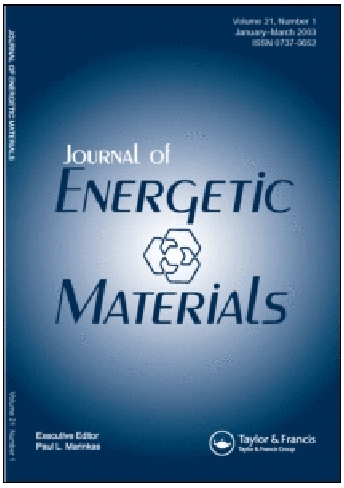

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A Novel and Highly Efficient Catalytic System for Trinitration of Aromatic Compounds: Ytterbium Perfluorooctanesulfonate and Perfluorooctanesulfonic Acid in Fluorous Solvents

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Ytterbium perfluorooctanesulfonate [Yb(OPf)$_3$] and perfluorooctanesulfonic acid [PfOH] catalyze the highly efficient nitric acid polynitration of aromatic compounds in fluorous media, affording trinitro derivatives even in a single stage. The reactions produce smaller amounts of waste acid than in traditional processes. The fluorous phase containing catalysts could be easily and efficiently recovered for reuse by simple phase separation.

Keywords: aromatic compound, fluorous biphasic catalysis, lanthanide, perfluorooctanesulfonic acid, trinitration

Introduction

Nitration is one of the key processes in synthetic chemistry and is widely used industrially [1,2]. Traditional nitration in

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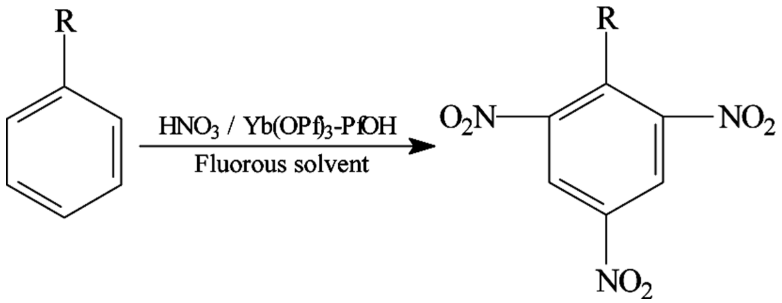
manufacturing process requires the use of potent mixtures of concentrated or fuming nitric acid with sulfuric acid, leading to excessive acid waste streams and added expense. Thus, aromatic nitration is one of the most troublesome functionalizations in the context of green chemistry. Despite some breakthroughs based on the use of solid catalysts [3] and the use of dinitrogen pentoxides [4] or nitrogen dioxides/ozone [5] as a nitrating agent, major problems remain, especially when polynitration is required for the production of energetic materials. Recently, it was found that lanthanide(III) triflates (1–10 mol%) [$Ln(OTf)_3$] can catalyze the nitration of a range of simple aromatic compounds such as nitrotoluenes and fluoroarenes in good to excellent yield using stoichiometric quantities of 69% nitric acid, the only by-product being water and the catalyst being readily recycled by simple evaporation [6]. However, this nitration was carried out in refluxing 1,2-dichloroethane, an environmentally hazardous solvent. In addition, the recovery of the catalyst from aqueous solution is not an economic process. On the other hand, a novel Lewis acid of ytterbium perfluorooctanesulfonate [$Yb(OPf)_3$] has been used as a recycled catalyst for the mononitration of aromatic compounds in moderate yield using concentrated nitric acid in fluorous solvents [7]. Crampton and coworkers reported that perfluorocarbons can be used effectively as solvents and bulking agents in the trinitration of toluene [4]. However, such trinitration required at least 5 equivalents of nitric aicd and sulfuric acid, which is a traditional nitration system with the plague of waste acid. Coon et al. [8] reported that trifluoromethanesulfonic acid (TfOH) could be used as a nitration solvent and catalyst for nitric acid nitrated process in which only mono or dinitro derivates were obtained and recycle of TfOH has not heretofore been achieved. Inspired by the recent work on the Friedel-Crafts acylation of unactivated benzenes catalyzed by $Yb(OPf)_3$ with the coexistence of perfluorooctanesulfonic acid [PfOH] [9], a strong monobasic acid with an acidity function H_0 being -12.08 (that of sulfuric acid is -11.90) [10] and especially high solubility in fluorous solvents [9], we have applied this catalytic system to the trinitration of aromatic compounds, such



Ytterbium perfluorooctanesulfonate [$Yb(OPf)_3$] and perfluorooctanesulfonic acid [PfOH] catalyze the highly efficient nitric acid polynitration of aromatic compounds in fluorous media, affording trinitro derivatives even in a single stage.

as toluene, benzene, chlorobenzene, and bromobenzene (Fig. 1). It was exciting to find that rather high yields of the corresponding trinitrobenzenes and the robustness of the catalytic system for recycling using by simple phase separation were obtained. We would like to report herein the work on this new application of the catalytic system.

Experimental

Typical Procedure for Preparation of $Yb(OPf)_3$

$Yb(OPf)_3$ was prepared according to the literature [9] (Method A). The mixture of PfOH solution (aq) and $YbCl_3 \cdot 6H_2O$ solution (aq) was stirred at room temperature (Method B). The mixture of PfOH solution (aq) and Yb_2O_3 powder was stirred at boiling. In both methods, the resulting gelatin-like solid was collected, washed, and dried at 150°C in vacuo to give a white solid, which does not have a clear melting point up to 500°C but shrinks around 380° and 450°C. IR (KBr) υ1 237 (CF_3), 1,152 (CF_2), 1,081 (SO_2), 1,059 (SO_2), 747 (S–O), and 652 (C–S) cm^{-1}. ICP: Calcd for $C_{24}O_9F_{51}S_3Yb$: Yb, 10.30%. Found: Yb, 9.88%. Anal. Calcd for $C_{24}O_9F_{51}S_3Yb \cdot H_2O$: C, 17.21%; H, 0.10%. Found: C, 17.03%; H, 0.18%.

Typical Procedure for Trinitration of Toluene

A mixture of Yb(OPf)$_3$ (209 mg, 0.125 mmol), PfOH (188 mg, 0.375 mmol), toluene (0.26 mL, 2.5 mmol), octane (4 mL), perfluorodecalin (8 mL), and pure HNO_3 (0.63 mL, 15 mmol). The mixture was stirred at 95°C for 8 h. (The nitration was safe enough for operation.) The fluorous layer on the bottom was separated for the next nitration. After cooling, octane (8 mL) was added into the reaction mixture (organic phase and water phase). Then, the mixed solution was subsequently washed with water (10 mL), 10% $NaHCO_3$ solution (10 mL), and water (10 mL), and dried over Na_2SO_4 to give a yellow organic phase (determination by GC or GC-MS showed that toluene was completely [$>$99] converted to TNT with no other isomeric nitro derivatives being detected). The solvent was removed under reduced pressure and the residue was recrystallized from 63% HNO_3 solution to give a yellowish solid TNT (0.53 g, 94%), with the m.p. being 80°C. The ^1H NMR spectrum in [$^2H_6$]-DMSO of expected products was identical with spectra of authentic samples. The chemical shifts were as followed: 9.01 (2H, m, Ar), 2.55 (3H, S, CH_3). The efforts were directed toward the determination of oxidative by-products in the nitration procedure. The above wash solution (water and $NaHCO_3$ solution) was collected and acidified with 36% HCl solution. Then, the acidified solution was extracted with CH_2Cl_2 (10 mL $\times$ 2). Determination by GC-MS and ^1H NMR of the CH_2Cl_2 layer showed that no oxidative products such as 2,4,6-trinitrobenzoic acid and 2,4,6-trinitrophenol could be detected.

Results and Discussion

The nitration of toluene was first carried out in perfluorodecalin ($C_{10}F_{18}$, *cis* and *trans*-mixture) using pure nitric acid, which was prepared by distillation from 98% sulfuric acid and potassium nitrate as the nitration reagent (Table 1). Based on the general concept of fluorous phase chemistry [11], we also used octane as a co-solvent for the nitration. It was found that, upon heating at 95°C, the organic phase is miscible with fluorous phase and the nitration became a biphasic reaction (top layer is the nitric acid; bottom layer is the fluorous solvent with aromatic compound). Using nitric acid alone allows the ready conversion of toluene to dinitrotoluenes, but no significant conversion to 2,4,6-trinitro-toluene (TNT) was observed even in the presence of excess acid or using $Yb(OPf)_3$ as a catalyst. Further increases of amount of the $Yb(OPf)_3$ did not significantly improve the yield of TNT. However, the use of PfOH resulted in moderate yield of trinitro derivate after prolonged reaction, which indicates that the presence of PfOH is essential for the occurrence of trinitration. Notably, the system containing 15 mol% PfOH and 5 mol% $Yb(OPf)_3$ with 6 equivalents of nitric acid gave the complete conversion of toluene to TNT at 95°C after 8 h. This compares with the conventional process, which involves stepwise nitrations, mono- to di- to trinitrotoluene, each involving excess nitric acid with sulfuric acid as solvent [12]. In addition, the reaction proceeded very cleanly (checked by GC-MS and ^{1}H NMR), and no other significant products such as oxidative by-products and isomeric nitro derivatives in the nitration procedure could be detected. When the reaction was finished, the reaction mixture was cooled to room temperature. The fluorous phase with $Yb(OPf)_3$ and PfOH catalysts can separate from the organic layer and return to the bottom layer. Use of fluorous phase, recycled without purification, was equally effective. The trinitrations of toluene were run for five consecutive cycles, furnishing the corresponding product with 99, 98, 98, 97, 96% yields. Based on the ^{19}F NMR and UV-Vis spectroscopic data and GC-MS, no loss of catalyst or fluorous solvent to the organic and water (nitric acid) phases can be detected. But we found that the loss of PfOH leaching to the water phase become obvious when the volume ratio of fluorous phase to water phase decreased. The results of ^{19}F NMR and UV-Vis showed that the loss of PfOH increased from 0.1 to 8.9% with the ratio mentioned above decreasing from 10:1 to 1:1. Thus, controlling high volume ratio of fluorous phase to water phase is an important strategy for the use of this novel catalytic system in nitration.

Table 1
Summary of the reactions for nitration of aromatics[a]

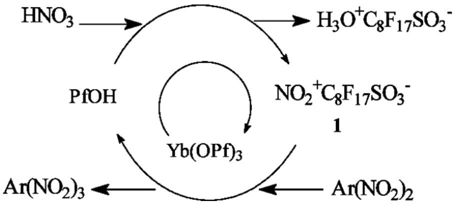
Substrate	HNO_3 (molar equiv.)	Catalyst (mol%) PfOH	Catalyst (mol%) $Yb(OPf)_3$	Temp. (°C)	Time (h)	Isomers of product/ composition (%)[b]
Toluene	6	—	—	95	6	2,4-DNT(81); 2,6-DNT(19); TNT(0)
Toluene	8	—	5	100	8	2,4-DNT(80); 2,6-DNT(20); TNT(0)
Toluene	10	—	10	100	8	2,4-DNT(80); 2,6-DNT(20); TNT(0)
Toluene	6	5	—	95	12	2,4-DNT(72); 2,6-DNT(7); TNT(21)
Toluene	6	15	—	95	12	2,4-DNT(39); 2,6-DNT(5); TNT(55)
Toluene	6	15	5	95	8	2,4-DNT(<1); 2,6-DNT(0); TNT(>99)
Benzene	8	15	5	95	16	1,3-DNB(31); 1,2-DNB(3); TNB(66)
Benzene	8	20	5	95	16	1,3-DNB(<1); 1,2-DNB(0); TNB(>99)
Chlorobenzene	10	22	5	110	24	2,4-DNCB(<1); 2,6-DNCB(0); TNCB(99)
Chlorobenzene[c]	10	22	5	110	24	2,4-DNCB(2); 2,6-DNCB(0); TNCB(98)
Bromobenzene	10	22	5	110	24	2,4-DNBB(26); 2,6-DNBB(2); TNBB(72)
Bromobenzene	12	25	5	120	24	2,4-DNBB(25); 2,6-DNBB(2); TNBB(73)

[a] Reaction conditions for trinitration: substrate (0.0025 mol), perfluorodecalin (8 mL), octane (4 mL). Convension of substrate was above 99.5% by GC analysis.

[b] Composition was determined by GC using an internal standard method.

[c] Recycled case.

We found that $Sc(OPf)_3$-PfOH catalyst had the similar activity for the reaction of toluene with a quantitive conversion to trinitro product in the presence of 15 mol% PfOH and 5 mol% $Sc(OPf)_3$ with 6 equivalents of nitric acid at 95°C over 8 h, while the systems containing other lanthanide perflates, namely $La(OPf)_3$ or $Eu(OPf)_3$, yielded TNT in 39 or 43%, respectively. This would be ascribed to the higher Lewis acidity of $Yb(OPf)_3$ and $Sc(OPf)_3$ than those of other lanthanide perflates. When using perfluorotoluene (C_7F_8) and perfluoromethylcyclohexane (C_7F_{14}) as fluorous solvents in $Yb(OPf)_3$-PfOH catalyzed cases, the nitration also proceeded smoothly to give desired product in 99 and 98% yield, respectively. However, perfluorotoluene (C_7F_8) is in fact miscible withreaction aromatic compounds at room temperature. Thus, it is impossible to recover fluorous phase by phase separation. In addition, it was found that during repeated nitration reactions, the loss of fluorous solvent is very serious when using perfluoromethylcyclohexane (C_7F_{14}) as a fluorous solvent because it is very volatile (bp 76°C). In the reaction of benzene, our efforts here were directed toward the formation of 1,3,5-trinitrobenzene (TNB) directly. Although the reaction became slower in the nitration of benzene, the advantages of the catalytic system were still clear, benzene giving a quantitive conversion to the TNB using 8 equivalents of nitric acid in the presence of 20 mol% PfOH and 5 mol% $Yb(OPf)_3$ over 16 h. Comparison of experimental data in the nitration between toluene and benzene indicates that there is a gradual enhancement of nitration ability in such reaction system as the amount of PfOH and nitric acid increases. Thus, the application of $Yb(OPf)_3$-PfOH in perfluorocarbons was extended to polynitration of chlorobenzene and bromobenzene under more favorable reaction conditions (Table 1). As expected, in the reaction of chlorobenzene with 10 equivalents of nitric acid gave 2,4,6-trinitrochlorobenzene (TNCB) in 99% yield in the presence of 20 mol% PfOH and 5 mol% $Yb(OPf)_3$ at 110°C over 24 h. However, in the case of bromobenzene, only 72% 2,4,6-trinitrobromobenzene (TNBB) was obtained with 28% proportions of 2,4- and 2,6-dinitrobromobenzene (DNBB) under the reaction



Scheme 1. The assumed mechanism for Yb(OPf)$_3$-PfOH catalyzed nitration.

conditions of chlorobenzene case. Increase of nitric acid and PfOH accompanied with even higher reaction temperature appeared not to work for the improvement of nitration.

Finally, the mechanism for Yb(OPf)$_3$-PfOH catalyzed nitration was discussed. Coon et al. [7] reported that $NO_2^+CF_3SO_3^-$ derived from nitric acid and TfOH was a efficient nitration agent in the case that TfOH was used as a solvent and catalyst. Thus, in our research the assumed catalytic cycle as shown in Scheme 1. A key nitration agent is proposed to be nitroperflate **1**, which possesses more strong nitration ability because of electro-drawing property of fluorous tail C_8F_{17}, which strengthens the electrophilicity of $NO_2{}^+$. **1** Reacts even with especially unactivated aromatic compounds, such as dinitro derivates, to afford the corresponding trinitrobenzenes accompanied by regeneration of PfOH. Yb(OPf)$_3$ is assumed to catalyze the nitration involving **1** by its complexation with **1**, which makes $NO_2{}^+$ release from the ion pair **1** easily. In addition, Yb(OPf)$_3$-promoted generation of **1** by virtue of its high oxophilicity in the catalytic cycle is proposed.

Conclusion

In conclusion, Yb(OPf)$_3$-PfOH-PFC system can be considered as the most attractive alternative to existing heterogeneous catalystic system for nitric acid polynitration of aromatic compounds. The reactions produce smaller amounts of waste acid than in traditional processes. The fluorous phase containing catalysts could be easily and efficiently recovered for reuse by simple phase separation.

Acknowledgement

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