Lewis versus Brønsted Acid Activation of a Mn(IV) Catalyst for Alkene Oxidation

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Supporting Information

ABSTRACT: Lewis acid (LA) activation by coordination to metal oxido species has emerged as a new strategy in catalytic oxidations. Despite the many reports of enhancement of performance in oxidation catalysis, direct evidence for LA-catalyst interactions under catalytically relevant conditions is lacking. Here, we show, using the oxidation of alkenes with H2O2, and the catalyst [Mn4(μ-O)3(tmtacn)2][PF6]2 (1), that Lewis acids commonly used to enhance catalytic activity, e.g., Sc(OTf)3, in fact undergo hydrolysis with adventitious water to release a strong Brønsted acid. The formation of Brønsted acids in situ is demonstrated using a combination of resonance Raman, UV/vis absorption spectroscopy, cyclic voltammetry, isotope labeling, and DFT calculations. The involvement of Brønsted acids in LA enhanced systems shown here holds implications for the conclusions reached in regard to the relevance of direct LA-metal oxido interactions under catalytic conditions.

INTRODUCTION

The interaction of Lewis acids (LAs) with transition metal complexes and clusters can profoundly change their reactivity, which is most clearly manifested in the critical role of calcium ions in the oxygen evolving complex of photosystem (PS) II.1-2 Recent reports have highlighted correlations between Lewis acidity and properties of transition metal complexes, such as redox potential,3-5 and by extrapolation the enhancements in activity that they bring in oxidation catalysis, e.g., using iron3-15 and manganese complexes.16-21 However, the causal nature of the effects of LAs and indeed the actual interactions between them and transition metal complexes under catalytic conditions are unclear. In particular, their binding to reactive species, although postulated, has not been confirmed in solution. For example, Watkinson and Nodzewska30 and the group of Yin31 have described the exceptional impact of Lewis acids on the oxidation of alkenes with H2O2 catalyzed by the complex [Mn4(μ-O)3(tmtacn)2][PF6]2 (I, where tmtacn is N,N,N′-trimethyl-1,4,7-triazacyclononane, Scheme 1). The catalytic activity of 1 is dependent on the presence of Lewis acidic metal triflates such as Sc(OTf)3; alkene oxidation is not observed under the same conditions without a Lewis acid. This dependence was ascribed to binding of the Lewis acid to either 1 or the reactive intermediate responsible for substrate oxidation. Direct interaction between, e.g., Sc3+, and 1, was inferred from spectroscopic data and by analogy with known M-O-LA structures obtained in the solid state.32-34 Definitive evidence for such binding in solution is not available, however, especially under reaction conditions with, e.g., H2O2, where water is added with the oxidant in excess.

In the present contribution we show through a combination of spectroscopy and DFT calculations that the changes that follow addition of Lewis acids to 1 are not due to LA binding to an oxido unit of 1, as proposed for related Fe39=O complexes.32-34 Instead, the effects observed are due to the release of a strong Brønsted acid upon hydrolysis of the metal triflates by adventitious water either present in the solvent or as water of crystallization in 1. The released Brønsted acid facilitates reduction of 1 by H2O2 and subsequent ligand exchange and redox reactions35 provide for the observed increase in catalytic performance.

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Scheme 1. Oxidation of Alkenes with H₂O₂ Catalyzed by [Mn₁₂(μ-O)₃(tmtacn)]²⁺ (1) and Proposed Roles of Lewis Acids

Scheme 2. Key Stages in the Oxidation of Styrene (Blue) Catalyzed by 1 (1 mM) with Sc(OTf)₃ (2 mM) Using H₂O₂ (Magenta) As Oxidant

RESULTS AND DISCUSSION

As reported by Watkinson and Nodzewska and the group of Yin, we find here that the addition of metal triflates to 1 prior to the addition of H₂O₂ results in conversion of styrene to styrene oxide, albeit still with a substantial loss of H₂O₂ through disproportionation (Scheme 2 and Figures S1 and S2). The addition of 2 equiv of Sc(OTf)₃ results in an increase in absorbance at 799 nm and a broad shoulder at 687 nm, whereas with Y(OTf)₃, both rapid decomposition of H₂O₂ and significant conversion of styrene were observed. The relative performance of the Lewis acids correlates with their relative rates of hydrolysis,38 however, the counterion plays a role in the outcome of the reaction also. These data prompted us to examine the interaction between the LAs, and especially Sc(OTf)₃, and 1.

Effect of Lewis Acids on the Electronic and Vibrational Spectroscopy of 1. The UV/vis absorption spectrum of 1 in acetonitrile shows a broad visible absorption at 490 nm and several more intense bands below 400 nm.39,40 The addition of 2 equiv of Sc(OTf)₃ results in an increase in absorbance over the range 400 and 650 nm and the appearance of weak bands at ca. 750 and 850 nm (Figure 1a). The relative rate of change in absorbance is constant across the entire spectrum, indicative of a single step process. Notably, the changes are not immediate but take >30 s. The Raman spectrum at λ_exc 355 nm undergoes concomitant changes with the resonantly enhanced Mn−O−Mn symmetric stretching band at 699 cm⁻¹ decreasing in intensity and a band at 687 cm⁻¹ appearing together with an increase in intensity of the band at 799 cm⁻¹ (Figure 1b). DFT calculations and ¹⁸O labeling indicate that the band at 699 cm⁻¹ is a vibrational mode of the Mn−(μ-O)₃−Mn core, while the band at 799 cm⁻¹ involves mostly the Mn−N bonds, with little displacement of the Mn−(μ-O)₃−Mn core (Figure S4). Similar changes are observed at λ_exc 457 nm (Figure S5). Weaker bands appear also that correspond to modes of the tmtacn ligand observed under nonresonant conditions (λ_exc 785 nm, Figure S6). The addition of Al(OTf)₃ resulted in identical changes to the UV/vis absorption and resonance Raman spectra of 1, whereas the addition of Y(OTf)₃ and Y(CF₃CO₂)₃ did not (Figure S7).

The changes in the UV/vis absorption spectrum are similar to those reported by Lv et al., who proposed the formation of a mononuclear manganese(IV) complex analogous to that reported earlier by Chiu Quee-Smith et al. (i.e., [Mn⁴⁺(tmtacn)(OMe)₃][PF₆]). However, the final UV/vis absorption spectrum is identical to that reported earlier by Hage et al. for 1 in concentrated H₂SO₄. The addition of excess water after the addition of Sc(OTf)₃ resulted in an immediate recovery of the initial UV/vis absorption and resonance Raman spectra of 1 (Figure 1), and indeed even 0.2 vol % of water is sufficient for full recovery (see Figures S8a and S2). The turnover numbers (TONs) achieved here in the presence of LAs, ca. 250, are consistent with the earlier reports (ca. 100). In-line monitoring of the oxidation of styrene reveals that, in the presence of Lewis acids, the reaction proceeds through two distinct phases (Scheme 2, Figure S2). The addition of H₂O₂ is followed by an induction period, after which both alkene oxidation and disproportionation of the H₂O₂ begin concomitantly. The duration of the induction period and the ratio of styrene conversion to H₂O₂ disproportion depends on the time, here referred to as standing time, between the addition of the Lewis acid to 1 in anhydrous acetonitrile and the subsequent addition of styrene and H₂O₂ (Scheme 2). Disproportionation of H₂O₂ is observed regardless of the standing time, whereas conversion of styrene is observed only when the standing time exceeds several minutes. During the reaction, a white precipitate forms that is a mixture of insoluble manganese and scandium salts (by ICP, see Experimental Section for details) of, most likely, acetate formed by hydrolysis of acetonitrile.36,37 Although the isolated precipitate is not catalytically active.

Other Lewis acids have similar effects to that of Sc(OTf)₃, in terms of induction period and rate of oxidation. With Al(OTf)₃ consistently higher, conversion of styrene was obtained, whereas with Y(OTf)₃, the decomposition of H₂O₂ was slow, and negligible conversion of styrene was observed (Figure S2). Notably, however, with Y(CF₃CO₂)₃, both rapid decomposition of H₂O₂ and significant conversion of styrene were observed. The relative performance of the Lewis acids correlates with their relative rates of hydrolysis, however, the counterion plays a role in the outcome of the reaction also. These data prompted us to examine the interaction between the LAs, and especially Sc(OTf)₃, and 1.
Furthermore, using H$_2$O$^{18}$O did not result in incorporation of $^{18}$O into I (by Raman spectroscopy, Figures S4 and S8c). Hence, the changes upon the addition of Sc(OTf)$_3$ are unlikely to be due to “opening” of the Mn−O−Mn bridges. Furthermore, DFT calculations indicate that although the formation of a Sc$^{III}$−O−(Mn$^{IV}$)$_2$ bond is thermodynamically feasible, the calculated frequencies of the relevant vibrational mode (symmetric) do not match the shifts observed experimentally by Raman spectroscopy (Figure S9). In contrast the shifts calculated for 1 and H$_2$I$^+$ match well (Figure S4). These data indicate that, in solution, Lewis acidic metal ions (e.g., Sc$^{III}$) do not bind to a bridging oxygen of 1, but instead 1 is protonated by Brønsted acids, vide infra.

**Effect of Lewis Acids on the Cyclic Voltammetry of 1.**

A key role of Brønsted acids in activating 1 in catalytic oxidations is to shift its reduction potential to more positive potentials. This shift facilitates reduction of 1 by H$_2$O$_2$ from a Mn$^{IV}$ state to dinuclear Mn$^{II}$ and Mn$^{III}$ species. The latter species are catalytically active as established earlier where 1 was used in the presence of carboxylic acids. DFT calculations indicate that binding of Sc$^{III}$ to the Mn−(μ−O)−Mn core is thermodynamically favorable and changes the Mn−O bond lengths substantially (see SI). The Sc−O bond is predicted to have a significant covalent bond character, close to that of the O−H bond in H$_2$I$. Hence, notwithstanding the discussion above, binding of Sc(OTf)$_3$ could shift the reduction potential of 1 in a similar manner to that induced by protonation and thereby facilitate reduction by H$_2$O$_2$. Indeed, cyclic voltammetry shows that the reduction of 1 at −0.6 V vs SCE moves to ca. 0.4 V upon the addition of Sc(OTf)$_3$ (Figure 2). The increase in current indicates a multielectron process, and new oxidation waves at ca. 1.0 V on the return cycles are consistent with the formation of new species as shown earlier by de Boer et al.

Notably these changes are almost identical to those observed upon the addition of TfOH to 1 (Figure 2). As with Lewis acids, the addition of water results in only a minor shift of the redox waves back toward negative potentials, and essentially the same general shape of the redox wave is observed (Figure S10), despite that H$_2$I$^+$ reverts to 1. It should be noted that even weak acids that are not able to fully protonate 1 can provide sufficient acidity to enable reduction due to the fast equilibriums involved (Figure S11). After standing for several minutes, additional redox waves at 0.6 V are observed with both TfOH and Sc(OTf)$_3$ (Figures S12 and S13). The new redox waves at 0.65 and 1.05 V that appear over time in the presence of Sc(OTf)$_3$ and of TfOH correspond to those of [Mn$^{III}$$_2$(μ−O)(μ−OAc)$_2$(tmtacn)$_2$]$^{2+}$ in the presence of acid (Figure S14).

**Comparison of the Lewis and Bronsted Acids on the Spectroscopy of 1 and Its Catalytic Activity.** As for the cyclic voltammetry, Sc(OTf)$_3$ and TfOH have essentially identical effects on the UV/vis absorption and resonance Raman spectra of 1 (Figure 1). Indeed, these same spectroscopic changes are observed upon the addition of concentrated H$_2$SO$_4$ (or D$_2$SO$_4$, Figure S15) to 1 in acetonitrile, and the changes are consistent with formation of...
the monoprotonated complex H1+. Notably the changes induced by Brønsted acids are instantaneous, in contrast to the gradual changes (>30 s) observed upon the addition of Sc2(O2)3. This difference is consistent with release of Brønsted acids by hydrolysis of Sc2(O2)3 prior to protonation of 1. It should be noted that 1 supplies 1 equivalent of water as water of crystallization, in addition to residual water already present in acetonitrile.

Having confirmed the spectroscopic similarities between the addition of TIOH and Sc2(O2)3 to 1, the Brønsted acid assisted oxidation16,28,46 of styrene was examined. Essentially identical catalytic behavior was observed when using TIOH or Sc2(O2)3, including a lag period followed by rapid onset of addition of TfOH and Sc2(O2)3 to residual water already present in acetonitrile. Equivalents of water as water of crystallization, in addition to protonation of 1. It should be noted that 1 supplies 1 equivalent of water as water of crystallization, in addition to residual water already present in acetonitrile.

Similar trends were observed with trifluoroacetic acid (Figure S16), reinforcing that triflic acid is not unique and other Brønsted acids are capable of activating 1 in the same way, i.e., by protonation assisted reduction from the MnIV,IV oxidation18,28,46 of styrene was examined. Essentially identical catalytic behavior was observed when using TIOH or Sc2(O2)3, including a lag period followed by rapid onset of addition of TfOH and Sc2(O2)3 to residual water already present in acetonitrile. Equivalents of water as water of crystallization, in addition to protonation of 1. It should be noted that 1 supplies 1 equivalent of water as water of crystallization, in addition to residual water already present in acetonitrile.

In the present report, 1 equiv of water is present by default due to the fact that 1 is a monohydrate, but as discussed by Spencer et al. even if this is not the case water can form due to background reactions. Indeed, even when anhydrous, the water content is at a minimum 0.001–0.005 vol %, which corresponds to approximately 0.5–3 mM of H2O. This is in the same concentration range as the manganese complex (1 mM) and metal triflates (2 mM). Furthermore, in addition to water added with the oxidant H2O2 even when in 90 wt % concentration, the disproportionation of H2O2 generates H2O and O2 and during epoxidation 1 equiv of H2O is released also.

The pKₐ of 1 is lower than most strong acids and hence the leveling effect of water means that when present in excess of the TIOH formed, the strongest acid present is the hydronium ion, which is unable to protonate 1 to an extent detectable by spectroscopic methods. Neither yttrium(III) salts nor CF3CO2H induce changes in the UV/vis absorption and Raman spectra of 1, although they provide sufficient Brønsted acidity to facilitate reduction of 1 by H2O2, as observed with carboxylic acids earlier. Indeed, there is no reason that the pKₐ of Sc(H2O)₃ species formed by hydrolysis should be lower than that of TIOH and hence the species responsible for protonation of 1 cannot be defined. It is of note, however, that cyclic voltammetry with TIOH is nearly identical to that with Sc2(O2)3. Hence, although we have characterized Brønsted acidity in the present study as being due to the formation of TIOH in situ, in reality the nature of the species that protonates 1 to form H1+ is ill-defined. Ultimately, the actual Brønsted acid responsible is of little concern in this case, but rather the effects observed are due to Brønsted rather than Lewis acidity. A point that is certain is that once water is added in molar excess, e.g., with H2O2, or formed by side reactions, the hydronium ion is the Brønsted acid involved. Notably the hydronium ion is a much weaker acid than H1+, and its addition, as shown above, results in a recovery of the original spectral features of 1. Nevertheless, the equilibrium position is sufficient (see cyclic voltammetry) to provide enough H1+ in solution for H2O2 to be able to initiate reduction. The initial reduction triggers an autocatalytic transformation of 1 into species in lower oxidation states as shown earlier.

**CONCLUSION**

In summary, we have shown here that Lewis acidic metal triflates undergo rapid hydrolysis to generate strong Brønsted acids in acetonitrile under the conditions used for catalytic oxidations with H2O2. Indeed, even in anhydrous acetonitrile, residual water (ca. 0.5 to 3 mM H2O) and water of crystallization (1 molecule per 1) can be sufficient for hydrolysis of the Lewis acid (Sc2(O2)3). In the case of oxidation of alkenes with H2O2 and 1, the hydrolysis occurs well before the onset of substrate conversion. Hence, the postulated binding of Lewis acids to 1, or a putative reactive species, does not occur and the changes in spectral properties and enhancements in catalytic activity observed are due to Brønsted acids formed in situ. Indeed, Brønsted acids, i.e., carboxylic acids, were shown earlier to suppress disproportionation and allow for H2O2 to be used with complete efficiency in the oxidation of alkenes catalyzed by 1 with, e.g.,...
CCl3CO2H, with turnover numbers (TONs) exceeding 3000.\textsuperscript{35,47}

Although Sc\textsuperscript{3+}-bound species have been observed crystallographically,\textsuperscript{32-34} the reactivity changes induced by such Lewis acids in solution are highly likely to be due to the release of Bronsted acids. The role of Lewis as a source of Bronsted acids shown here impacts more broadly, for example, in the study of Lewis acid activation of iron and other metal catalysts. Beyond this, however, in recognizing the possibility to introduce strong Bronsted acids into reactions via Sc(OTf)\textsubscript{3} the use of often difficult to handle strong acids directly can be circumvented.

## EXPERIMENTAL SECTION

### General Information.
All reagents were of commercial grade (Sigma-Aldrich, TCI) and were used as received unless stated otherwise. H2O\textsubscript{2}: Sigma-Aldrich, 50 wt %. H2\textsubscript{3}O\textsubscript{2}: Rotem Industries Ltd., 98%. Anhydrous CH3CN (Sigma-Aldrich): 99.8%, <0.005% H2O (3 mM). The 1.5 M Na\textsubscript{18}OH (in H2\textsubscript{16}O) was prepared by adding a piece of Na metal (33 mg, 0.29 mmol) to 1.0 mL of H2\textsubscript{16}O. The mixture of 1 M H2O\textsubscript{2} and 1.5 M Na\textsubscript{18}OH in H2\textsubscript{16}O was prepared by mixing a solution of 50 wt % H2O\textsubscript{2} (13 mL) and H2\textsubscript{16}O (250 μL) with the previously prepared 1.5 M Na\textsubscript{18}OH (aq; 200 μL). [Mn(μ-O\textsubscript{2})(tmtacn)2](PF\textsubscript{6})2 was generously supplied by Catsel Ltd., and it was analyzed by elemental analysis (calcd for Mn, C\textsubscript{8}H\textsubscript{7}N\textsubscript{4}O\textsubscript{2}F\textsubscript{4}P\textsubscript{2}F\textsubscript{6}, 23.0% C; 28.3% H; 12.0% N; 17.7% P; 5.5% F; 25.5% O). The mixture of 1 M H2O\textsubscript{2} and 1.5 M Na\textsubscript{18}OH (aq.; 200 μL) was added to the reaction mixture, after which the solution turned dark red, and was stirred at room temperature during which it turned dark red, and was stirred at room temperature for approximately 45 min. Then, 1 M H2SO\textsubscript{4} in H2\textsubscript{16}O (150 μL) was added to the reaction mixture to reach pH 2. The dark red reaction mixture was subsequently filtered by gravity over paper into a 10 mL flask. KPF\textsubscript{6} (45 mg, 0.24 mmol) was added to the filtrate, upon which a precipitate formed immediately. The flask was kept in the fridge overnight to form microcrystalline needles, after which the solution was removed from the vial by Pasteur pipet, and the solid was washed with diethyl ether. The crystalline product was dried in the vial with gentle heating to remove residual water. The 1\textsuperscript{8}O-labeled product H2\textsubscript{3}O\textsubscript{2} was characterized by Raman spectroscopy (λ\textsubscript{exc} 785 nm (Figure S6)) and UV/vis absorption spectroscopy in CH3CN.

### Physical Measurements.
Inductively Coupled Plasma Atomic absorption (ICP-AAS) spectra were recorded on a PerkinElmer Optima 7000 DV ICP. Electrochemical measurements were carried out on a model 760C Electrochemical Analyzer (CH Instruments). Analyte concentrations were typically 1.0 mM in anhydrous CH3CN, 3 μmol. MnSO\textsubscript{4}·H2O (3 mM). The 1.5 M Na\textsubscript{18}OH (in H2\textsubscript{16}O) was prepared by adding a piece of Na metal (33 mg, 0.29 mmol) to 1.0 mL of H2\textsubscript{16}O. The mixture of 1 M H2O\textsubscript{2} and 1.5 M Na\textsubscript{18}OH in H2\textsubscript{16}O was prepared by mixing a solution of 50 wt % H2O\textsubscript{2} (13 mL) and H2\textsubscript{16}O (250 μL) with the previously prepared 1.5 M Na\textsubscript{18}OH (aq; 200 μL). [Mn(μ-O\textsubscript{2})(tmtacn)2](PF\textsubscript{6})2 was generously supplied by Catsel Ltd., and it was analyzed by elemental analysis (calcd for Mn, C\textsubscript{8}H\textsubscript{7}N\textsubscript{4}O\textsubscript{2}F\textsubscript{4}P\textsubscript{2}F\textsubscript{6}, 23.0% C; 28.3% H; 12.0% N; 17.7% P; 5.5% F; 25.5% O). The mixture of 1 M H2O\textsubscript{2} and 1.5 M Na\textsubscript{18}OH (aq.; 200 μL) was added to the reaction mixture, after which the solution turned dark red, and was stirred at room temperature for approximately 45 min. Then, 1 M H2SO\textsubscript{4} in H2\textsubscript{16}O (150 μL) was added to the reaction mixture to reach pH 2. The dark red reaction mixture was subsequently filtered by gravity over paper into a 10 mL flask. KPF\textsubscript{6} (45 mg, 0.24 mmol) was added to the filtrate, upon which a precipitate formed immediately. The flask was kept in the fridge overnight to form microcrystalline needles, after which the solution was removed from the vial by Pasteur pipet, and the solid was washed with diethyl ether. The crystalline product was dried in the vial with gentle heating to remove residual water. The 1\textsuperscript{8}O-labeled product H2\textsubscript{3}O\textsubscript{2} was characterized by Raman spectroscopy (λ\textsubscript{exc} 785 nm (Figure S6)) and UV/vis absorption spectroscopy in CH3CN.

### Procedure Employed for Catalysis Studies.
The Lewis acid (30 μL of 100 mM solution in CH3CN, 3 μmol) or Bronsted acid (30 μL of 300 mM solution in CH3CN, 9 μmol) was added to 1.21 mL of a 1.24 mM solution of 1 (1.5 μmol) in anhydrous CH3CN, and this mixture was stirred for a certain standing time, after which styrene (172 μL, 1500 μmol) was added. The final concentrations in 1.5 mL reaction mixture: 1 (1 M), Lewis acid (2 mM) or Bronsted acid (6 mM), styrene (1 M), H2O\textsubscript{2} (1 M). Reaction progress was determined by Raman spectroscopy (λ\textsubscript{exc} 785 nm) with the initial time (t = 0) defined as the point of addition of H2O\textsubscript{2} (85 μL of 50 wt % in H2O\textsubscript{2}, 1500 μmol). The conversion of styrene and consumption of H2O\textsubscript{2} were monitored for approximately 30 min. Epoxide formation was confirmed by 1\textsuperscript{H} NMR spectroscopy.

### Caution! Complete disproportionation of H2O\textsubscript{2} to oxygen and water can occur and hence the reactions should not be carried out in sealed vessels.

Note: Comparison of reaction progress data obtained in the present study with that in previous reports by Nodzewska and Watkinson showed the same reaction time (3–4 min),\textsuperscript{31} however, applied general reaction conditions to each tested substrate, and therefore a reaction time of 2 h was reported for styrene. It is of note that in the aforementioned studies 0.1 M styrene was used, in contrast to the present study with 1 M and hence the effect of standing time would not have manifested itself in a difference in conversion in those studies.

ICP analysis confirms that the white precipitate formed during catalysis contained 10–16 wt % of Mn and 5–20 wt % of Sc in the form of insoluble salts. The insolubility and %metal content is consistent with the anion being acetate. The FTIR spectrum indicates that the counterion is an organic compound which is affected by deuteration of the solvent (d\textsubscript{4}-acetoniitrile) but does not contain a nitrile group (Figure S17). This precipitate is formed in the absence of substrate, and a precipitate is formed in the absence of the manganese complex also. Hence although the organic component could be due to a degradation product of the tmtacn ligand, more probably, hydrolysis of acetoniitrile is responsible since the spectrum is solvent deuteration dependent. Comparison of these spectra with those of commercially available, and relatively anhydrous, scandium and manganese acetates is hampered by the effect of water (hydration state) on the spectrum, but the spectrum of the precipitate is close to that of NaOAc (Figure S18).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b02737.

Additional spectroscopic and electrochemical data (PDF)
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