is in the d_{xy} orbital, and its transition to $[d_{xz}, d_{yz}](\nu_1), d_{x^2-y^2}(\nu_2)$, and $d_{z^2}(\nu_3)$ happens with increasing energies.^{62,63} In the case of the $[V^{IV}(O)Cl(TPA)]^+$ species, the weak visible absorptions at ~731 and 574 nm can be respectively assigned to the ν_1 and ν_2 bands, and the ν_3 band has a low intensity at ~363 nm, which has been obscured by the intensive charge transfer transition occurring at the same region (Figure 5a). In the literature, it was reported that the O^{2-} group competes for the same vacant d_{xz} V orbital with the Cl⁻ group in the $[V^{IV}(O)Cl(TPA)]^+$ species.^{64,65} Accordingly, the UV-vis change at ~731 nm is likely to be related to the interaction of Al^{3+} with both O^{2-} and Cl⁻ groups. In investigating the interaction of a Brönsted acid, such as p-toluenesulfonic acid and HClO₄, with the V^{IV}=O group in the $[V^{IV}(O)Cl(TPA)]$ complex, Sasaki even reported that an excess of *n*-Bu₄NCl is essential to avoid the dissociation of the chloride from the $[V^{IV}(O)Cl(TPA)]^+$ species. Here, adding strong Lewis acids such as Al³⁺ causes dissociation of the chloride from the [V^{IV}(O)Cl(TPA)]⁺ species; meanwhile, it may also interact with the V^{IV}=O group, as well as the proton (Brönsted acid) disclosed by Sasaki.⁵⁹ Similar interaction of Al^{3+} with vanadium(V) oxido group was also indicated for the dioxidovanadium(V) complexes (vide infra).

The interaction between $[V^{IV}(O)Cl(TPA)]^+$ species and Al^{3+} was also indicated in EPR studies. For the paramagnetic mononuclear oxidovanadium(IV) complex, it has a characteristic eight-line signal for the oxidovanadium(IV) species in the EPR spectrum, and increasing the density of the unpaired electron on the oxidovanadium(IV) center would lead to an increased A_0 value.^{66,67} In Figure 6, curve (a) displays the EPR signal of [V^{IV}(O)Cl(TPA)]PF₆ in acetonitrile at 298 K, revealing its characteristic eight-line signal with the g_0 value of 1.984 and a hyperfine coupling constant of $A_0 = 89.6 \times 10^{-4}$ cm^{-1} . Adding 1 equiv of Al(OTf)₃ to the above solution leads to the formation of a new oxidovanadium(IV) species with the decay of the original one, while adding 2 equiv of $Al(OTf)_3$ caused complete transformation of the original oxidovanadium-(IV) species to the new one having the g_0 value of 1.986 with $A_0 = 99.8 \times 10^{-4}$ cm⁻¹. The increased A_0 value was likely the result of the interaction of the $[V^{IV}(O)Cl(TPA)]^+$ species with Al³⁺.^{68,69} Similar EPR signal changes were also observed by adding Al(OTf)₃ to $[V^{IV}(O)(OTf)(TPA)]PF_6$, in which



Figure 5. UV-vis absorption change by adding Al(OTf)₃ to (a) $[V^{IV}(O)Cl(TPA)]PF_6$ and (b) $[V^{IV}(O)(OTf)(TPA)]PF_6$, using 3 mL of CH₃CN at 298 K. Conditions for panel (a): $[V^{IV}(O)Cl(TPA)]PF_6 = 1$ mM, Al(OTf)₃ = 0, 0.25, 0.5, 1, and 2 mM; conditions for panel (b): $[V^{IV}(O)(OTf)(TPA)]PF_6 = 1$ mM, Al(OTf)₃ = 0 and 1 mM.



Figure 6. EPR spectra of $[V^{IV}(O)Cl(TPA)]PF_6$ with Al(OTf)₃. Conditions: 3 mL of CH₃CN, 298 K. $[V^{IV}(O)Cl(TPA)]PF_6$, 1 mM, and Al(OTf)₃ content = (a) 0, (b) 1 mM, and (c) 2 mM. A_0 values: (a) 89.6 × 10⁻⁴ cm⁻¹, (b) 95.8 × 10⁻⁴ cm⁻¹, and (c) 99.8 × 10⁻⁴ cm⁻¹.

 $[V^{IV}(O)(OTf)(TPA)]PF_6$ alone shows the g_0 value of 1.984 with $A_0 = 92.3 \times 10^{-4}$ cm⁻¹, while adding 1 equiv of Al³⁺ changed it to a g_0 value of 1.984 with $A_0 = 95.8 \times 10^{-4}$ cm⁻¹ (Figure S2 in the Supporting Information). The final EPR spectra differences between the one observed by adding 2 equiv of Al(OTf)₃ to the $[V^{IV}(O)Cl(TPA)]^+$ species (Figure 6) and that by adding 1 equiv of Al(OTf)₃ to the $[V^{IV}(O)(OTf)-(TPA)]$ species (Figure S2) are possibly related with their different ion components in the solution, which causes the coordination environment difference of the vanadium(IV) species, as well as those in UV-vis studies (*vide supra*).

Similar to the $[V^{IV}(O)Cl(TPA)]^+$ species, Al^{3+} may also interact with the $[V^{V}(O)_2(TPA)]^+$ species via the V^V =O functional group, and in the literature, it was reported that adding a Brönsted acid leads to the formation of the $V^{V}(O)(OH)$ species in certain dioxidovanadium(V) complexes.^{70,71} Here, as shown in Figure S3(a) in the Supporting Information, the UV-vis spectrum of $[V^{V}(O)_2(TPA)]PF_6$ changed gradually by adding 2 equiv of $Al(OTf)_3$, and an orange precipitate was generated after 1 h, indicating the direct interaction between the dioxidovanadium(V) complex with Al^{3+} in acetonitrile. This precipitate is not the vanadium(V) oxide, because it is soluble in dimethylsulfoxide (DMSO) and dimethyl formamide (DMF), and no free TPA ligand is detected via thin layer chromatography (TLC) analysis. In another test, adding 3 equiv of HOTf as a Brönsted acid to the $[V^{V}(O)_{2}(TPA)]PF_{6}$ solution also leads to the formation of precipitate, but it is much slower and much less than that of adding Al(OTf)₃. In addition, the interaction was further confirmed by the Al³⁺-accelerated reduction of vanadium(V) through hydrogen abstraction from CHD. As shown in Figure 7, in the absence of Al(OTf)₃, there is no significant



Figure 7. EPR spectra of $[V^V(O)_2(TPA)]PF_6$ reacting with 1,4-cyclohexadiene in the absence (black) and presence (red) of Al(OTf)₃. Conditions: CH₃CN, 3 mL; CHD, 100 mM; $[V^V(O)_2(TPA)]PF_6$, 1 mM; Al(OTf)₃, 2 mM; 303 K, 10 min.

vanadium(IV) signal observed by EPR detection after mixing $[V^{V}(O)_{2}(TPA)]PF_{6}$ with CHD in acetonitrile at 303 K. In the presence of Al(OTf)₃, the clean vanadium(IV) signals occur in 10 min, indicating the Al³⁺-promoted hydrogen abstraction by the V^V=O moiety. The two generated vanadium(IV) species can be tentatively assigned to the $[V^{IV}(O)(OTf)(TPA)]^{+}$ species and its interaction with the Al(OTf)₃, as well as that in Figure S2. In the literature, similar enhanced hydrogen atom abstraction ability of the active metal oxido moieties from C–H bond was even observed by Lau, in which adding a Lewis acid clearly accelerated cyclohexane oxidation by permanganate.^{72,73}

For the $[V^{V}(O)(O_{2})(TPA)]PF_{6}$ complex, it was reported that the presence of Brönsted acid leads to the protonation on the peroxo group,⁶¹ and the proton tending to activate the peroxo group in the vanadium(V) center was also proposed in many vanadium haloperoxidase (VHPO) models.^{74,75} Here, although the UV-vis absorption of $[V^{V}(O)(O_{2})(TPA)]PF_{6}$ in CH₃CN just changed slightly by adding Al(OTf)₃ (Figure



Figure 8. UV-vis changes of $[V^{IV}(O)Cl(TPA)]PF_6$ with $Al(OTf)_3$ in the presence of 1,4-cyclohexadiene under dioxygen. Conditions: CH₃CN, 3 mL; CHD, 100 mM; $[V^{IV}(O)Cl(TPA)]PF_6$, 1 mM; $Al(OTf)_3$, 2 mM; under a dioxygen balloon, 303 K.

S3(b)), the interaction was clearly indicated by ²⁷Al NMR studies. As shown in Figure S5 in the Supporting Information, Al(OTf)₃ alone displayed a major chemical shift at ~ 0.5 ppm, indicating that Al^{3+} has an octahedral coordination environment. 56,76,77 By adding different amounts of $[V^{V}(O)(O_{2})-$ (TPA)]PF₆, it changed to a broadened resonance gradually, clearly indicating the interaction between $[V^{V}(O)(O_{2})(TPA)]^{+}$ species and Al³⁺. This interaction was further supported by Al³⁺-enhanced stoichiometric hydrogen abstraction from CHD (Table S1 in the Supporting Information). In the absence of Al(OTf)₃, the $[V^{V}(O)(O_{2})(TPA)]^{+}$ species alone is incapable of hydrogen abstraction from CHD under argon at 303 K, while adding Al(OTf)₃ provided 31.0% yield of benzene within 24 h. In addition, this observation also supports that the $V^{V}(O_{2})$ functional group is very sluggish in hydrogen abstraction, even though it was proposed as the active species in VHPO and many other oxidation reactions.^{78,7}

In the complementary experiments with other Lewis acids, it was found that adding Sc(OTf)₃ caused similar dissociation of the chloride from the coordination sphere of the $[V^{IV}(O)Cl$ -(TPA)]⁺ species, which was evidenced by similar UV-vis and EPR changes to those of adding $Al(OTf)_3$; however, adding $Y(OTf)_3$ or others did not cause the dissociation of the chloride at ambient temperature (303 K) (Figure S6 in the Supporting Information). These interactions between different Lewis acids and oxidovanadium(IV) complex are remarkably linked with their promotional effects in dioxygen activation toward hydrogen abstraction (Table 1). That is, adding Al^{3+} and Sc^{3+} can efficiently promote hydrogen abstraction with the $[V^{IV}(O)]$ -Cl(TPA)]PF₆ catalyst at 303 K; for other Lewis acids, higher temperature with longer reaction time is needed to achieve similar activity, implying that the dissociation of the chloride may facilitate the attack of dioxygen on the oxidovanadium(IV) center to initiate dioxygen activation. As evidence, when $[V^{IV}(O)Cl(TPA)]PF_6$ and $Al(OTf)_3$ were premixed for 1 h in advance, the hydrogen abstraction from CHD demonstrated a relatively faster kinetic behavior, as shown in Figure S7 in the Supporting Information.

Roles of Lewis Acid in Dioxygen Activation by the Oxidovanadium(IV) Complex. It has been reported that oxidovanadium(IV) complexes can be oxidized by dioxygen to vanadium(V)-oxido-peroxo species in the presence of THF or other ethereal solvents.^{25,31,59,80,81} Here, similar conversion was also observed for the $[V^{IV}(O)Cl(TPA)]PF_6$ complex in the presence of Al(OTf)₃ and CHD in acetonitrile. As reported, the $[V^{IV}(O)Cl(TPA)]^+$ species has very weak absorption at 574 nm

 $(\varepsilon = 25 \text{ M}^{-1} \text{ cm}^{-1})$ and 731 nm ($\varepsilon = 45 \text{ M}^{-1} \text{ cm}^{-1}$), while the $[V^{V}(O)(O_{2})(TPA)]^{+}$ species shows characteristic absorption at 447 nm ($\varepsilon = 287 \text{ M}^{-1} \text{ cm}^{-1}$) assigned to the peroxo-to-vanadium charge transfer transition.⁵⁹ Here, in UV-vis kinetic studies (Figure 8), in the presence of Al(OTf)₃, the absorption at 447 nm gradually increased in the acetonitrile solution containing both the $[V^{IV}(O)Cl(TPA)]^{+}$ species and CHD (UV-vis data were collected from the reaction mixture under a dioxygen balloon at set intervals), whereas it remains its original absorbance of $[V^{IV}(O)Cl(TPA)]^{+}$ species in the absence of Al(OTf)₃. This transformation was also verified by mass studies (Figure 9). In the absence of Al(OTf)₃, $[V^{IV}(O)Cl(TPA)]^{+}$



Figure 9. Mass spectra of hydrogen abstraction from 1,4-cyclohexadiene by $[V^{IV}(O)Cl(TPA)]PF_6$ with Al(OTf)₃. Conditions: CH₃CN, 3 mL; CHD, 100 mM; $[V^{IV}(O)Cl(TPA)]PF_6$, 1 mM; Al(OTf)₃, 2 mM; under a dioxygen balloon, 303 K, 5 h.

species shows its mass peak at 392.05912, and it does not change after long-standing; in the presence of Al^{3+} and CHD, this mass peak changed to 389.08087, corresponding to the $[V^{V}(O)(O_{2})(TPA)]^{+}$ species. Since the $[V^{V}(O)_{2}(TPA)]^{+}$ species has no absorption above 400 nm, ⁵⁹ the final absorption at 447 nm indicated a crude 92% yield of $[V^{V}(O)(O_{2})(TPA)]^{+}$ species formation in the solution, clearly indicating the Al^{3+} -promoted dioxygen activation via the oxidovanadium(IV) complex. Note that, in the absence of CHD, no such transformation is observed for the $[V^{IV}(O)Cl(TPA)]^{+}$ complex, if even Al(OTf)₃ was added, as shown in Figure 5 (*vide supra*).

In dioxygen activation, the primary step is the formation of the metal superoxo species, which further proceeds by electron transfer to generate the metal peroxo species or proceeds by hydrogen atom abstraction to generate the metal hydroperoxide species.^{38–41} As shown in Figure 8, in the presence of CHD, adding Al(OTf)₃ to the acetonitrile solution of $[V^{IV}(O)Cl-$

Scheme 1. Proposed Mechanism for Lewis Acid Enhanced Dioxygen Activation by Oxidovanadium(IV) Complex Towards Hydrogen Abstraction from 1,4-Cyclohexadiene



(TPA)]PF₆ complex leads to the formation of $[V^{V}(O)(OOH)-(TPA)]^{2+}$ species having absorbance at ~550 nm,⁸¹ which was gradually converted to the $[V^{V}(O)(O_{2})(TPA)]^{+}$ having absorbance at 447 nm. In addition, the formation of $[V^{V}(O)(O_{2})(TPA)]^{+}$ species has also been evidenced by mass studies (Figure 9, vide supra). The formation of the $[V^{V}(O)(O_{2})(TPA)]^{+}$ species, as well as the $[V^{V}(O)(OOH)-(TPA)]^{2+}$, species may release $H_{2}O_{2}$ in the hydrogen abstraction process.^{82,83} As evidence, along with the formation of benzene and the $[V^{V}(O)(O_{2})(TPA)]^{+}$ species, the accumulation of $H_{2}O_{2}$, up to 40 mM, was also observed by HPLC analysis during the hydrogen abstraction from CHD (Figure S8 in the Supporting Information).

Although it is generally believed that formation of the metal superoxo species is the first step in dioxygen activation, here, the attempts to directly observe the vanadium(V) superoxo species were not successful by UV-vis, EPR, and mass studies, even in the presence of $Al(OTf)_3$, suggesting that the lifetime of the superoxo species is very short, because the equilibrium is very unfavorable for dioxygen activation, as shown in eq 1, and/ or it exhibits a rapid transformation to other products. Alternatively, the superoxo species was indicated by chemical scavenger tests in this work. In the literature, benzoquinone is a popular scavenger for the superoxo species, or, for example, superoxide, in wastewater treatment.^{84–87} Here, adding benzoquinone to the acetonitrile solution containing CHD, $Al(OTf)_{3}$ and $[V^{IV}(O)Cl(TPA)]PF_{6}$ would completely quench the hydrogen abstraction reaction, and there is no $[V^V(O)]$ -(OOH)(TPA)²⁺ or $[V^{V}(O)(O_{2})(TPA)]^{+}$ species formation observed by UV-vis studies, clearly supporting that, in Al³⁺promoted dioxygen activation by an oxidovanadium(IV) complex, the superoxo species occurs in the solution and plays the key role in hydrogen atom abstraction.

In the control experiments shown in Table 2, $[V^{IV}(O)-(OTf)(TPA)]PF_6$ alone is inactive for hydrogen abstraction from CHD through dioxygen activation, whereas adding $Al(OTf)_3$ to $[V^{IV}(O)(OTf)(TPA)]PF_6$ provided 95.2% conversion with 85.1% yield of benzene, indicating the crucial role of Al^{3+} in dioxygen activation, not only for the removal of the chloride from the oxidovanadium(IV) complex to generate a vacation site. In the literature, Fukuzumi even reported that the binding of Lewis acids to the superoxide species can make electron transfer from (TPP)Co to O₂ become possible.^{47,48} Alder also reported that Al^{3+} played the important roles in the vanadium-mediated NADH oxidation under dioxygen, and it was suggested that the addition of Al^{3+} enhances the production of the superoxide radical.⁸⁸ Here, the interaction of Al^{3+} with the vanadium(V) superoxo species may also drive the equilibrium to the right side in eq 1, to a certain degree, thus promoting dioxygen activation and leading to an efficient hydrogen abstraction.

Oxidative Reactivity of the Vanadium(V) Superoxo **Species.** As disclosed above, the presence of Al^{3+} can promote dioxygen activation via the $[V^{IV}(O)Cl(TPA)]PF_6$ complex, leading to efficient hydrogen abstraction with the stoichiometric formation of $[V^{V}(O)(O_{2})(TPA)]^{+}$ species (up to 92% yield). Similar formation of the $[V^{V}(O)(O_{2})(TPA)]^{+}$ species could also be observed by adding 9,10-dihydroanthracene in place of CHD; however, it is a much more sluggish process (see Figure S9 in the Supporting Information, versus Figure 8). Krüger and Mayer even reported that the vanadium(V) superoxo species is also capable of hydrogen abstraction from tetrahydrofuran (THF), which has a BDE_{CH} value of 92 kcal/ mol; however, the induction period could be long (on the order of days).^{25,31} These findings clearly support that the vanadium-(V) superoxide species is capable of hydrogen abstraction, and the presence of a Lewis acid such as Al³⁺ can accelerate dioxygen activation, leading to an efficient hydrogen abstraction in a catalytic process.

However, in the case of using sulfide or olefin in place of CHD, no oxygenation products were observed, which suggested that the in situ-generated vanadium(V) superoxo species is incapable of oxygenation to sulfide or olefin, even in the presence of $Al(OTf)_3$. However, in the presence of both CHD and sulfides such as thioanisole, diphenyl sulfide, and benzyl phenyl sulfide, adding $Al(OTf)_3$ can promote the formation of both benzene and sulfide oxidation products, but the hydrogen abstraction efficiency is much poorer than that in the absence of sulfide. For example, under the conditions of 1 mM [V^{IV}(O)Cl(TPA)]PF₆, 2 mM Al(OTf)₃, and 100 mM CHD with 25 mM thioanisole, after stirring at 303 K for 24 h, only 42.2% conversion of CHD was achieved with a 37.2% vield of benzene formation (comparing with 92.8% conversion with a 82.5% yield in 5 h at 303 K, see Table 1, entry 14); meanwhile, 80% of the sulfide was converted with a 62% yield of sulfide oxide and 6% yield of sulfone formation. In the control experiments, $[V^{V}(O)_{2}(TPA)]PF_{6}$ is incapable of sulfide oxygenation, and $[V^{V}(O)(O_{2})(TPA)]PF_{6}$ can only lead to trace oxygenation product, even in the presence of $Al(OTf)_3$. These results suggest that none of the vanadium(V) superoxo, oxido, and peroxo species are efficient for sulfide oxygenation, while the vanadium(V) hydroperoxide species, which was generated from hydrogen abstraction from CHD by the vanadium(V) superoxo species, is responsible for sulfide oxygenation in this

system. However, this vanadium(V) hydroperoxide species is incapable of epoxidizing olefin to the corresponding epoxide, even though similar hydroperoxide intermediates from titanium, manganese, and iron have been reported for efficient olefin epoxidation.^{89–91}

Mechanism of Lewis-Acid-Promoted Dioxygen Activation by Oxidovanadium(IV) Complex toward Hydrogen Abstraction. Regarding the facts disclosed above, including (1) the presence of AI^{3+} can promote the dissociation of the chloride from [V^{IV}(O)Cl(TPA)]⁺ species, and meanwhile interacts with the $V^{IV} = O$ functional group, (2) the presence of Al^{3+} can promote dioxygen activation by $V^{IV}(O)$ -Cl(TPA) PF₆ leading to efficient hydrogen abstraction from CHD, and (3) in addition to the formation of benzene as hydrogen abstraction product, up to 92% yield of the $[V^{V}(O)(O_{2})(TPA)]^{+}$ species were generated by UV-vis analysis with large amount of H_2O_2 (40 mM) release in the reaction solution, a brief Al³⁺-enhanced dioxygen activation via the oxidovanadium(IV) complex toward hydrogen abstraction was proposed as depicted in Scheme 1. In this mechanism, the conversion of vanadium(V)-oxido-hydroperoxide species can proceed via three pathways, including the release of H₂O₂ to generate vanadium(V)-oxido-hydroxide species, the formation of vanadium(V)-oxido-peroxo product by deprotonation, and via homolytic cleavage to generate the VIV=O and HOO•, which leads to a radical process in hydrogen abstraction, as reported in the literature. $^{92-95}$ Both $\rm H_2O_2$ and vanadium(V)oxido-peroxo product have been detected by UV-vis and HPLC analysis. According to Scheme 1, the formation of H₂O₂ would be equivalent to that of benzene formation, that is, under the catalysis of vanadium complex with $Al(OTf)_3$, hydrogen abstraction from CHD by O2 would produce equivalent amount of H_2O_2 and benzene. However, the detected H_2O_2 (40 mM) is approximately half of the benzene formation, indicating that much of the H₂O₂ was depleted during the hydrogen abstraction reaction, which is consistent with the occurrence of the induction period in hydrogen abstraction. Note that this induction period may not be attributed to trace organic peroxide as an impurity in acetonitrile solvent or commercial CHD substrate, because, in the absence of $Al(OTf)_{3}$, using oxidovanadium(IV) or vanadium(V) complex alone always displayed a very sluggish hydrogen abstraction kinetics.

CONCLUSIONS

This work demonstrated that adding certain nonredox metal ions, such as Al(III), as a Lewis acid can significantly enhance dioxygen activation via an oxidovanadium(IV) complex, which leads to efficient hydrogen abstraction. The promotional effect can be attributed to the multiple roles of the Lewis acid, including assisting the dissociation of the chloride from the oxidovanadium(IV) complex to generate a vacant site for dioxygen binding; interacting with the vanadium(V) superoxo species, which drives dioxygen activation; and interacting with the vanadium(V) oxido functional group, thus improving its hydrogen abstraction efficiency. The generated vanadium(V) superoxo species is capable of hydrogen abstraction, but incapable of oxygenation, while the vanadium(V) hydroperoxide species is capable of oxygenation to sulfide, but not to olefin. The results demonstrated here may shed some light on dioxygen activation toward efficient catalysis at ambient temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02277.

Complementary data for hydrogen abstraction, EPR tests, UV-vis studies, and H_2O_2 formation analysis (PDF)

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The authors declare no competing financial interest.

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