Solvent-free esterification catalyzed by surfactant-combined catalysts at room temperature†

Li Gang,*[ab] Li Xinzong[ab] and Wumanjiang Eli[a]

Received (in Montpellier, France) 24th October 2006, Accepted 9th January 2007
First published as an Advance Article on the web 26th January 2007
DOI: 10.1039/b615448d

Solvent-free esterifications of various carboxylic acids and alcohols can be catalyzed by surfactant-combined catalysts dodecylbenzene sulfonic acid (DBSA) and copper dodecylbenzene sulfonate (CDBS) in moderate to excellent yield at room temperature. The esterification method has two notable advantages: first, there is no need for any solvent, even water, and secondly, no need for energy, the reaction can proceed smoothly at room temperature.

Introduction

Direct esterification of organic acids and alcohols is one of the most fundamental and important reactions in organic chemistry industry. These ester products are essential fine chemicals used widely in the manufacturing of flavors, pharmaceuticals, plasticizers, polymerization monomers, and as emulsifiers in the food and cosmetic industries.[1] Recently, an increasing interest in esterification has been stimulated by the great promise shown by alkyl esters as biodiesel to substitute for fossil fuels.[2]

Catalysts are key factors of esterification. Traditional industry esterifications are catalyzed by use of concentrated sulfuric acid in organic solvents. Water formed during the process is removed continuously from the system by means of azeotropic distillation. However, there are many serious disadvantages in such catalysis esterification: the processes are accompanied with many co-reactions such as oxidation, sulfonation and etherization, and a high amount of energy is required to remove water to promote the equilibrium process to shift towards the product side. Therefore, many substitutes for sulfuric acid to catalyze esterification reactions have been reported in the literature, such as solid acid,[3] ion exchange resin,[4] molecular sieve[5] and biocatalyst lipase.[6]

Surfactants are a class of chemicals comprised of a hydrophilic polar head group and a hydrophobic chain and can assemble automatically in water or organic solvents. Brønsted- or Lewis acid-type surfactants have been used to catalyze many organic reactions such as aldol, Mannich, Michael and alkylation reactions.[7] Esterifications of carboxylic acids with alcohols catalyzed by *para*-dodecylbenzene sulfonic acid (DBSA) have also been reported in a few examples. Saam *et al.* and Kobayashi *et al.*, respectively, reported polyesterification of nonanedioic acid and 1,10-decanediol at 80 °C and direct esterifications of various carboxylic acids and alcohols at 40 °C using 10 mol% dodecylbenzene sulfonic acid catalyst in water,[8] Although dehydration esterifications in water are exciting and novel, the method lacks practicability in actual production processes since a high amount of wastewater, which is difficult and troublesome to deal with, is produced during the reaction process.

The focus of the present work is the direct esterification of carboxylic acids with alcohols at room temperature in the presence of 5 mol% surfactant-catalyst: *para*-dodecylbenzene sulfonic acid or copper *para*-dodecylbenzene sulfonate, in the absence of solvent. Furthermore, the catalysis esterification mechanism is investigated.

Direct esterifications of various carboxylic acids and alcohols were catalyzed by 5 mol% DBSA and CDBS at room temperature as shown in Table 1. It is readily seen that conversions of carboxylic acids are dependent upon the solubility of the reactants and product ester in water: the poorer the solubility of reactants and product ester in water, the higher the conversion to carboxylic acids. The conversions were excellent for water-insoluble reactants or product esters (entries 1–6). For acetic acid and ethanol, because they are fully soluble in water (entry 10) and since the product ethyl acetate is also partially soluble in water, the conversions to acetic acid catalyzed by DBSA and CDBS were only 76.8 and 75.9%, much lower than the 98.7 and 97.2% of esterification of oleic acids with 1-octanol (entry 1). There are mainly two reasons for this: one is that most of the water formed is still present in a continuous phase because of a degree of solubility of the reactant and product in water, which results in hydrolysis of the product ester. The other is that the reactants partly dissolve in water in the micelle interior. For the case where the reactants are soluble in water but the products are not, the conversions were good (entries 7–9). Although *iso*-alcohols reacted smoothly (entry 11), esterification of secondary alcohols was very slow due to strong steric hindrance (entries 13 and 14). For acrylic acid (entry 12), the esterification was slow due to the conjugation effect of carbonyl and ethylene. Higher conversion could be obtained by heating or prolonged reaction. Esterification at room temperature using DBSA or CDBS as catalysts is also excellent for strongly hydrophobic substrates.

---

[a] *Xinjiang Technology Institute of Physics and Chemistry, The Chinese Academy of Science, Urumqi, 830011, People's Republic of China. E-mail: ligang@ms.xjb.ac.cn; Fax: +86 991-3838957; Tel: +86 991-3858347*
[b] *Graduate University of the Chinese Academy of Sciences, Beijing, 100049, People's Republic of China*

† Electronic supplementary information (ESI) available: IR spectrograms of part product esters. See DOI: 10.1039/b615448d

Table 1 DBSA and CDBS catalyzed direct esterifications of various substrates

$$\mathrm{RCOOH + R'OH \xrightarrow[24\ h]{rt\ 5\ mol\%cat} RCOOR' + H_2O}$$

Entry	R	R′	Conversion (%) DBSA	Conversion (%) CDBS
1	$CH_3(CH_2)_7CH{=}CH(CH_2)_7$–	$CH_3(CH_2)_7$–	98.7	97.2
2	$CH_3(CH_2)_7CH{=}CH(CH_2)_7$–	$CH_3(CH_2)_4$–	98.4	95.7
3	$CH_3(CH_2)_7CH{=}CH(CH_2)_7$–	$CH_3(CH_2)_3$–	97.1	94.4
4	$CH_3(CH_2)_7CH{=}CH(CH_2)_7$–	$CH_3(CH_2)_2$–	95.4	92.6
5	$CH_3(CH_2)_7CH{=}CH(CH_2)_7$–	CH_3CH_2–	94.6	90.8
6	$CH_3(CH_2)_6$–	$CH_3(CH_2)_4$–	94.8	94.9
7	$CH_3(CH_2)_2$–	$CH_3(CH_2)_4$–	91.8	85.3
8	CH_3CH_2–	$CH_3(CH_2)_4$–	88.5	83.6
9	CH_3–	$CH_3(CH_2)_4$–	86.9	83.8
10	CH_3–	CH_3CH_2–	76.8	75.9
11	$CH_3(CH_2)_6$–	$CH_3CH(CH_3)CH_2$–	90.8	90.9
12	$CH_2{=}CH$–	$CH_3(CH_2)_7$–	71.3 86.7[a]	59.0 78.6[a]
13	$CH_3(CH_2)_6$–	$CH_3CH_2CH(CH_3)$–	54.9	48.9
14	$CH_3(CH_2)_6$–	$CH_3CH(CH_3)$–	64.5 76.5[b]	60.2 64.3[b]

[a] 72 h. [b] 60 °C.

To understand the mechanism of direct esterification of carboxylic acids with alcohols catalyzed by surfactant-combined catalysts DBSA and CDBS, the catalysis results of DBSA and CDBS were compared with those of other catalysts (5 mol%) in esterification of oleic acid with 1-octanol as typical substrates.

As shown in Table 2, when the esterification reaction of oleic acid with 1-octanol was catalyzed by 5 mol% surfactant-combined catalysts DBSA and CDBS at room temperature, the conversions of oleic acid were excellent, up to 98.7 and 97.6%, respectively (entries 1 and 2). Comparatively, the ordinary surfactant sodium *para*-dodecylbenzene sulfonate (SDBS) was hardly active towards esterification (entry 3) though the only difference between SDBS and DBSA and CDBS is the nature of the cations (Na^+ for SDBS; Brønsted acid H^+ for DBSA; and Lewis acid Cu^{2+} for CDBS). This showed that Brønsted acid H^+ or Lewis acid Cu^{2+} are the key factors to catalyze esterification. With simple non-surfactant Lewis acids ($CuCl_2$, $Cu(OTs)_2$) and Brønsted acids (TsOH, H_2SO_4), esterification under the same conditions (entries 4–7), was much inferior to that of DBSA and CDBS. This fact indicated that the long alkyl chains of DBSA and CDBS were also vital for the efficient catalysis. However, the cation surfactant cetyltrimethylammonium bromide (CTAB) was hardly efficient for esterification (entry 8). These results demonstrate that two qualifications are indispensable for efficient catalytic esterifications of carboxylic acids with alcohols: (i) long-alkyl chain of surfactant; (ii) Brønsted acid H^+ or Lewis acid Cu^{2+}. DBSA and CDBS fully meet these two requirements.

Table 2 Direct esterifications with various catalysts

Entry	Catalyst	Conversion (%)
1	DBSA	98.7
2	CDBS	97.2
3	SDBS	2.1
4	H_2SO_4	20.1
5	$CuCl_2$	18.5
6	TsOH	55.2
7	$Cu(OTs)_2$	48.5
8	CTAB	0.9

Most of the esterification catalysts used in organic synthesis are Brønsted acids such as H_2SO_4, CH_3SO_3H or heterogeneous solid acids. The mechanisms of esterification catalysis have been deeply researched.[2b,9] The mechanism of DBSA catalyzed esterification is similar. DBSA promotes the protonation of the carbonyl oxygen on the carboxylic group to favor of nucleophilic attack by the alcohol to form a tetrahedral intermediate as shown in Fig. 1. Dehydration of the intermediate leads to the product ester.

Lewis acids such as Cu^{2+}, Mg^{2+} and Al^{3+} have been used as catalysts for esterification in a few reports.[10] Barbosa *et al.* provided a plausible mechanism for esterification reaction using $SiO_2/ZnCl_2$ in solid-phase catalysis.[11] Based on these studies, we presume the mechanism as shown in Fig. 2 for CDBS catalyzed esterifications of carboxylic acids and alcohols. The mechanism of CDBS catalysis is described as follows: the carbonyl oxygen of the carboxylic group combines

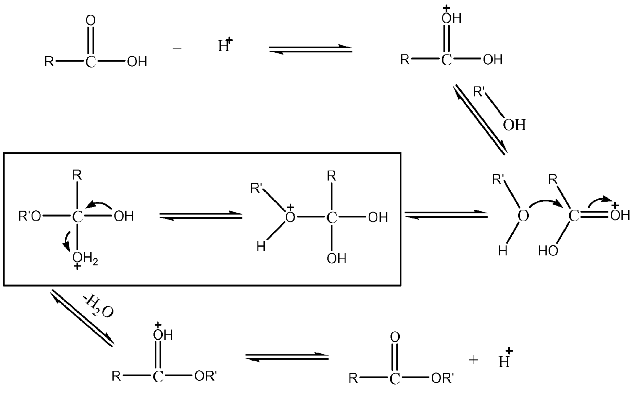

Fig. 1 Mechanism of the DBSA catalyzed esterification.

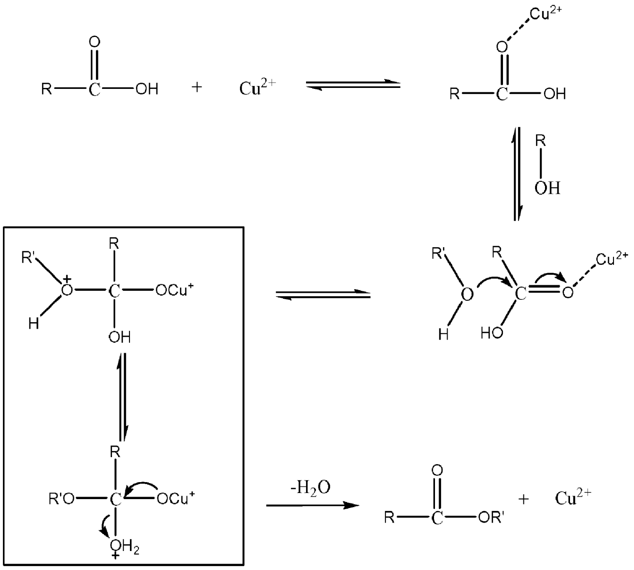

Fig. 2 Proposed mechanism of the CDBS catalyzed esterification.

with Cu^{2+} of CDBS to form an activated complex which is attacked by the nucleophile alcohol to form a tetrahedral intermediate. The product ester is obtained after the intermediate eliminates water.

Significantly, DBSA and CDBS as surfactants in hydrophobic substrates can self-assemble reverse clusters, which provide a large interface between the catalyst and reactant where the reaction takes place, so greatly enhancing the reaction rate. Also the formation of DBSA and CDBS clusters would congregate catalytic species H^+ and Cu^{2+} at the reaction interface, which could catalyze the esterification more efficiently. The process of esterification catalyzed by DBSA and CDBS is illustrated in Fig. 3. Furthermore, because of hydrophobic property of the continuous substrate phase and hydrophilicity of the cluster interior, water molecules produced could automatically enter the cluster interior while the product ester enters the continuous phase. With progress of the reaction, surfactant clusters are enlarged to form inverse micelles with the aid of alcohol as a co-surfactant. Separation of water from the ester avoids reverse reaction hydrolysis and rapidly promotes the equilibrium reaction towards product.

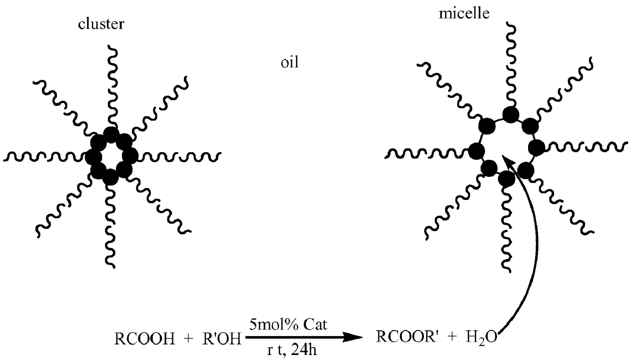

Fig. 3 Illustration of auto-isolation of water produced during the esterification process.

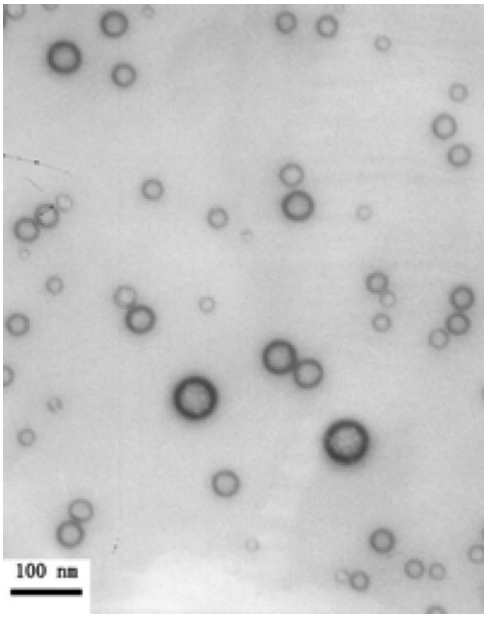

Fig. 4 TEM images of the oleic acid/1-octanol/DBSA system.

Formation of micelles by DBSA in the reaction system was confirmed by TEM as shown in Fig. 4. The reverse micelles resemble micro separators which automatically separate water produced by esterification from the product ester. Thus neither azeotropic distillation equipment, energy nor a drying agent is required.

Conclusion

This study indicates that the catalysts DBSA and CDBS show a twofold function during the esterification. First, as Brønsted and Lewis acids, they catalyze the esterification reaction. Secondly, as surfactants, they can form reverse micelles in substrates to separate water produced from the product ester.

The results further show that the conversions of carboxylic acid are dependent on the solubility of the reactants and product ester in water: the poorer the solubility of reactants and product ester in water, the higher the conversion to carboxylic acids. Also, the reaction can smoothly proceed at room temperature with no need for energy imput or equipment to remove produced water, which automatically enters the micelle interiors owing to the system hydrophobicity. Additionally there is no need for any solvent, even water. Therefore, the esterification catalyzed by surfactant-combined catalysts DBSA and CDBS should be promising in practical production.

Experimental

Chemicals

Dodecylbenzene sulfonic acid (DBSA, 98% purity), sodium dodecylbenzene sulfonate (SDBS, chemical purity), 1-octanol, 2-butanol, *n*-butyric acid and *para*-toluenesulfonate acid (TsOH, chemical purity) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Oleic acid, 1-propanol, 1-butanol, KOH, 1,3-propanediol, Copper oxide, cetyltrimethylammonium bromide (CTAB), propionic acid and acetic acid were purchased from Shanghai Shanpu chemical industry Co., Ltd (China). Ethanol, 2-propanol, sulfuric acid (H_2SO_4 98%), isobutanol, diethyl ether, acrylic acid and octanoic acid were obtained from Tianjin Chemical Reagent Factory (China). Benzene sulfuric acid (BSA) were obtained from Alfa Aesar Co., Ltd. Benzyl alcohol, 1-pentanol and valeric acid were all from Tianjin Guangfu Institute of Fine Chemical Industry Chemical Reagent Factory (China). All the other chemicals used were of analytical grade and were used without further purification.

Preparation of catalysis

Copper *para*-dodecylbenzene sulfonate was synthesized from copper oxide and DBSA in a 1 : 1 molar ratio. The detailed process was as follows: 32.6 g of DBSA was taken in a 100 ml glass reactor. 7.95 g of copper oxide powder was added slowly within 30 min at room temperature and was mixed using a magnetic stirrer (500 rpm). The mixture was heated slowly to 110 °C (2 °C min^{-1}) and then the system was kept at 110 °C for 3 h in order to remove water formed during the reaction process. The reaction was then cooled to room temperature.

Esterification reaction

A carboxylic acid, alcohol and 5 mol% catalyst were added to a 50 ml one-necked round-bottom flask with a reflux condenser. The reaction mixture was continuously stirred using a magnetic stirrer (800 rpm) for 24 h at room temperature.

TEM sample preparation

Oleic acid and 1-octanol (1 : 1 molar ratio) were added to a glass bottle to which 5 mol% DBSA was added. The reaction mixture was continuously stirred using a magnetic stirrer (800 rpm) for 24 h at room temperature. After the end of the reaction, a special copper net for TEM was dipped into the system using tweezers. Then the net was placed in the TEM apparatus and observed.

Analysis

After completion of the reaction, the percentage conversion of carboxylic acids was measured by standard titration.[12] The detailed procedure was as follows: After completion of the reaction, the mixture was dissolved in ethanol–diethyl ether (1 : 2, v/v) and phenolphthalein solution in ethanol (10 g L^{-1}) as indicator was added, and the titration was performed by means of 0.1 mol L^{-1} KOH solution in ethanol. The volume of KOH solution consumed was recorded, and the percentage conversion of carboxylic acids was calculated using the following expression:

$$\text{Conv. carboxylic acid (\%)} = \left[1 - \frac{V - V_2 M_2}{V_1 M_1}\right] \times 100\%$$

V_1 (ml mol^{-1}) and V_2 (ml mol^{-1}) represent the volume of KOH solution, respectively consumed by carboxylic acid per gram and catalysis per gram, which were titrated by KOH–ethanol solution solely according to same method. V (ml) represents the volume consumed by the reaction mixture after completion of the esterification. M_1 (mol) and M_2 (mol) represent carboxylic acid and catalyst added in reactor, respectively.

After the titration, low-boiling point solvents and water in the reaction mixture were removed by a rotory evaporator, and the pure esters were obtained by decompression distillation. The ester structures were confirmed by IR (Nicolet-5DX).

Acknowledgements

This work is financially supported by "XIBUZHIGUANG" Science Foundation of the Chinese Academy of Sciences.

References

1 (*a*) Y. Liu, E. Lotero and J. G. Goodwin, Jr, *J. Mol. Catal. A: Chem.*, 2006, **245**, 132–140; (*b*) M. R. Altiokka and A. Citak, *Appl. Catal., A*, 2003, **239**, 141–148; (*c*) G. D. Yadav and P. H. Mehta, *Ind. Eng. Chem. Res.*, 1994, **33**, 2198–2208.
2 (*a*) R. Aafaqi, A. R. Mohamed and S. Bhatia, *J. Chem. Technol. Biotechnol.*, 2004, **79**, 1127–1134; (*b*) E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce and J. G. Goodwin, Jr, *Ind. Eng. Chem. Res.*, 2005, **44**, 5353–5363.
3 (*a*) X. Chen, Z. Xu and T. Okuhara, *Appl. Catal., A*, 1999, **180**, 261–269; (*b*) J. H. Sepulveda, J. C. Yori and C. R. Vera, *Appl. Catal., A*, 2005, **288**, 18–24.
4 (*a*) S. Blagova, S. Paradaa, O. Bailerb, P. Moritzb, D. Lamc, R. Weinandd and H. Hassea, *Chem. Eng. Sci.*, 2006, **61**, 753–765; (*b*) Y. Zhang, L. Ma and J. Yang, *React. Funct. Polym.*, 2004, **61**, 101–114.
5 (*a*) S. R. Kirumakki, N. Nagaraju and S. Narayanan, *Appl. Catal., A*, 2004, **273**, 1–9; (*b*) I. K. Mbaraka and B. H. Shanks, *J. Catal.*, 2005, **229**, 365–373; (*c*) M. Alvaro, A. Corma, D. Das, V. Fornés and H. García, *J. Catal.*, 2005, **231**, 48–55.
6 (*a*) A. R. M. Yahya, W. A. Anderson and M. M. Young, *Enzyme Microb. Technol.*, 1998, **23**, 438–450; (*b*) G. Steinke, P. Weitkamp, E. Klein and K. D. Mukherjee, *J. Agric. Food Chem.*, 2001, **49**, 647–651.
7 (*a*) K. Manabe, Y. Mori, S. Nagayama, K. Odashima and S. Kobayashi, *Inorg. Chim. Acta*, 1999, **296**, 158–163; (*b*) K. Manabe and S. Kobayashi, *Org. Lett.*, 1999, **1**, 1965–167; (*c*) Y. Mori, K. Kakumoto, K. Manabe and S. Kobayashi, *Tetrahedron Lett.*, 2000, **41**, 3107–3111; (*d*) G. Cerichelli, S. Cerritelli, M. Chiarini, P. D. Maria and A. Fontana, *Chem.–Eur. J.*, 2002, **8**, 5204–5210.
8 (*a*) M. Baile, Y. J. Chou and J. C. Saam, *Polym. Bull.*, 1990, **23**, 251–255; (*b*) K. Manabe, X. Sun and S. Kobayashi, *J. Am. Chem. Soc.*, 2001, **123**, 10101–10102; (*c*) K. Manabe, S. Iimura, X. Sun and S. Kobayashi, *J. Am. Chem. Soc.*, 2002, **124**, 11971–11978.
9 T. N. Shah and S. M. C. Ritchie, *Appl. Catal., A*, 2005, **296**, 12–20.
10 (*a*) M. Wang, Z. Wang, Z. Sun and H. Jiang, *React. Kinet. Catal. Lett.*, 2005, **84**, 223–228; (*b*) L. Gooßen and A. Döhring, *Adv. Synth. Catal.*, 2003, **345**, 943–947; (*c*) Y. Wang, W. Li and React Kinet, *Catal. Lett.*, 2004, **83**, 195–203.
11 S. L. Barbosa, M. J. Dabdoub, G. R. Hurtado, S. I. Klein, A. C. M. Baroni and C. Cunha, *Appl. Catal., A*, 2006, **313**, 146–150.
12 (*a*) M. Habulin, V. Krmelj and Z. Knez, *J. Agric. Food Chem.*, 1996, **44**, 338–342; (*b*) M. Leitgeb and Z. Knez, *J. Am. Oil Chem. Soc.*, 1990, **67**, 775–778; (*c*) International Standard Organization 660, 1996.