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Lewis acid properties of some metal salts for lactic acid formation in water: ³¹P NMR spectroscopy with trimethylphosphine oxide as a molecular probe

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ABSTRACT

³¹P NMR spectroscopy was applied to the evaluation of water-tolerant Lewis acid catalysis of various metal triflates and chlorides in water using trimethylphosphine oxide (TMPO) as a probe molecule. Direct interaction of the TMPO molecule with the Lewis acid in water changes the original ³¹P NMR chemical shift and line width. ScCl₃, Sc(OTf)₃ and In(OTf)₃ exhibit larger changes in the ³¹P chemical shift by the formation of a Lewis acid -TMPO complex than other triflates and chlorides. This is due to strong interaction between the Lewis acid and TMPO, which leads to the slow exchange between TMPO and H₂O in ScCl₃, Sc(OTf)₃ and In(OTf)₃. Lewis acids with large change in the ³¹P chemical shift exhibit high catalytic activities for lactic acid formation from 1,3-dihydroxyacetone (1.3-DHA) and pyruvic aldehyde in water: Strong interaction with TMPO on the Lewis acid is a dominant factor for lactic acid formation. © 2013 Elsevier B.V. All rights reserved.

1. Introduction

Lewis acid catalysts such as AlCl₃, BF₃ and TiCl₄ have been utilized in the chemical industry for carbon–carbon bond forming reactions, represented by the Friedel–Crafts alkylation and acylation of petroleum-derived aromatic compounds [1,2]. Lewis acids activate the nucleophilic functional group in a reactant molecule by the formation of a Lewis acid–nucleophile adduct and subsequently promotes various carbon–carbon bond forming reactions. The high stability of the Lewis acid–nucleophile adduct causes deactivation of the original Lewis acidity [3]. As a result, stoichiometric amounts of Lewis acid catalysts are usually required for the reaction system. In addition, most Lewis acids are easily decomposed into the corresponding metal hydroxides in the presence of water, which also results in a loss of the original Lewis acid reactivity. The use of Lewis

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¹ Materials Research Center for Element Strategy, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8503, Japan. acid catalysts therefore requires that a strictly anhydrous organic solvent is employed.

Some metal trifluoromethanesulfonates (-OTf: -OSO₂CF₃) and chlorides, represented by Sc(OTf)₃, have been reported to function as water-tolerant Lewis acid catalysts [4]. Water, a green reaction medium, is desirable to use as a solvent for various organic reactions to reduce the environmental load. Metal triflates are effective Lewis acid catalysts for typical carbon-carbon bond forming reactions, such as the Mukaiyama-aldol reaction, the Mannich-type reaction, and allylation reaction, in the presence of water [4–7]. The catalytic activity of metal triflates for various carbon-carbon bond forming reactions is strongly related to the metal species. Kobayashi et al. proposed that the hydrolysis constants (pK_h) and water exchange rate constants (WERC) of metal triflates and chlorides are dependent on the catalytic performance for the Mukaiyama-aldol reaction [8]. Metal salts with small pK_h are easily decomposed in water into the corresponding metal hydroxides, and metal salts with large pK_h show less interaction of electrophilic molecules, including water, and are thus non-catalytsis. On the other hand, a Lewis acid with a large WERC is likely to exchange water molecules upon hydration of the Lewis acid with other nucleophilic molecules, including reactants with carbonyl groups, which exhibit high







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catalytic performance in water. Although the Lewis acid catalysis of metal triflates can be inclusively discussed with respect to two factors, the direct interaction of Lewis acid sites with nucleophilic molecules in water has not been investigated to date.

In this study, we examine the correlation of the catalytic activity of some metal triflates and chlorides containing various metal species (Sc, Y, La, Lu, In, and Zn) with their Lewis acidity in water. Lewis acidity of metal salts in water was studied using ³¹P NMR spectroscopy with trimethylphosphine oxide (TMPO) as a probe molecule. ³¹P NMR spectroscopy with TMPO has been widely used for characterization of the type (Brønsted and Lewis) and strength of acid sites on solid surfaces [10,11]. This is due to the 100% natural abundance of ³¹P atoms and the large chemical shift range over 430 ppm. Trimethylphosphine (TMP) has been conventionally applied to the evaluation of Lewis acidity for solid catalysts [10,11]. However, TMP is only available for the estimation of Lewis acids with same metal center [12]. In addition, oxidation of TMP into TMPO with O₂ easily occurs over Lewis acid sites, which restrict the use of TMP as a probe molecule in this study. Yang et al. applied liquid-state ³¹P NMR with TMPO to evaluate the acid strength of various homogeneous Brønsted acid catalysts [13]. They revealed that the ³¹P NMR chemical shift of TMPO reflects the Brønsted acid strength. TMPO is therefore also expected to be an excellent probe molecule available to evaluate the Lewis acidity of metal salts in water.

Catalytic activity was tested by the conversion of 1,3dihydroxyacetone (1,3-DHA) into lactic acid in water. The reaction involves the dehydration of 1,3-DHA into pyruvic aldehyde and the subsequent isomerization of pyruvic aldehyde into lactic acid [9]. Lewis acids were found to promote the isomerization of pyruvic aldehyde in water much more effectively than Brønsted acids, because Lewis acids are capable of forming a stable 5-membered Lewis acid-pyruvic aldehyde complex [9]. Therefore, the development of optimal Lewis acid catalysts for coordinating with pyruvic aldehyde is required for lactic acid synthesis.

2. Experimental

2.1. Catalytic reaction

Lewis acid catalysis of metal triflates and chlorides was examined through lactic acid production from 1,3-DHA and pyruvic aldehyde in water. $Sc(OTf)_3$, $In(OTf)_3$, $Y(OTf)_3$, $Lu(OTf)_3$, $La(OTf)_3$, and $Zn(OTf)_2$ obtained from Aldrich were used as metal triflates in this study. Prior to NMR measurements and catalytic reaction experiments, the metal triflates were dehydrated at 423 K for 3 h under vacuum to remove physisorbed water. $ScCl_3 \cdot 6H_2O$ (Strem Chemicals Inc.), YCl_3 (Strem Chemicals Inc.) and $LaCl_3 \cdot 7H_2O$ (Wako) were also tested as received.



Fig. 1. Time course for the transformation of 1.3-DHA into lactic acid with (a) In(OTf)₃, (b) H₂SO₄ and (c) H₃PO₄. Reaction conditions: catalyst 0.1 mmol, 2.0 mL of 0.1 M 1.3-DHA aqueous solution, 383 K.



The catalytic reaction was performed by heating a sealed Pyrex tube containing a mixture of catalyst (0.1 mmol) and 2.0 mL of 0.1 M aqueous pyruvic aldehyde or 1.3-DHA at 383 K for 1 h. The resulting solutions were analyzed using high performance liquid chromatography (HPLC) equipped with a refractive index (RI) detector.

2.2. ³¹ P NMR analysis

Direct interaction of Lewis acids with TMPO in water was evaluated using liquid-state ³¹P NMR spectroscopy (Bruker, AVANCE III 400) at resonance frequencies of 400.1 MHz and 162.0 MHz for ¹H and ³¹P, respectively. Same quantity of metal salt and TMPO was dissolved in D₂O (Metal salt and TMPO concentrations, 0.25 M; metal salt/TMPO ratio, 1). The Lewis acidities of the metal salts were compared according to the chemical shift and line width of the TMPO signal in the ³¹P NMR spectra. NMR measurements were performed at 303 K under ¹H decoupling to remove the influence of ¹H-³¹P spin-spin coupling. The number of scans and the recycle delay were set at 32 times and 5 s, respectively. The ³¹P chemical shift was referenced using 0.25 M TMPO/D₂O solution at 53.5 ppm as an external standard relative to 85% H₃PO₄ aq. at 0 ppm.

Solid state ³¹P MAS NMR experiment was carried out with ECA 400 spectrometer running at resonance frequencies and 399.0 MHz and 161.5 MHz for ¹H and ³¹P, respectively, with a T6 double-tune probe and 7 mm zirconia rotor. NMR spectra were acquired with high-power ¹H decoupling, a recycle delay of 10 s, a $\pi/2$ pulse length of 5.5 us, 128 times scans and a spinning speed at 8 k Hz. 85% H₃PO₄ aq. was used for the external reference of ³¹P chemical shift at 0 ppm.

Adsorption of TMPO on solid Sc(OTf)₃ and In(OTf)₃ was performed by simple impregnation technique. TMPO was dissolved in anhydrous CH_2Cl_2 and prepared 0.1 M TMPO/ CH_2Cl_2 solution. Dehydrated Sc(OTf)₃ and In(OTf)₃ at 323 K for 1 h under vacuum were added to TMPO-containing CH_2Cl_2 solution (0.1 M) under an argon atmosphere. After removal of the solvent under vacuum, TMPO-adsorbed Sc(OTf)₃ and In(OTf)₃ were obtained. The sample was packed into the zirconia rotor in glove box.

2.3. Density functional theory (DFT) calculations

Molecular structures for TMPO, mono-hydrated pyruvic aldehyde, and 1.3-DHA were optimized with consideration of the solvation effects (of water). The self-consistent reaction field method was implemented using Gaussian 03 software [14] with the polarizable continuum model. The B3LYP hybrid functional and 6-311G basis sets were used in this case. Contour maps for the highest occupied molecular orbitals (HOMOs) were constructed using GaussView software [15]. The contour surfaces are shown at an electron density of 0.15 e Å⁻³.

3. Results and discussion

3.1. Catalysis using metal triflates and chlorides for lactic acid production from 1,3-DHA and pyruvic aldehyde in water

The catalytic activity for lactic acid formation from 1,3-DHA in water was first examined with typical Brønsted and Lewis acid catalysts. Fig. 1 shows time courses for 1,3-DHA conversion and product yields in the presence of In(OTf)₃, H₂SO₄ and H₃PO₄. The reaction proceeds through the dehydration of 1,3-DHA into pyruvic aldehyde and the subsequent isomerization of pyruvic aldehyde into lactic acid (Scheme 1). In(OTf)₃, a typical water-tolerant Lewis acid, consumes almost 1.3-DHA within 2 h and gives a lactic acid yield of *ca*. 95%. This means that water-tolerant Lewis acid catalysis is effective for the consecutive reactions. In contrast, H₂SO₄

and H₃PO₄ only produce pyruvic aldehyde with ca. 95% selectivity. H₂SO₄ gives 80% 1,3-DHA conversion and pyruvic aldehyde yield after 2h. H₃PO₄ exhibits lower catalytic performance than H₂SO₄, which indicates that the strong Brønsted acid facilitates the dehydration of 1,3-DHA. It should be noted that these Brønsted acids cannot produce lactic acid under the present reaction conditions. The difference in catalysis for the reaction between the Brønsted and Lewis acids is attributed to the reaction pathway for the isomerization of pyruvic aldehyde. Scheme 1 shows the proposed reaction pathway for the isomerization of pyruvic aldehyde into lactic acid over a Lewis acid. Pyruvic aldehyde is firstly produced from 1,3-DHA by dehydration. ¹H NMR analysis confirmed that pyruvic aldehyde is a highly reactive dicarbonyl compound and present in water as the original aldehyde, monohydrated, and dihydrated forms with typical distributions of trace levels, 57% and 43%, respectively (monohydrated pyruvic aldehyde: δ 2.20 ppm (3H), 5.18 ppm (1H), dihydrated pyruvic aldehyde: δ 1.27 ppm (3H), 4.73 ppm (1H)) [16,17]. Monohydrated pyruvic aldehyde is subsequently converted into lactic acid through hydride transfer over the Lewis acid. As the reaction proceeds, most of the dihydrated pyruvic aldehyde is continuously converted into the monohydrated form to maintain an equilibrium distribution, and the monohydrated pyruvic aldehyde is finally converted into lactic acid. In the case of a Brønsted acid, the reaction proceeds through a methyl anion transfer via a benzilic acid rearrangement [16]. This reaction cannot be promoted under mild conditions. On the other hand, it has



Fig. 2. Catalytic activities for the transformation of (a) pyruvic aldehyde and (b) 1.3-DHA on various metal salts. Reaction conditions: catalyst 0.1 mmol, 2.0 mL of 0.1 mM pyruvic aldehyde or 1.3-DHA aqueous solution, 383 K, 1 h.

been reported that Lewis acids can effectively catalyze the hydride transfer of glucose into fructose [18,19] and pyruvic aldehyde into lactic acid [16] in water through the Meerwein–Ponndorf–Verley (MPV) reduction mechanism. In the case of In(OTf)₃, the reaction is expected to proceed by the formation of a 5-membered intermediate with In(OTf)₃, followed by lactic acid formation via a 1,2-hydride transfer reaction of the monohydrated pyruvic aldehyde, as in the presence of other Lewis acids (Scheme 1).

Catalysis over some metal triflates (metal center: Sc, Y, La, Lu, In, Zn), chlorides (metal center: Sc, Y, La) and Brønsted acids (H₂SO₄ and H₃PO₄) was also examined by lactic acid formation from pyruvic aldehyde and 1,3-DHA in water, and the results are shown in Fig. 2. While the Brønsted acids show no catalysis for the reaction, all the Lewis acids tested can convert pyruvic aldehyde into lactic acid. Sc(OTf)₃, ScCl₃ and In(OTf)₃ have high catalytic performance for the reaction; lactic acid yield and selectivity of these catalysts reached 87% and 90%, 83% and 85%, and 95% and 96%, respectively as shown in Fig. 2a. On the other hand, the other triflates and chlorides have lower lactic acid yields (10%-55%) and selectivities (20%-65%) than Sc(OTf)₃, ScCl₃ and In(OTf)₃. Fig. 2b shows the catalytic activities of the Lewis acids for the conversion of 1,3-DHA into lactic acid at 383 K for 1 h. While Y(OTf)₃, La(OTf)₃, and Lu(OTf)₃ have high 1,3-DHA conversion of ca. 70%, the combined yield of pyruvic aldehyde and lactic acid for all the tested catalysts, except for Sc(OTf)₃, ScCl₃, and In(OTf)₃, are below 30%. 1,3-DHA and pyruvic aldehyde have reactive carbonyl (C=O) groups, so that complex intermolecular reactions, such as aldol condensation, by Lewis acid catalysts would result in the formation of complex polymerized species. Therefore, in the case of these Lewis acids, the formation of polymerized byproducts proceed preferentially to the dehydration of 1,3-DHA and hydride transfer of pyruvic aldehyde. On the other hand, ScCl₃ and In(OTf)₃ have higher lactic acid yields, although Sc(OTf)₃ and ScCl₃ exhibit low lactic acid selectivity in contrast to the case of hydride transfer of pyruvic aldehyde, as shown in Fig. 2a: Sc(OTf)₃, ScCl₃, and $In(OTf)_3$ have lactic acid yields of 59%, 50%, and 84%, respectively. These results indicate that the water-tolerant Lewis acids are effective catalysts for lactic acid formation from 1,3-DHA in water, which is strongly dependent on the metal center.

3.2. ³¹P NMR measurement with TMPO as a basic probe molecule

The Lewis acid properties of metal triflates and chlorides were elucidated using ³¹P NMR measurements with TMPO as a probe molecule. Activation of the reactant by the Lewis acid is closely related to the energy level of the HOMO of the nucleophile and the lowest unoccupied molecular orbital (LUMO) of the electrophile [3]. A small HOMO-LUMO energy gap between the Lewis acid and nucleophile enables the formation of a Lewis acid-nucleophile complex. Fig. 3a shows a HOMO and LUMO energy diagram for TMPO, 1,3-DHA, monohydrated pyruvic aldehyde, and H₂O on the basis of density functional theory (DFT) calculations. The higher HOMO energies of these nucleophilic molecules, including TMPO, than that of $H_2O(-8.1 \text{ eV})$ means that the Lewis acids interact with these reactant molecules in preference to H₂O molecules. It should be noted that TMPO has a similar HOMO energy level (-7.5 eV) to 1,3-DHA (-7.1 eV) and monohydrated pyruvic aldehyde (-7.4 eV). In addition, the electrons in the HOMO of TMPO are located on the oxygen atom of the phosphoryl group as well as the HOMOs of 1,3-DHA and monohydrated pyruvic aldehyde, which electrons are found on the oxygen atom of carbonyl groups (Fig. 3b). Such an electronic analogy among these nucleophiles indicates that TMPO is a suitable probe molecule for the evaluation of Lewis acid catalysis for these reactions. Fig. 4 shows ³¹P NMR spectra of TMPO in the presence of equimolecular amounts of metal triflates and chlorides in D₂O. TMPO in D₂O have one resonance at 53.5 ppm that is assigned to the interaction of TMPO with water molecules (Scheme 2b). The addition of Sc(OTf)₃, ScCl₃, and In(OTf)₃ to the TMPO/D₂O solution results in a large shift of the TMPO signal to the higher frequency



Fig. 3. (a) HOMO and LUMO energy diagrams for TMPO, monohydrated pyruvic aldehyde, 1.3-DHA and water, and (b) schematic structure of the HOMOs for (i) TMPO, (ii) monohydrated pyruvic aldehyde, and (iii) 1.3-DHA.



Fig. 4. ³¹P NMR spectra for TMPO in TMPO/D₂O solution with various Lewis acid catalysts. The concentrations of Lewis acid (c_{acid}) and TMPO (c_{TMPO}) were set at 0.25 M (Lewis acid/TMPO = 1). (a) TMPO without Lewis acid catalyst, (b) Sc(OTf)₃, (c) Y(OTf)₃, (d) La(OTf)₃, (e) Lu(OTf)₃, (f) In(OTf)₃, (g) Zn(OTf)₂, (h) ScCl₃, (i) YCl₃, (j) LaCl₃, (k) H₂SO₄ and (l) H₃PO₄.

region. Fig. 4(b), (f) and (h) show TMPO signals on Sc(OTf)₃, ScCl₃, and In(OTf)₃ appear at 64.5, 63.4, and 61.9 ppm, respectively. This change can be simply interpreted by the formation of a Lewis acid–TMPO complex and hydrous TMPO in equilibrium, as shown in Scheme 2. The single and broad peak in Fig. 4(b), (f), and (h) is due to the slow exchange between the Lewis acid and D₂O on TMPO in solution. In this case, the peak position of TMPO (Ω_{peak}) is given by Eq. (1), where [1]_{eq}, [2]_{eq} and Ω^0_1 , Ω^0_2 denote the equilibrium concentrations and the original chemical shifts of species 1 and 2, respectively [20].

$$\Omega_{peak} = \frac{[1]_{eq}\Omega_1^0 + [2]_{eq}\Omega_2^0}{[1]_{eq} + [2]_{eq}}$$
(1)

A large change in chemical shift indicates that the preference of most TMPO molecules is to form TMPO–Lewis acid complexes as opposed to with H_2O molecules. The line width of the TMPO signal on Sc(OTf)₃, ScCl₃ and In(OTf)₃ is considerably broader than those of other Lewis acids. While the change in chemical shift reflects the affinity between the Lewis acid and TMPO, the line width of the TMPO resonance provides information on the chemical exchange between a Lewis acid–TMPO complex and hydrous TMPO (Scheme 2). The broad NMR resonance is indicative of a slow



Scheme 2. Schematic illustration of the chemical equilibrium between the $M(OTf)_{x}$ -TMPO complex and hydrous TMPO.

exchange rate between the two species; therefore, $Sc(OTf)_3$, $ScCl_3$ and $In(OTf)_3$ are capable of forming stable TMPO–Lewis acid complexes in water. In contrast, $Y(OTf)_3$, $La(OTf)_3$, $Lu(OTf)_3$, $Zn(OTf)_2$, YCl_3 and LaCl_3 have a sharp TMPO signal at 53–55 ppm (Fig. 4(c), (d), (e), (g), (i) and (j)). The small change in the ³¹P chemical shift suggests that the TMPO molecules coordinated with these metal triflates are readily replaced with H₂O molecules. As a result, most of the Lewis acid in water is present in the hydrated state. This is due to the weak interaction of the metal center with TMPO. Typical Brønsted acids (H₂SO₄ and H₃PO₄) were also studied as reference materials, which showed small ³¹P chemical shift change under same experimental conditions.

Therefore, the Lewis acids tested here are categorized into two groups based on the ³¹P NMR measurements with TMPO; (i) $Sc(OTf)_3$, $ScCl_3$ and $In(OTf)_3$ with a large change in ³¹P chemical shift for TMPO and (ii) Y(OTf)₃, YCl₃, Lu(OTf)₃, La(OTf)₃, LaCl₃ and $Zn(OTf)_2$ with a small or no change in ³¹P chemical shift for TMPO. The former form Lewis acid-TMPO complexes in water more preferentially than the latter. Such Lewis acids effectively activate the reactant molecules by the formation of a Lewis acid-reactant complex and thereby exhibit high catalytic performance for lactic acid formation from 1,3-DHA and pyruvic aldehyde in water. Lewis acidity of solid Sc(OTf)₃ and In(OTf)₃ was examined by adsorption of TMPO using solid-state ³¹P MAS NMR. Fig. 5 shows ³¹P MAS NMR spectra for TMPO-adsorbed Sc(OTf)₃ and In(OTf)₃ in dried powder form. TMPO resonance on Sc(OTf)₃ and In(OTf)₃ appears at 67.7 and 65.4 ppm, respectively, which are comparable to those on dissolved Sc(OTf)₃ and In(OTf)₃ in D₂O (Fig. 4). Small difference of TMPO resonance on dissolved metal triflate in D₂O is due to fast exchange between Lewis acid-TMPO and hydrous TMPO as shown in Scheme 2. No decrease in Lewis acidity of $Sc(OTf)_3$ and $In(OTf)_3$ in water strongly suggests that the exchange between water and nucleophilic molecule occurs on these metal triflate.

In contrast, the latter Lewis acids have weak interaction with the nucleophilic molecules of TMPO, 1,3-DHA and pyruvic aldehyde, which causes lower catalytic performance for the reactions. This difference is due to strong/weak interaction between the Lewis acid and the nucleophile, which results in much slower exchange between the nucleophile and H₂O for the former Lewis acids than for the latter Lewis acids. Preliminary result on density



Fig. 5. ³¹ P MAS NMR spectra for TMPO loading on (a) Sc(OTf)₃ and (b) In(OTf)₃.

functional theory (DFT) calculation suggests that lowest unoccupied molecular orbital (LUMO) levels of Sc(OTf)₃ and Y(OTf)₃ were estimated to be *ca.* -2.2 and -1.0 eV, respectively, from crystalline Sc(OTf)₃·9H₂O[21] and Y(OTf)₃·9H₂O[22] structure. Higher HOMO levels of pyruvic aldehyde and TMPO than that of H₂O means that Lewis acid is bonded to nucleophiles such as 1,3-DHA, pyruvic aldehyde, and TMPO in preference to H₂O. In addition, low LUMO level of Sc(OTf)₃ suggests that the interaction between Sc(OTf)₃ and these nucleophiles is larger than that of Y(OTf)₃, due to small HOMO–LUMO energy gap. Strong interaction of reactant molecules with Sc(OTf)₃ would form active Lewis acid–reactant complexes, resulting in high catalytic performance.

4. Conclusion

The changes in the ³¹P NMR chemical shift and line width by the formation of a TMPO-Lewis acid complex in water are effective indicators to evaluate the catalytic performance of homogeneous water-tolerant Lewis acids in water. Sc(OTf)₃, ScCl₃, and In(OTf)₃ show 61, 51, and 96% yield for lactic acid formation, respectively. High performance of ScCl₃, Sc(OTf)₃, and In(OTf)₃ was evident from the large chemical shift and broad line width of the TMPO-Lewis acid complexes observed in the ³¹P NMR spectra, which indicate the formation of stable reactant-Lewis acid complexes in water. Similar HOMO level and electronic state of TMPO to carbonyl group in reactant (1.3-DHA and pyruvic aldehyde), in addition to 100% natural abundance of ³¹P atoms, make TMPO as an effective probe molecule for the evaluation of Lewis acid catalysis in water. Efficient activation of 1.3-DHA and pyruvic aldehyde as well as TMPO in water by the Lewis acids results in high catalytic performance for Lewis acid-catalyzed reactions.

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