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Reaction rate enhancement by addition of anionic surfactant SDS in the ruthenium catalyzed hydrogen transfer from a 1,4-diol to 4-phenyl-3-buten-2-one

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Abstract

Hydrogen transfer from *cis*-1,2-cyclohexanedimethanol to (*E*)-4-phenyl-3-buten-2-one catalyzed by [RuCl((*S*)-binap)(benzene)]Cl was accelerated by addition of SDS (sodium dodecyl sulfate). The long alkyl chain is essential for the enhancement of catalytic activity.

Key words: Ruthenium; Hydrogen transfer; Catalysis

1. Introduction

Ruthenium complexes are widely used as homogeneous catalysts in various kinds of organic transformations. Well-designed organic ligands have been developed to perform with better efficiency and higher selectivity [1]. On the other hand, less attention has been paid to the microenvironment of the catalytic centre, as defined by counter anions, salts existing in the reaction mixture, and the solvent cage. Recently, G. Oehme and his co-workers reported the increase of catalytic activity and enantioselectivity in Rh^I catalyzed asymmetric hydrogenations using amphiphiles [2]. Water was employed as solvent and the amphiphalic nature of surfactants was expected to help catalysts disperse into aqueous solvents this enhancing catalytic activity [3*]. The authors interpreted the enhancement of rate in terms of the formation of micelles which contain catalyst, but no clear explanation for this phenomenon has yet been offered. Here, we report enhancement of the reaction rate by addition of anionic surfactants, as observed in Ru^{II} catalyzed homogeneous reactions from *cis*-1,2-cyclohexanedimethanol to (*E*)-4-phenyl-3-buten-2-one.

2. Results and discussion

Oxidation of a 1,4-diol by hydrogen transfer was examined in the presence and absence of additives. *cis*-1,2-Cyclohexanedimethanol (**1**) was treated with [RuCl((*S*)-binap)(benzene)]Cl [4] (binap: 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) in the presence of (*E*)-4-phenyl-3-buten-2-one as a hydrogen acceptor [5*]. Addition of Et_3N was required for satisfactory catalytic activity [6*,7*]. Lactone **2** was obtained accompanied by hemiacetal **3** in the yields described in Table 1 [8*]. In order to compare the total amount of transferred hydrogen, the total yield of **2** and **3** is also shown in Table 1. As lactone **2** is formed by loss of two molecules of hydrogen and hemiacetal **3** by removal of one molecule of H_2, the total yield is given by the sum of the yield of **2** and the half of the yield of **3**. All the reactions were carried out at 60°C for 44 h. Addition of SDS (sodium dodecyl sulfate, n-$C_{12}H_{25}OSO_3Na$, 3 equiv to Ru) improved the total yields of **2** and **3**. Rate enhancement was observed in toluene (runs 2 and 3), 1,2-dichloroethane (runs 7 and 8), THF (runs 9 and 10), and iso-octane (2,2,4-trimethylpentane) (runs 11 and 12). The coordinating solvent THF retarded the

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* Reference number with asterisk indicates a note in the list of references.

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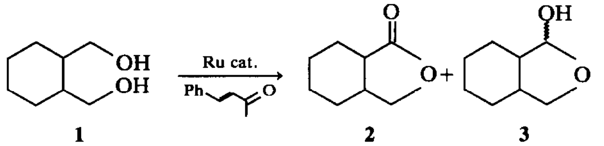
reaction especially without SDS (runs 9 and 10). Protic solvents were not used since they might have been oxidized under the reaction conditions. The reaction mixture was homogeneous in toluene, 1,2-dichloroethane, or THF, but both the catalyst and SDS were almost insoluble in iso-octane. Other anionic surfactants, such as sodium decanesulfonate (n-$C_{10}H_{21}SO_3$-Na) and AOT (bis(2-ethylhexyl) sodium sulfosuccinate) also accelerated the reaction (runs 5, 13, and 15), while the cationic surfactant cetyltrimethylammonium chloride (n-$C_{14}H_{25}NMe_3Cl$) was inert (run 16). The use of sodium methyl sulfate (CH_3OSO_3Na) and sodium methanesulfonate (CH_3SO_3Na), analogues of SDS (n-$C_{12}H_{25}OSO_3Na$) and sodium decanesulfonate (n-$C_{10}H_{21}SO_3Na$) without long alkyl chains, as additives resulted in lower yields (runs 4, 6, and 14). It is noteworthy that the enantioselectivities of the lactone obtained were hardly affected by the addition of surfactants.

Further study was carried out in a homogeneous system to clarify the role of the anionic surfactants using toluene as solvent. A cationic complex [RuCl((*S*)-binap)(benzene)] · n-$C_{12}H_{25}OSO_3$ (**4**) (containing 1.0 equiv of CH_2Cl_2 as crystal solvent) was prepared from [RuCl((*S*)-binap)(benzene)]Cl and SDS [9*]. The complex **4** worked as efficiently as catalyst system [RuCl((*S*)-binap)(benzene)]Cl–SDS to afford **2** (total yield of 87%, lactone **2** 85%, 12% *ee* (1*S*,6*R*), hemiacetal **3** 4%).

In the mechanistic study, it is not clear at this state whether n-$C_{12}H_{25}OSO_3^-$ is bound to the ruthenium centre in the catalytically active species or not, although the similar *ee*s obtained with and without addition of SDS may suggest that the anion n-$C_{12}H_{25}OSO_3^-$ exists relatively far from the enantioselection site of catalyst. We could say that the catalytic centre should be under the influence of n-$C_{12}H_{25}OSO_3^-$ anion since clear improvement of yields is observed after the addition of SDS.

In conclusion, addition of anionic surfactants, especially SDS, improved the catalytic activity of Ru^{II} complexes in hydrogen transfer reaction from *cis*-1,2-cyclohexanedimethanol (**1**) to (*E*)-4-phenyl-3-buten-2-one in various organic solvents. The enantioselectivities of the products were not influenced in any cases [10*]. The observation that long alkyl chains are essential for this effect leads us to consider that anions with a bulky hydrophobic group may change the aggregation form of ruthenium complexes in the reaction mixture to give higher catalytic activity [11]. In all the cases examined

TABLE 1. Effects of surfactants in the oxidation of *cis*-1,2-cyclohexanedimethanol (**1**) by hydrogen transfer reaction catalyzed by [RuCl((*S*)-binap)(benzene)]Cl



1 **2** **3**

Run	Solvent	Additive	Total yield [a] of 2 and 3 (%)	Yield of 2 % (% ee [b])	Yield of 3 (%)
1	– [c]	–	67	61 (23)	12
2	toluene	–	64	57 (13)	14
3	toluene	SDS	89	89 (11)	0
4	toluene	CH_3OSO_3Na	66	64 (– [d])	4
5	toluene	n-$C_{10}H_{21}SO_3Na$	78	76 (– [d])	3
6	toluene	CH_3SO_3Na	56	49 (– [d])	13
7	$ClCH_2CH_2Cl$	–	57	53 (18)	7
8	$ClCH_2CH_2Cl$	SDS	63	62 (9)	1
9	THF	–	21	13 (– [d])	13
10	THF	SDS	46	44 (9)	3
11	iso-octane	–	40	16 (– [d])	47
12	iso-octane	SDS	90	87 (12)	6
13	iso-octane	n-$C_{10}H_{21}SO_3Na$	64	55 (16)	18
14	iso-octane	CH_3SO_3Na	33	20 (24)	25
15	iso-octane	AOT	63	61 (10)	5
16	iso-octane	n-$C_{16}H_{33}N(CH_3)_3Cl$	34	14 (28)	39

[a] The sum of the lactone yield and the half of the hemiacetal yield.

[b] Shown in parentheses are the ees of the **2** obtained. All the predominant products possessed (1*S*,6*R*) configuration.

[c] The reaction was carried out without solvent.

[d] Not determined.

in this work, the possibility of formation of molecular assembly such as micelles or vesicles seems unlikely for the following reasons: (1) the purified complex **4** worked as effectively as the catalyst system [RuCl((*S*)-binap)(benzene)]Cl–SDS; (2) the rate enhancement effect was observed in both non-polar and polar solvents.

3. Experimental details

3.1. General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of the standard Schlenk technique under argon atmosphere purified by passing through a BASF-Catalyst R3-11 column. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, and ^{31}P NMR) were measured on JNM-EX270 spectrometer. Gas chromatographic (GLC) analyses were conducted on a Hitachi 263-30 equipped with a flame ionization detector.

3.2. General procedure for Ru^{II} catalyzed hydrogen transfer reaction from cis-1,2-cyclohexanedimethanol to (E)-4-phenyl-3-buten-2-one

In a 20 ml Schlenk tube were suspended [RuCl((*S*)-binap)(benzene)]Cl (4.4 mg, 0.0050 mmol), Et_3N (0.0030 ml, 0.022 mmol), and SDS (sodium dodecyl sulfate, n-$C_{12}H_{25}OSO_3Na$, 4.3 mg, 0.015 mmol) in toluene (1.0 ml). To the resulting mixture were added *cis*-1,2-cyclohexanedimethanol (**1**) (36 mg, 0.25 mmol) and (*E*)-4-phenyl-3-buten-2-one (73 mg, 0.50 mmol). The mixture was stirred at 60°C for 44 h and the dark brown reaction mixture was then concentrated by rotary evaporator. The conversion of the diol **1** into lactone **2** and hemiacetal **3** was determined by ^{1}H NMR spectra of the crude mixture using triphenylmethane as an internal standard. The crude products were purified by silica-gel column chromatography (hexane/ethyl acetate = 5/1) affording (–)-(2*R*,3*S*)-*cis*-8-oxabicyclo[4.3.0]nonan-7-one (**2**) as a colourless oil accompanied by a small amount of hemiacetal **3**. The ratio of the enantiomers of the lactone **2** was determined by GLC with a chiral column (Chiradex B-PH, 150°C).

3.3. Preparation of [RuCl((S)-binap)(benzene)] · n-$C_{12}H_{25}OSO_3$ (4) from [RuCl((S)-binap)(benzene)]Cl and SDS

In a 20 ml Schlenk tube were suspended [RuCl((*S*)-binap)(benzene)]Cl (70 mg, 0.080 mmol) and SDS (115 mg, 0.40 mmol) in dichloromethane (10 ml). The mixture was stirred at dichloromethane reflux for 1 h and then passed through a pad of Celite to remove NaCl and excess SDS. Removal of the solvent *in vacuo* gave [RuCl((*S*)-binap)(benzene)] · n-$C_{12}H_{25}OSO_3$ (**4**) as a brown solid which contained 1.0 equiv of CH_2Cl_2 as crystal solvent. Mp (benzene) (dec.) 152–163°C. ^{31}P NMR ($CDCl_3$) δ 30.3 (d, $J = 64.1$ Hz), 38.3 (d, $J = 64.1$ Hz). ^{1}H NMR ($CDCl_3$) δ 0.81 (t, $J = 6.6$ Hz, 3H), 1.17 (bs, 16H), 1.23 (m, 2H), 1.61 (m, 2H), 4.04 (t, $J = 6.9$ Hz, 2H), 5.60 (bs, 6H), 5.88 (d, $J = 8.6$ Hz, 1H), 6.41 (d, $J = 8.9$ Hz, 1H), 6.80–7.80 (m, 30H). Found: C, 63.89; H, 5.60. Calcd. for $C_{62}H_{63}ClO_4P_2RuS \cdot CH_2Cl_2$: C, 63.71; H, 5.52%.

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