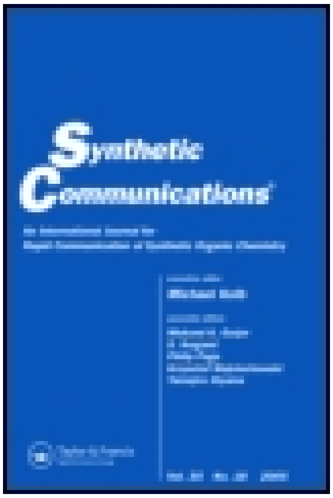
This article was downloaded by: [University of Illinois Chicago]
On: 17 October 2014, At: 04:49
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Novel Atom-Economic Nitration of Benzene with a Nitrogen Dioxide-Oxygen System using Cocatalyst of Solid Oxides and Lanthanide(III) Metal Triflates

Xiaohua Du [a], Xiaoqing Li [a] & Zhenyuan Xu [a]
[a] State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou, China

Published online: 19 Oct 2007.

To cite this article: Xiaohua Du, Xiaoqing Li & Zhenyuan Xu (2007) Novel Atom-Economic Nitration of Benzene with a Nitrogen Dioxide-Oxygen System using Cocatalyst of Solid Oxides and Lanthanide(III) Metal Triflates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:21, 3741-3749, DOI: 10.1080/00397910701569502

To link to this article: http://dx.doi.org/10.1080/00397910701569502

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthetic Communications®, 37: 3741–3749, 2007

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910701569502

Novel Atom-Economic Nitration of Benzene with a Nitrogen Dioxide–Oxygen System using Cocatalyst of Solid Oxides and Lanthanide(III) Metal Triflates

Xiaohua Du, Xiaoqing Li, and Zhenyuan Xu
State Key Laboratory Breeding Base of Green Chemistry–Synthesis
Technology, Zhejiang University of Technology, Hangzhou, China

Abstract: Benzene is nitrated by a novel atom-economic nitration procedure with a NO_2-O_2 system in the presence of a mixture of solid oxides and $Ln(OTf)_3$. The only by-product in this novel method is water. The efficiency of NO_2 is much high than 50%, the theoretical efficiency of NO_2 of the known methods. Among the solid oxides and $Ln(OTf)_3$ studied, HZSM-5 and $Sm(OTf)_3$ were the most efficient catalysts in this process. Therewith, the yield of the benzene nitration reached 72.5%, calculated by NO_2.

Keywords: benzene, lanthanide(III) metal triflate, nitration, nitrogen dioxide, oxygen, solid oxides

INTRODUCTION

Nitration of organic compounds is one of the most important and extensively studied organic reactions. The nitroaromatic compounds so produced are themselves widely utilized and act as chemical feedstocks for a great range of useful materials such as dyes, pharmaceuticals, perfumes, and plastics.[1] Unfortunately, classical nitration has long been carried out using concentrated or fuming nitric acid with sulfuric acid on a high-volume scale, which leads to

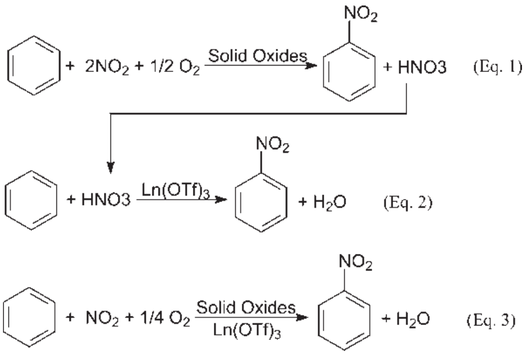
Received in Japan January 22, 2007
Address correspondence to Xiaohua Du, State Key Laboratory Breeding Base of Green Chemistry–Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, China. E-mail: greensyn@zjut.edu.cn

excessive acid waste streams, overnitration, and oxiding by-products. The obvious disadvantages associated with this procedure prompted research on alternative methods to classical nitration such as using solid acid catalysts, strong Lewis acid catalysts, and other nitrating agents.

The nonacid method for aromatic nitration using a NO_2/O_3 system as nitrating agent has demonstrated an excellent conversion of a wide variety of aromatic compounds to the corresponding nitro derivatives under mild conditions (Kyodai nitration).[2] However, because ozone used in the nitration reaction can only be obtained by discharging oxygen at a high voltage, an expensive ozone generator and large amounts of electricity are needed for the mass production of ozone. Further efforts to find an alternative means to solve the problom has led to the Fe(III)-catalyzed nitration of aromatic compounds with an NO_2-O_2 system.[3] Rather unfortunately, a long reaction time (e.g., 12 to 36 h) is needed even though large amounts of nitrogen dioxide (31 equivalents) and catalyst are used. In anothor modified means, zeolite was used as catalyst for this process, and high yields and significant selectivities were obtained. However, a long reaction time and large amount of nitrogen dioxide were necessary.[4] Furthermore, according to the reaction equation [Scheme 1, Eq. (1)], the theoretical efficiency of NO_2 is only 50%. The other 50% of NO_2 converts into nitric acid as a waste acid, which is an disadvantage of this procedure.

On the other hand, it has been reported that lanthanide(III) metal triflate [$Ln(OTf)_3$][5] and other perfluorinated rare-earth metal salts[6] can be used as recyclable catalysts for the nitration of simple arenes with stoichiometric quantities of nitric acid. The only by-product is water, and the catalyst may be readily recycled and reused repeatedly.

To develop an atom-economic process for aromatic nitration, we applied the mixture of solid oxides and $Ln(OTf)_3$ as catalyst for NO_2-O_2 system nitration. As shown in Scheme 1, our approach to the nonacid process for



***Scheme 1*.** Proposed mechanism for nitration of benzene with NO_2-O_2 system as nitrating agent catalyzed by solid oxides and $Ln(OTf)_3$.

nitration of benzene consisted of two steps: first, a solid oxide catalyzed the NO_2-O_2 system to nitrate benzene and generated a by-product of nitric acid at the same time. Second, $Ln(OTf)_3$ catalyzed nitric acid to nitrate benzene in situ. The total reaction is shown in Eq. (3). The theoretical efficiency of NO_2 is 100%, and the only by-product is water. To the best of our knowledge, such cocatalyst is rare in nitration methodology. Therefore, the obtained facts may open new alternatives for atom-economic aromatic nitration.

RESULTS AND DISCUSSION

Initially, HZSM-5 and $Sm(OTf)_3$ were investigated in our approach. To optimize the amount of $Sm(OTf)_3$ for maximum yield, nitration of benzene was studied with varied $Sm(OTf)_3$ amounts ranging from 0 to 2 mol% and 2.0 g of HZSM-5. The results (Table 1) showed that the yield of nitrobenzene increases with the amount of $Sm(OTf)_3$ until $Sm(OTf)_3$ loading reaches 1 mol%, and more $Sm(OTf)_3$ was not beneficial to yield.

A similar process was studied with varied HZSM-5 amounts ranging from 0 to 2 g with $Sm(OTf)_3$ loading of 1 mol% to optimize the amount of HZSM-5 for maximum yield. The results (Table 2) showed that the yield of nitrobenzene increases with HZSM-5 until HZSM-5 loading reaches 1.0 g. More HZSM-5 has no obvious effects on the yield.

Varied pressure ranging from 0.2 to 0.8 MPa was studied to determine the most suitable reaction pressure. The data (Table 3) show that the highest yield was obtained at 0.5 MPa. Pressure higher than 0.5 MPa was not beneficial to yield.

To optimize the reaction temperature, varied temperature ranging from 85 to 115°C was studied. The results (Table 4) show that at low temperature, the

Table 1. Effects of $Sm(OTf)_3$ amount on the yield of nitrobenzene[a]

Entry	$Sm(OTf)_3$ (mol%)	Yield[b] (%)
1	0	51.4
2	0.5	59.5
3	1	65.4
4	1.5	65.8
5	2	65.6

[a] Reaction condition: 1,2-dicholoethane = 50 mL; benzene = 9 mL (0.105 mol); HZSM-5 = 2.0 g; liquid nitrogen dioxide = 3.2 g (0.07 mol); reaction temperature = 85°C; reaction pressure = 0.8 MPa; reaction time = 7 h.

[b] Isolated yields based on the amount of NO_2.

Table 2. Effect of HZSM-5 amount on the yield of nitrobenzene[a]

Entry	HZSM-5 amount (g)	Yield[b] (%)
1	0	59.4
2	0.5	63.2
3	1.0	65.8
4	1.5	65.7
5	2.0	65.5

[a] Reaction condition: 1,2-dicholoethane = 50 mL; benzene = 9 mL (0.11 mol); $Sm(OTf)_3$ = 1 mol%; liquid nitrogen dioxide = 3.2 g (0.07 mol); reaction temperature = 85°C; reaction pressure = 0.8 MPa; reaction time = 7 h.

[b] Isolated yields based on total amount of NO_2.

yield increased along with reaction temperature, and the highest yield was obtained at 100°C. However, yield decreased if reaction temperature increased further.

To optimize the reaction time, the process was studied at varied reaction times ranging from 3 to 9 h. The results (Table 5) show that the highest yield was obtained at 7 h. The yield was not changed when the reaction time was further prolonged.

We then carried out similar reactions in which various solid oxides or $Ln(OTf)_3$ were used as catalysts instead of HZSM-5 or $Sm(OTf)_3$ to determine which solid oxide, if any, would be the most applicable to benzene nitration. As shown in Tables 6 and 7, the reaction occurred in the presence of all of the solid oxides and $Ln(OTf)_3$. Among the solid oxides

Table 3. Effects of reaction pressure on the yield of nitrobenzene[a]

Entry	Reaction pressure (MPa)	Yield[b] (%)
1	0.2	28.5
2	0.4	63
3	0.5	65.7
4	0.6	65.4
5	0.8	65.5

[a] Reaction condition: 1,2-dicholoethane = 50 mL; benzene= 9 mL (0.11 mol); $Sm(OTf)_3$ = 1 mol%; HZSM-5 = 2.0 g; liquid nitrogen dioxide = 3.2 g (0.07 mol); reaction temperature = 85°C; reaction time = 7 h.

[b] Isolated yields based on total amount of NO_2.

Table 4. Effects of the reaction temperature on the yield of nitrobenzene[a]

Entry	Reaction temperature (°C)	Yield[b] (%)
1	85	65.7
2	95	71.8
3	100	72
4	105	71.8
5	115	68.2

[a] Reaction condition: 1,2-dicholoethane = 50 mL; benzene= 9 mL (0.11 mol); $Sm(OTf)_3$ = 1 mol%; HZSM-5 = 2.0 g; liquid nitrogen dioxide = 3.2 g (0.07 mol); reaction pressure = 0.5 MPa; reaction time = 7 h.

[b] Isolated yields based on total amount of NO_2.

and $Ln(OTf)_3$ studied, HZSM-5 and $Sm(OTf)_3$ gave the most encouraging yield of 72.5% (entries 1 and 2).

Control experiments were performed according general procedure. The absence of eitheir solid oxide (entry 9, Table 6) or $Ln(OTf)_3$ (entry 7, Table 7) decreased the product yields remarkably. The results clearly indicated that both solid oxide and $Ln(OTf)_3$ are indispensable for nitration of benzene in our method. Moreover, all entries using catalyst made up of solid oxide and $Ln(OTf)_3$ gave yields of more than 50%, which means by cocatalyzing the solid oxide and $Ln(OTf)_3$, the efficiency of NO_2 was increased more than 50%, the theoretical efficiency of NO_2 in the prior methods.

In summary, we have discovered a novel atom-economic aromatic nitration process with an NO_2-O_2 system in the presence of a mixture of solid oxides and $Ln(OTf)_3$. The only by-product in this process is water,

Table 5. Effects of reaction time on the yield of nitrobenzene[a]

Entry	Reaction time (h)	Yield[b] (%)
1	3	41.4
2	6	59.4
3	7	72.5
4	9	72.3

[a] Reaction condition: 1,2-dicholoethane = 50 mL; benzene = 9 mL (0.105 mol); $Sm(OTf)_3$ = 1 mol%; HZSM-5 = 1.0 g; liquid nitrogen dioxide = 3.2 g (0.07 mol); reaction temperature = 100°C; reaction pressure = 0.5 MPa.

[b] Isolated yields based on total amount of NO_2.

Table 6. Nitration of benzene catalyzed by $Sm(OTf)_3$ and various solid oxides[a]

Entry	Solid oxide	Yield[b] (%)
1	HZSM-5	72.5
2	V_2O_5	72.2
3	Al_2O_3	60.4
4	SiO_2	65.6
5	Cr_2O_3	65.4
6	ZrO_2	60.2
7	CeO_2	64.3
8	WO_3	59.4
9[c]	—	32.1

[a] Reaction condition: 1,2-dicholoethane = 50 mL; benzene= 9 mL (0.105 mol); $Sm(OTf)_3$ = 1 mol%; HZSM-5 = 1.0 g; liquid nitrogen dioxide = 3.2 g (0.07 mol); reaction temperature = 85°C; reaction pressure = 0.5 MPa.

[b] Isolated yields based on total amount of NO_2.

[c] No solid oxide was used.

and the efficiency of NO_2 is in excess of 50%. Efforts are under way to elucidate more mechanistic details of the nitration reaction catalyzed by this novel mixture catalyst and to identify systems enabling the nitration of other aromatic compounds and the subsequent transformations thereof.

Table 7. Nitration of benzene catalyzed by HZSM-5 and various $Ln(OTf)_3$[a]

Entry	$Ln(OTf)_3$	Yield[b] (%)
1	$Sm(OTf)_3$	72.5
2	$Yb(OTf)_3$	68.4
3	$Nd(OTf)_3$	61.7
4	$Gd(OTf)_3$	60.3
5	$Er(OTf)_3$	64.5
6	$Dy(OTf)_3$	62.5
7[c]	—	27.1

[a] Reaction condition: 1,2-dicholoethane = 50 mL; benzene = 9 mL (0.105 mol); $Sm(OTf)_3$ = 1 mol%; HZSM-5 = 2.0 g; liquid nitrogen dioxide = 3.2 g (0.07 mol); reaction temperature = 85°C; reaction pressure = 0.5 MPa.

[b] Isolated yields based on total amount of NO_2.

[c] No $Ln(OTf)_3$ was used.

EXPERIMENTAL

General

Sm_2O_3, Yb_2O_3, Nd_2O_3, Gd_2O_3, Er_2O_3, Dy_2O_3, V_2O_5, Al_2O_3, Al_2O_3, Cr_2O_3, ZrO_2, CeO_2, WO_3 were procured from Sinopharm Chemical Reagent Co., Ltd., China. Silica gel was obtained from Qingdao Haiyang Chemical Co., Ltd., China. NaZSM-5 was purchased from Wenzhou Huahua Group Co., China. Benzene was procured from Quzhou Juhua Chemical Reagent Co., Ltd., China. 1,2-Dichloroethane was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. The purity of the product was analyzed by GC-MS (Agilent 6890 N/5973) and/or GC (GC-1102, China).

Catalyst Preparation

$Ln(OTf)_3$ (Ln = Sm, Yb, Nd, Gd, Er, Dy)

The triflate salts were prepared following a reported procedure.[7] Typically, an excess of lanthanide(III) oxide (99.9% purity) was added to an aqueous solution of trifluoromethanesulfonic acid (50% v/v) and heated at boiling for 30 min to 1 h. The mixture was filtered to remove the unreacted oxide. The filtrate was concentrated, and the resulting hydrate was dried by heating at 120°C for 48 h.

HZSM-5

NaZSM-5 (50 g) was treated with 500 mL of 1 M aqueous ammonium chloride at 90°C for 2 h. The procedure was repeated five times, followed by filtration of the sample and washing with distilled water until the filtrate showed the absence of the chloride ions. The obtained sample was oven dried at 120°C for 10 h followed by calcination at 550°C for 4 h in an air atmosphere.

General Procedure for Nitration of Benzene

1,2-Dicholoethane (50 mL), benzene (9 mL, 0.11 mol), solid oxides, $Ln(OTf)_3$, and liquid nitrogen dioxide (2.2 mL, 0.07 mol) were poured into an autoclave. Next, oxygen was injected at a pressure of 0.2 to 0.8 MPa, and then the mixtures were reacted at 85 to 115°C for 3 to 9 h while the same level of pressure was maintained. After completion of the reaction, the reaction mixture was filtrated to remove the solid oxides, washed with water to recycled $Ln(OTf)_3$, and dried with $MgSO_4$. The solvent was removed under reduced pressure to afford nitrobenzene. The purity of the product was analyzed by GC-MS (Agilent 6890 N 5973) and/or GC (GC-1102, China).

ACKNOWLEDGMENT

We thank the Zhejiang Natural Science Foundation, China (Y404033), for financial support.

REFERENCES

1. Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration: Methods and Mechanisms*; VCH: New York, 1989.
2. (a) Mori, T.; Suzuki, H. Ozone-mediated nitration of aromatic compounds with lower oxides of nitrogen (the Kyodai nitration). *Synlett.* **1995**, *5*, 383–392; (b) Suzuki, T.; Noyori, R. Ozone-mediated nitration with lower oxides of nitrogen (the Kyodai nitration). *Chemtracts.* **1997**, *10*, 813–817; (c) Peng, X.; Suzuki, H. Regioselective double Kyodai nitration of toluene and chlorobenzene over zeolites: High preference for the 2,4-dinitro isomer at the second nitration stage. *Org. Lett.* **2001**, *22*, 3431.
3. Suzuki, H.; Yonezawa, S.; Nonoyama, N.; Mori, T. Iron(III)-catalyzed nitration of non-activated and moderately activated arenas with nitrogen dioxide–molecular oxygen under neutral conditions. *J. Chem. Soc., Perkin Trans.* 1, **1996**, 2385–2389.
4. (a) Akolekar, D. B.; Lemay, G.; Sayari, A.; Kaliaguine, S. High pressure nitration of toluene using nitrogen dioxide on zeolite catalysts. *Res. Chem. Interm.* **1995**, *21*, 7–16; (b) Peng, X.; Suzuki, H.; Lu, C. Zeolite-assisted nitration of neat toluene and chlorobenzene with a nitration dioxide/molecular oxygen system: Remarkable enhancement of para-selectivity. *Tetrahedron Lett.* **2001**, *42*, 4357–4359; (c) Smith, K.; Almeer, S.; Peters, C. Regioselective mononitration of aromatic compounds by zeolite/dinitrogen tetroxide/air in a solvent-free system. *Chem. Commun.* **2001**, 2748–2749; (d) Smith, K.; Almeer, S.; Vlack, J. K. para-selective nitration of halogenobenzenes using a nitrogen dioxide–oxygen–zeolite system. *Chem. Commun.* **2000**, 1571–1572.
5. (a) Waller, F. J.; Barrett, A. G.; Braddock, D. C.; Ramprasad, D. Lanthnide(III) triflates as recycleable catalysts for atom-economic aromatic nitration. *Chem. Commun.* **1997**, 613–614; (b) Waller, F. J.; Barrett, A. G.; Braddock, D. C.; Mckinnell, R. M.; Ramprasad, D. Lanthnide(III) and group (IV) metal triflate catalysed electrophilic nitration: "Nitrate capture" and the role of the metal centre. *J. Chem. Soc. Perkin Trans.* 1, **1999**, 867–871; (c) Braddock, C. Novel recyclable catalysts for atom-economic aromatic nitration. *Green Chem.* **2001**, *2*, 26–32; (d) Li, X.; Du, X.; Xu, Z. Toluene nitration catalyzed by metal triflates. *Chin. J. Org. Chem.* **2006**, *26*, 1111; (e) Yuan, Y.; Nie, J.; Wang, S.; Zhang, Z. Aromatic nitration catalyzed by metal bis[(perfluoroalkyl)-sulfonyl] imides. *Chin. J. Org. Chem.* **2005**, *25*, 394–398; (f) Kawada, A.; Takeda, S.; Yamashita, K.; Abe, H.; Harayama, T. Scandium(III) trifluoromethanesulfonate catalyzed aromatic nitration with inorganic nitrates and acetic anhydride. *Chem. Pharm. Bull.* **2002**, *50*, 1060–1065; (g) Waller, F. J.; Barrett, A. G. M.;

Braddock, D. C.; Ramprased, D. Hafnium(IV) triflates as superior recycleable catalysts for the atom-economic nitration of o-nitratoluene. *Tetrahedron Lett.* **1998**, *39*, 1641–1642.

6. (a) Shi, M.; Cui, S. Electrophilic aromatic nitration using a mixed catalyst of lithium, molybdenum, ytterbium on silica gel. *Adv. Synth. Catal.* **2003**, *345*, 1329–1333; (b) Shi, M.; Cui, S. Perfluorinated rare earth metals catalyzed nitration of aromatic compounds. *J. Fluorine Chem.* **2002**, *113*, 207–209; (c) Shi, M.; Cui, S. Electrophilic aromatic nitration using perfluorinated rare earth metal salts in fluorous phase. *Chem. Commun.* **2002**, 994–995.
7. Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. K.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. Use of lanthnide(III) ions as catalysts for the reactions of amines with nitriles. *J. Org. Chem.* **1987**, *52*, 1017–1021.