Lanthanide(III) complexes of aromatic sulfonic acids as catalysts for the nitration of toluene

Tatjana N. Parac-Vogt∗, Karen Deleersnyder, Koen Binnemans

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Abstract

Ytterbium(III) complexes of benzenesulfonic acid, Yb(BSA)3, p-toluenesulfonic acid, Yb(Tos)3, and 2-naphthalenesulfonic acid, Yb(NSA)3, were prepared and tested as possible catalyst for the nitration of toluene. With a loading of 5–10 mol% of Yb(BSA)3 and Yb(NSA)3, a quantitative conversion of toluene to nitrotoluene was achieved within 5 h, while Yb(Tos)3 was slightly less active and 77% of nitrated products were obtained. The catalysts can be easily recovered after the reaction, and 1H NMR spectroscopy of analogous diamagnetic lanthanide(III) catalysts showed that the recovered catalysts were identical to the freshly prepared ones. The ratio of ortho:meta:para products was in all reactions 52:6:42, which is consistent with a direct electrophilic attack by the nitronium ion, NO2+.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Nitration; Lanthanides(III); Green chemistry; Rare earths

1. Introduction

Nitration of aromatic compounds is one of the most important and extensively studied organic reactions [1]. The aromatic nitro compounds are widely utilized for the synthesis of great variety of materials such as dyes, plastics and pharmaceuticals. The classical nitration procedure requires the use of a potent mixture of concentrated nitric and sulphuric acids, yielding large amounts of waste streams of inorganic acids, which are environmentally unfriendly and expensive to dispose. In addition, the synthetic procedure is not very selective and often leads to overnitration or to oxidized by-products. The obvious disadvantages associated with this procedure prompted extensive research in finding new nitration methods such as using solid-acid catalysts, other sources of NO2+, organic nitrating agents, etc. [1,2].

Lanthanide triflates, [Ln(OTf)3], were found to be efficient catalysts for the nitration of a range of simple aromatic compounds using stoichiometric quantities of nitric acid, the only by-product being water and the catalyst being readily recycled by simple evaporation of the solvent [3]. In order to avoid the use of chlorinated solvents and recovery of the catalyst from an aqueous solution an alternative method was developed, which employed perfluorinated lanthanide salts [Ln(OSO2CF3)3] as the catalyst, and various fluoruous compounds as solvents [4]. Although the procedure was devoid of chlorinated solvents and required very small catalyst loading (0.05 mol%) for achieving moderate to good yields (40–60%) of nitrated toluene, the method is still unlikely to be utilized on a large industrial scale; the fluorinated solvents are much more expensive than most of the conventional solvents, and in addition, their large global warming potential could pose serious environmental problems [5].

Lanthanide complexes have in recent years attracted considerable attention as reagents for variety of organic reactions [6]. Among them, the lanthanide salts of triflic acid, [Ln(OTf)3], have been particularly successfully applied as catalyst for a large number of organic transformations [7]. They are expected to be strong Lewis acids due to the electron-withdrawing trifluoromethanesulfonate group. Indeed, triflic acid is one of the strongest acids known today, and its pK∞ value has been estimated to be smaller than −12 [8]. For aromatic nitration, the extreme acidity of triflic acid is thought to be necessary to increase the polarising power of the metal ion, which plays a crucial role in formation of de facto nitrating agent NO2+ [9].

So far, the complexes of lanthanides with aromatic sulfonic acids have not been explored as catalysts in organic reactions. The aromatic sulfonic acids are much weaker

∗ Corresponding author. Fax: +32-16-327992.
E-mail address: tatjana.vogt@chem.kuleuven.ac.be (T.N. Parac-Vogt).
acids than triflic acid, (the p-toluene sulfonic acid is for example about 10\(^6\) times weaker acid than triflic acid) [10], and therefore their complexes with lanthanides are expected to be much weaker Lewis acids than Ln(OTf)\(_3\). However, the advantages of aromatic sulfonic acids over triflic acid, which include much cheaper costs and easier handling, prompted us to explore lanthanide complexes of benzenesulfonic acid, Ln(BSA)\(_3\), p-toluene sulfonic acid, Ln(Tos)\(_3\), and 2-naphthalenesulfonic acid, Ln(NSA)\(_3\), as possible catalyst for the atom economic aromatic nitration of toluene [11].

2. Experimental

Reagents were obtained from Aldrich Chemical Co. Inc., Acros Organics and Rhodia Electronics and Catalysis, and used without further purification. \(^1\)H NMR spectra were run on a Bruker Avance 300, operating at 300 MHz. Gas chromatography (GC) analyses were performed on ThermoFinnigan Trace GC. Elemental analysis was performed on a CE Instruments EA-1110 elemental analyzer.

2.1. Synthesis of ytterbium(III) p-toluenesulfonate, ytterbium(III) benzenesulfonate, and ytterbium(III) naphthalenesulfonate

The compounds were synthesized by the reaction of 1.1 eq. of ytterbium oxide (Rhodia 99.99%), Yb\(_2\)O\(_3\), and 6 eq. of the corresponding sulfonic acid in aqueous solution. After stirring the solution in boiling water for 30 min, the excess of Yb\(_2\)O\(_3\) was removed by filtration. The filtered solution was evaporated to dryness and the resulting solid was dried in a vacuum oven at 50\(^\circ\)C overnight. The elemental analysis results are shown in Table 1. The diamagnetic lanthanum(III) complexes were synthesized by the same procedure, using La\(_2\)O\(_3\) instead of Yb\(_2\)O\(_3\).

2.2. General procedure for nitration of toluene

To a solution of a respective ytterbium(III) catalyst (5 mol%, 0.3 mmol) in nitric acid (67%, \(d = 1.41\), 0.200 ml, 3.0 mmol) was added a solution of toluene (0.240 ml, 3 mmol) in 4 ml of 1,2-dichloroethane. The mixture was stirred and heated at reflux. After a given period of time the solution was cooled and diluted with water. The yellow organic phase was dried with MgSO\(_4\), evaporated and analysed by \(^1\)H NMR and GC.

3. Results and discussion

Ytterbium(III) complexes of three different sulfonic acids, Tos, NSA, and BSA, shown in Fig. 1, were synthesized. As Table 1 shows, all three complexes were isolated as hydrated salts. Single crystal and thermal analytical studies of [Yb(TOS)\(_3\)] showed that this complex initially crystallizes with nine water molecules and that seven are being lost upon heating at ca. 55\(^\circ\)C [12]. The elemental analysis of our complexes (Table 1) showed that they contain two to four water molecules, and that some of the crystalline water was lost upon drying at 40\(^\circ\)C in vacuo.

All ytterbium(III) sulfonates proved to be efficient catalysts for the nitration of toluene. Ytterbium(III) was chosen over other lanthanides because due to its small radius ytterbium(III) should have greater polarizing power compared to larger lanthanide(III) ions, and because ytterbium(III) compounds are relatively cheap in comparison with lutetium(III) and scandium(III) compounds. Previous studies have indeed shown that in many cases Yb(OTf)\(_3\) was a more powerful catalyst than the complexes containing larger lanthanide(III) ions [3,9].

As Table 2 shows, high yields of nitrated products were obtained with catalyst loadings of 5–10 mol%. Within 6h, 10 mol% of Yb(NSA)\(_3\) and Yb(BSA)\(_3\) catalyzed quantitative conversion of toluene to nitrotoluene. Control experiments have shown that the uncatalyzed reaction was very slow, and that less than 10 mol% of the nitrated products were formed in the absence of the catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb(Tos)(_3)</td>
<td>55</td>
</tr>
<tr>
<td>Yb(NSA)(_3)</td>
<td>61</td>
</tr>
<tr>
<td>Yb(BSA)(_3)</td>
<td>64</td>
</tr>
</tbody>
</table>

(a) 5 mol% catalyst loading, 3h; (b) 10 mol% catalyst loading, 3h; (c) 10 mol% catalyst loading, 6h.

Table 1: Analysis of the ytterbium(III) sulfonates

<table>
<thead>
<tr>
<th>Complex</th>
<th>Chemical formula</th>
<th>Analysis (%)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb(Tos)(_2)·2H(_2)O</td>
<td>C(_9)H(_8)O(_7)·3Yb</td>
<td>35.03 (34.91) 3.69 (3.49)</td>
</tr>
<tr>
<td>Yb(NSA)(_2)·3H(_2)O</td>
<td>C(_9)H(_8)O(_7)·3Yb</td>
<td>42.51 (42.45) 3.71 (3.21)</td>
</tr>
<tr>
<td>Yb(BSA)(_2)·4H(_2)O</td>
<td>C(_9)H(_8)O(_7)·3Yb</td>
<td>30.00 (30.16) 3.16 (3.23)</td>
</tr>
</tbody>
</table>

\(^a\) The calculated values are given in parentheses.

Fig. 1. Sulfonates used as counterions for ytterbium(III) catalysts: BSA: benzenesulfonate; Tos: tosylate; NSA: 2-naphthalenesulfonate.
After the reaction, the catalysts were easily recovered from the water solutions in almost quantitative yields by simple evaporation of the solvent. In order to check whether the catalysts remained unchanged after the nitration reaction, the diamagnetic lanthanum(III) complex La(BSA)₃ was synthesized. Within 16 h the quantitative conversion of toluene to nitrotoluene was observed, and the ¹H NMR spectrum of recovered lanthanum(III) catalyst was identical to the ¹H NMR spectra of freshly prepared complex. The recovered catalyst was used for the further nitration of toluene, and within the same period of time quantitative yield of the nitrotoluene was observed, with no changes in the relative ratio of isomers.

The relative ratio of ortho- meta- and para-isomers was in all cases 52:6:42 and it remained same regardless of the reaction time and the catalyst used (Scheme 1). This is consistent with direct electrophilic attack by the nitronium ion, NO₂⁺. The nitronium ion was also indicated as de facto nitrating agent in Ln(OTf)₃ catalyzed nitration of aromatic compounds [3]. The postulated mechanism involves binding of nitric acid to lanthanide metal via displacement of water ligands upon which the strong polarization due to the metal results in proton liberation. Reaction of the proton with another molecule of nitric acid liberates NO₂⁺ in the classical manner [1] as shown in Scheme 2. It is likely that a similar mechanism applies for the nitration catalyzed by complexes examined in this study, since they differ from Ln(OTf)₃ only in the nature of the counterions. Studies on Ln(OTf)₃ and Ln(Tos)₃ complexes in solution indicate that in aqueous media the nine water molecules occupy the first coordination sphere, and triflate and tosylate counterions are essentially spectator ions [13,14]. It has been suggested that the triflate counterion is crucial for the catalytic activity since it is the conjugate base of extremely strong acid allowing that nitric acid is preferentially protonated which can lead to production of nitronium ion [9]. However, the conjugate bases of aromatic sulfonic acids, which are much weaker acid than the triflic acid, also fulfill the role played by the triflate counterions.

4. Conclusions

In this study, we have shown that complexes of lanthanide(III) ions with aromatic sulfonic acids are very efficient catalysts for the nitration of toluene. Although the aromatic sulfonic acids are about 10⁶ times weaker acids than triflic acid, their complexes with lanthanide(III) are still strong Lewis acids which are able to catalyze the nitration of toluene. Therefore, the extreme acidity and corrosivity of triflic acid, used for the preparation of Ln(OTf)₃ catalyst, can be avoided by the use of the alternative catalysts reported in this study.

Acknowledgements

This study was supported by the K.U.Leuven (VIS/01/006.01/2000/02-06/2004 and GOA 03/03) and by the FWO-Flanders (G.0117.03). Mr. K.B. acknowledges the FWO-Flanders for a Postdoctoral Position and for a “Krediet aan Navorschers”. The authors wish to thank Rhodia Electronics and Catalysis for a gift of Yb₂O₃. The authors also thank Ms. Petra Bloemen for doing the elemental analysis.

References