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Nanoflow microreactor for dramatic increase not only in reactivity but also in selectivity: Baeyer–Villiger oxidation by aqueous hydrogen peroxide using lowest concentration of a fluorous lanthanide catalyst

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Abstract

Not only the reaction rate but also the regioselectivity in the scandium bis(perfluorooctanesulfonyl)amide-catalyzed Baeyer–Villiger reaction is remarkably increased by the development of the fluorous nanoflow microreactor system continuously controlled by the nanofeeder *DiNaS* (Direct Nanoflow System) even in the lowest concentration of the catalyst (≪0.1 mol%). The Baeyer–Villiger reaction completes within few seconds as a contact time in the nanoflow microreactor to give the lactone products with high regioselectivity without hydrolysis.

Keywords: Nanoflow; Microreactor; Fluorous lanthanide catalyst; Baeyer–Villiger reaction

1. Introduction

Fluorous phase is the third phase orthogonal to organic and aqueous phases. Molecules can be rendered fluorous by the attachment of perfluoroalkyl groups, which are referred to as ponytails [1]. In the fluorous biphasic catalysis, a fluorous catalyst is immobilized in the fluorous phase by one to several fluorous ponytails. The strongly electron-withdrawing properties of perfluoroalkyl ponytails could have a dramatic effect on the catalytic activity of the fluorous catalyst. This is the reason why hydrocarbon spacers have to be set on ligands to minimize the electron-withdrawing effect on the late transition metal catalysts.

The weaker van der Waals interactions of perfluoroalkyl groups result in lower boiling points of the perfluoroalkanes and their low miscibility with organic solvents. Fluorous biphasic catalysis is based on this low miscibility with conventional organic solvents at room temperature. Fluorous solvents are highly hydrophobic and its miscibility to organic solvent is critically temperature dependent. When fluorous ponytails are present in sufficient length and/or quantity, fluorous phase affinities (fluorophilicities) of fluorous lanthanide catalysts can be extremely high. We have thus developed the lanthanide(III) tris(perfluorooctanesulfonyl)amide complexes without any hydrocarbon spacer, which are super Lewis acidic and soluble in both aliphatic fluorocarbons and fluoroaromatic solvents such as benzotrifluoride (BTF) as fluorous/organic hybrid solvents [2,3].

The miniaturization of analytic device using micro-total analysis systems (μ-TAS) has shown a new paradigm especially in biochemical field [4]. Recently, a miniaturized chemical reactor, that is, microreactor, attracts much attention of synthetic organic chemists [5]. The inherent benefits of microreactors are efficient heat transfer, rapid generation of small but detectable quantities of reaction products, fluidic control and short molecular diffusion distance can be applied in organic synthesis [6].

Strict control of the flow rates of the reaction media is the key to develop the fully integrated microreactor system. Usual

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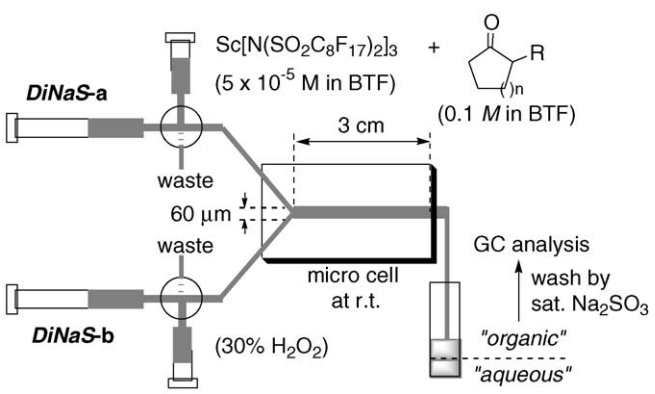
flow rate in the recent micro-pumping systems is in the range of 10–500 μL/min [5]. The development of high-performance nanoscale flow pumping system (''nanoflow system'') has been required for further downsizing of the microreactors by three orders from micro to nano. Electro osmotic flow (EOF) and hydrodynamic pumping technique are employed in microreactors [7]. However, the flow rate is simply proportional to the polarity of the solvent in EOF, and hence, non-polar solvents such as fluorous media cannot be used. By contrast, our nanoflow microreactor system can be employed through strict fluidic control in nano-ordered level even by using non-polar fluorous solvents.

The Baeyer–Villiger (B–V) reaction has been widely employed in organic synthesis by virtue of the unique transformation. An oxygen atom can be inserted into a carbon–carbon single bond by an oxidant [8]. Particularly, hydrogen peroxide is an environmentally friendly oxidant to waste only water. This environmental advantage can make hydrogen peroxide attractive for industrial use. Hydrogen peroxide has, in turn, disadvantages: less reactivity, formation of the regioisomeric mixtures from α-substituted cyclopentenone substrates in particular, and hydrolysis of the ester or lactone products particularly in the presence of strong acids [9]. To overcome these disadvantages, a wide variety of homogeneous and heterogeneous metal catalysts have been developed for the B–V oxidation [8].

We report the remarkable increase not only in the reaction rate but also in the regioselectivity of the B–V oxidation with 30% H_2O_2 even in the low concentration of a fluorous lanthanide complex [10,11] with bis(perfluorooctanesulfonyl)amide ponytail [2] (e.g., $Sc[N(SO_2C_8F_{17})_2]_3$) in our nanoflow microreactor system. This fluorous lanthanide catalyst can be fully employed through the microfabricated flow device strictly controlled by nanofeeder Direct Nanoflow System [12–14] (*DiNaS*) (Scheme 1).

2. Results and discussion

The nanoflow microreactor system is illustrated in Scheme 1. *DiNaS* can now be supplied from KYA TECH Corp. as a high pressure (up to 20.0 MPa) syringe delivery system controlling the tunable flow of solution from 1 to 200,000 nL/min [12]. The



Scheme 1. The Baeyer–Villiger reaction by nanoflow microreactor.

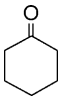
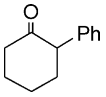
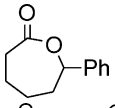
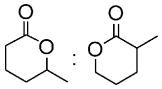
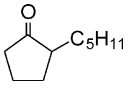
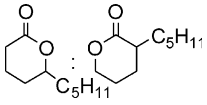
borosilicate microreactors are delivered from Fuji Electric Co. and fabricated by using a standard fabrication procedure [15]. The reaction path dimension is 3 cm length × 30 μm depth × 30 μm width. With decreasing cell dimensions the surface area to volume ratio increases, thereby arising the most striking property of the micro-cell. Due to small dimensions and internal volumes, the reaction rate remarkably increases. Fick's second law of diffusion indicates that the time of transportation T is reduced by shortening the width as shown in the diffusion equation: $T \sim L^2/D$ (L: width, D: diffusion coefficient) [16].

The nature of fluid flow is of great influence on the mixing in the cell. Under laminar flow conditions, molecular diffusion is the only mechanism for exchange of molecules. In turbulent flow, a fluid portion does not stay within a certain layer but moves in a random manner across the flow path. As compared to the length of molecular diffusion for mixing of fluid in laminar flow, the distance traveled by small volume elements in the turbulent flow is much higher, leading to fast and continuous mixing [17]. Due to low flow rates (25–200 nL/min) and small characteristic dimensions, laminar flow conditions are sometimes encountered. Scheme 1 shows the introduction of two solutions (aq. H_2O_2 and BTF) into a microreactor at constant flow rates for different runs [14]. Diffusion between the adjacent domains leads to a homogeneous mixing at molecular level and larger interfacial areas lead to enhance mass and heat transfer as well as promotion of chemical reactions [17].

A batch system of fluorous Sc-amide complex was first examined for the B–V oxidation of 2-methylcyclopentanone in $CF_3C_6F_{11}$ biphasic system with 30% H_2O_2 but no product was observed even after 3 h stirring. By using BTF as a fluorous-organic hybrid solvent, the lactone product (regioselectivity ratio 67:33) was formed. In the nanoflow microreactor, a substrate and $Sc[N(SO_2C_8F_{17})_2]_3$ (5×10^{-5} M) in BTF [18] and 30% H_2O_2 were separately introduced via two micro-inlets (Scheme 1); significantly the B–V oxidation reactions of cyclic ketones were completed within few seconds at r.t. even in very low concentration (5×10^{-5} M) of $Sc[N(SO_2C_8F_{17})_2]_3$. The flow rate was continuously controlled by 100 nL/min for both phases and thus the reactions were examined for 8.1 s as biphasic contact time through 30 μm × 30 μm × 3 cm microchannel. Virtually complete regioselectivity of the product as well as high chemical yield were obtained (Table 1). By contrast, lower yield and regioselectivity were obtained in the batch system. It should be noted here that the virtually complete regioselectivity could be achieved along with quantitative yield by the nanoflow microreactor even with cyclopentanone substrates.

The success in the nanoflow system shows that the faster dispersion of H_2O_2 into BTF including the substrate and the Sc catalyst can be achieved. The perfect regioselectivity and significant increased chemical yield by the nanoflow microreactor can be rationalized by the formation of the metal peroxide [19,20] by the faster dispersion of H_2O_2 into BTF including the fluorous Sc catalyst. The metal peroxide can increase the nucleophilicity of HO_2^-.

Table 1
The B–V reaction in the nanoflow microreactor and batch systems[a]

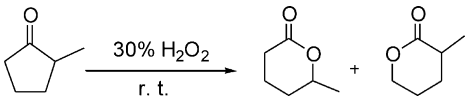
Substrate	Product	Time (s)	% Yield	Regioisomer ratio
		8.1 (5 h)	63 (22)[b]	
		8.1 (5 h)	91 (28)	100:0 (69:31)[b]
		8.1 (5 h)	74 (17)	100:0 (100:0)[b]
		8.1 (5 h)	99 (53)	97:3 (67:33)[b]
		8.1 (5 h)	92 (55)	99:1 (70:30)[b]

[a] Substrates (0.1 M), 30% H_2O_2 aqueous solution and a catalyst (0.05 mol%) in BTF were used in the nanoflow system and flow rates for both layer were maintained by 100 nL/min at r.t.
[b] Catalyst (1 mol%) in BTF was used in batch system.

In order to support for the metal peroxo formation in the nanoflow system [20], two experimental procedures were compared in the batch system (round bottomed flasks) for 2-methylcyclopentanone (Table 2). In the standard batch experiment (Method a) under almost the same condition as the nanoflow system except for the high Sc catalyst concentration (otherwise, oxidation did not proceed within reasonable reaction times). To the Sc catalyst in BTF (1×10^{-3} M), the substrate was added (0.1 M), followed by 30% H_2O_2. The low regioselectivity was observed in the first batch experiment (Scheme 2, Method a). In the premixing batch experiment (Method b), the Sc catalyst was premixed with aq. H_2O_2 for 30 min prior to substrate addition in the same concentrations of the substrate (0.1 M) and the Sc catalyst (1×10^{-3} M) as the Method a. In contrast to the standard Method a, the higher regioselectivity was achieved in the premixing Method b.

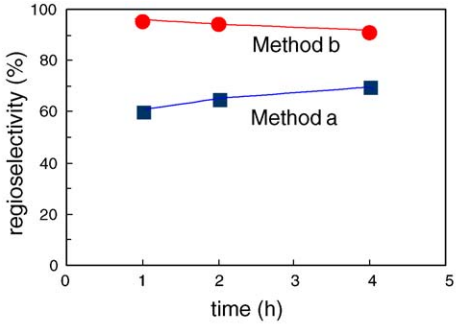
On the basis of these experimental observations in the batch system, the significant increase in regioselectivity can be illustrated in terms of efficient metal peroxide formation in the nanoflow system as shown in Scheme 2. It is crucial either the complexation of the Sc catalyst with H_2O_2 to give more nucleophilic Sc peroxide species (path b) or the coordination of the Sc catalyst to the ketone (path a).

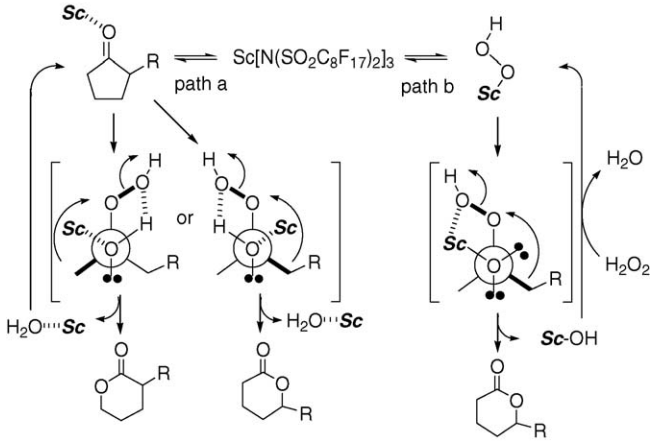
Table 2
The pre-complexation of the Sc peroxo species[a]



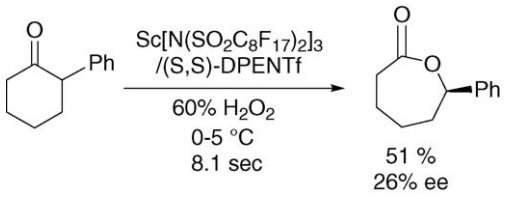
Time (h)	Method a		Method b	
	Regioselectivity	% yield	Regioselectivity	% yield
1	60:40	17	95:5	17
2	65:35	22	94:6	22
4	70:30	39	91:9	43

[a] Substrates (0.1 M) and catalyst (1 mol%) in BTF were used in batch system; yield and regioselectivity were determined by GC analysis.





Scheme 2. The mechanism of the metal peroxo formation followed by the regiospecific oxygen atom insertion.



Scheme 3. Asymmetric Baeyer–Villiger reaction in nanoflow microreactor.

In path b, the intramolecular nucleophilic attack of the hydroperoxide moiety regioselectively proceeds from the Sc complex to the coordinated ketone. The direction of O–O bond *anti* to the migratory carbon bearing R group leads to high regioselectivity with the formation of the Sc hydroxide complex. In the nanoflow microreactor, the faster dispersion of H_2O_2 into BTF phase can efficiently lead to the re-form of the Sc peroxide from the Sc hydroxide complex with H_2O_2. The highly regioselective path b is in contrast to path a, where the intermolecular H_2O_2 attack should proceed from both sides.

We have also examined the asymmetric B–V reaction by our nanoflow system in moderate enantioselectivity. The reaction rate is significantly increased with 60% H_2O_2 even by use of a fluorous lanthanide complex with (*S*,*S*)-1,2-*N*,*N*′-bis-(trifluoromethanesulfonylamino)-1,2-diphenylethane (DPENTf) (5×10^{-2} mol%) (Scheme 3). The fluorous Sc complex and DPENTf ligand were premixed to form the Sc–DPENTf complex in BTF before introducing into the nanoflow microreactor. The reaction proceeded within several seconds (∼50% conversion) in the microreactor to give moderate level of kinetic resolution (26% ee).

In summary, we have developed that the Sc-amide-catalyzed B–V reaction is significantly increased not only in the regioselectivity but also in the reaction rate along with moderate level of kinetic resolution by nanoflow microreactor even in the low concentration of the catalyst (≪0.1 mol%).

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were measured on a Varian GEMINI 300 (300 MHz), a JEOL GSX-500 (500 MHz) and a JEOL EX-270 (270 MHz) spectrometers. Chemical shifts of ^{1}H NMR were expressed in parts per million relative to chloroform (δ 7.26) or tetramethylsilane (δ 0.00) as an internal standard in chloroform-*d*. Chemical shifts of ^{13}C NMR were expressed in parts per million relative to chloroform-*d* (δ 77.0) as an internal standard. IR spectra were measured on a JASCO FT/IR-5000 spectrometer. GC analysis was carried out in SHIMADZU GC-1700. *DiNaS* was supplied from KYA TECH Corp. as a high pressure (up to 20.0 MPa) syringe delivery system controlling the continuous and tunable flow of solution from 1 to 200,000 nL/min. The borosilicate microreactors used in this nanoflow reaction system were prepared by Fuji Electric Co. using a standard fabrication procedure.

3.2. The B–V reaction of cyclic ketones for the batch and nanoflow systems

3.2.1. For batch system

In the BTF (1 ml) solution was added 1 mol% of $Sc[N(SO_2C_8F_{17})_2]_3$ (3 mg, 1×10^{-3} mmol) and solubilize it by stirring at room temperature. Cyclic ketones (0.1 mmol) were added to the fluorous catalyst solution. The reaction mixture was stirred at room temperature for 30 min followed by the addition of 30% aq. hydrogen peroxide solution. The mixture including *n*-decane (0.1 mmol) as an internal standard was allowed to stir at that temperature for 5 h monitoring by TLC. The reaction mixture was quenched with 10% aqueous Na_2SO_3 solution, extracted with Et_2O, washed with brine and dried over anhydrous magnesium sulfate. After evaporation under reduced pressure, the resultant residue was purified by flash column chromatography to give the lactone products. The yield and regioselectivity were determined by GC analysis.

3.2.2. For nanoflow system

The B–V reactions were performed by introducing a BTF solution containing cyclic ketones (0.1 mmol), and $Sc[N(SO_2C_8F_{17})_2]_3$ [5×10^{-5} M (5×10^{-2} mol%)] and *n*-decane (0.1 mmol) as an internal standard through *DiNaS-A* nanofeeder and 30% aq. hydrogen peroxide solution through *DiNaS-B* nanofeeder, respectively, at room temperature. The product was collected in a vial containing ethyl acetate as an eluating solvent. Contact time of the starting materials in the nanoflow device were determined by total volume of the flow path and volume flow rates of the two phases. The yield and regioselectivity were determined by GC analysis.

3.2.3. For the asymmetric B–V reaction

The asymmetric B–V reaction as performed by introducing a BTF solution containing 2-phenylcyclohexanone (0.1 M), (*S*,*S*)-DPENTf and $Sc[N(SO_2C_8F_{17})_2]_3$ [5×10^{-5} M (0.05 mol%)] and *n*-decane (0.1 M) as an internal standard through *DiNaS-A* and 60% aqueous hydrogen peroxide solution through *DiNaS-B* at 0–5 °C temperature. The product was collected in a vial containing ethyl acetate as an eluating solvent. Reaction time of the reacting materials in the microreactor device were determined by total volume of the flow path and volume flow rates of the two phases. The flow rate was maintained by 100–200 nL/min. The product conversion and enantioselectivity were determined by chiral GC analysis (SHIMADZU GC14B, column: CP-cyclodextrin 0.25 mm × 25 m).

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