Ultrasonics Sonochemistry 21 (2014) 620–627

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Ultrasound assisted the preparation of 1-(4-nitrophenyl) imidazole under a new multi-site phase-transfer catalyst – Kinetic study

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ARTICLE INFO

Article history:
Received 27 June 2013
Received in revised form 9 September 2013
Accepted 2 October 2013
Available online 11 October 2013

Keywords:
Sonochemistry
Imidazole
Interfacial reaction
Kinetics
MPTC
1-Chloro-4-nitrobenzene

ABSTRACT

In this work, the nitroarylation of imidazole catalyzed by a new novel dual-site phase-transfer catalyst was carried out in an alkaline solution/imidazole in chlorobenzene two-phase medium with ultrasonic irradiation (40 kHz, 300 W). This new synthesized phase-transfer catalyst, N^1,N^6-diethyl-N^1,N^1,N^6,N^6-tetraisopropylhexane-1,6-diaminium dichloride (MPTC), which possesses two-site activity, was obtained from the reaction of 1,6-dichlorohexane and N-ethyl-N-isopropylpropane-2-amine. The reaction of imidazole and alkali was carried out at the interface to generate sodium imidazole anion which can further react with MPTC form quaternary ammonium imidazole anion along with ultrasonic irradiation (40 kHz, 300 W). This ion-pair further react with 1-chloro-4-nitrobenzene which is present in the organic phase to produce 1-(4-nitropheny) imidazole. The reaction follows a pseudo first-order rate law. Kinetics of the reactions such as effect of the catalysts, ultrasonic effect, agitation speed, temperature, alkaline concentration, amount of 4-nitrochlorobenzene and the solvent effect on the reaction rate were investigated in detail. Peculiar phenomenon for the dependence of the reaction rate on the amount of MPTC and ultrasonication are explained satisfactorily.

1. Introduction

As the chemical reactants reside in immiscible phases, phase-transfer catalysts have the ability to carry out the heterogeneous reactions by one of the reactants penetrating from its normal phase (generally aqueous phase) to the organic phase where the reaction take place, which gives a high conversion and selectivity for the desired product under mild reaction conditions [1]. The quaternary onium salts as an effective catalysts for enhancing the two-phase reaction, this methodology occupies a unique niche in organic synthesis and it is a commercially matured discipline with over six hundred applications [2–7] covering a wide spectrum of industries such as pharmaceuticals, agrochemicals, dyes, perfumes, flavours, specialty polymers, pollution control, etc. As the application of phase-transfer catalysts (PTC) grow, much effort was placed on the development of phase-transfer catalysts with higher catalytic efficiency. To this end, researchers have developed "multi-site" phase-transfer catalysts (MPTC) for much higher activity than normal phase-transfer catalysts. Recently, the catalytic behavior of multi-site phase-transfer catalysts have been attracted much attention, due to the fact that multiple molecules of the aqueous reactant can be carried into the organic phase once a reaction cycle, thus the catalytic efficiency is enhanced [8–12].

Currently, a new analytical and process experimental techniques which are environmental benign techniques viz., ultrasound and microwave irradiation have become immensely popular in promoting various organic reactions [13–17]. Ultrasound irradiation is a transmission of a sound wave through a medium and is regarded as a form of energy enhance the rate of the reaction due to mass transfer and effective mixing [18–20].

The effect of ultrasonic energies in organic syntheses (homogeneous and heterogeneous reactions) has been boosted in recent years [21–27]. Sonication of multiphase systems accelerates the reaction by ensuring a better contact between the different phases [28,29]. Further, ultrasound irradiation also increase the reaction rate and avoid the use of high reaction temperatures [30]. These days this environmental benign technology is combined with phase-transfer catalysts (PTC) with primary objective of optimizing reaction conditions [31–33].

Our interest was entered on first time evaluating the influence of ultrasound in association with multi-site phase-transfer catalyst (MPTC) on the synthesis of 1-(4-nitrophenyl) imidazole from imidazole with 1-chloro-4-nitrobenzene (CNB) under heterogeneous condition. Since, the kinetic study of nitroarylation of imidazole using 1-chloro-4-nitrobenzene under controlled MPTC reaction conditions will be interesting and challenging, we followed the

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http://dx.doi.org/10.1016/j.ultsonch.2013.10.001

kinetic study using a newly synthesized multi-site phase-transfer catalyst (MPTC) viz., N^1,N^6-diethyl-N^1,N^1,N^6,N^6-tetraisopropylhexane-1,6-diaminium dichloride, as a catalyst under ultrasonic condition (40 kHz; 300 W). Further, to the best of our knowledge, there is no literature reports' regarding nitroarylation of imidazole under MPTC-ultrasonic irradiation condition.

2. Experimental

2.1. Chemicals

The reagents imidazole, 1-chloro-4-nitrobenzene (CNB), sodium hydroxide, benzene, toluene, chlorobenzene, biphenyl and other reagents are synthesis guaranteed grade (GR) chemicals and were used without further treatments.

2.2. Instrumentation

FT-IR spectra were recorded on a Brucker-Tensor 27 FT-IR spectrophometer. ^{1}H NMR and ^{13}C spectra were recorded on a Bruker 400 MHz and 100 MHz respective using TMS as an internal standard. Gas chromatography was carried out using a GC-Varian 3700 model. Ultrasonic water bath, Equitron, Media Instrument Manufacturing company, Chennai, India-600004. The ultrasonic generator was a thermostatic bath equipped with dual frequencies (28/40 kHz) and electric power 300 W with 0.0126 W/mL of power density.

3. Ultrasonic process equipment

Ultrasonic energy is transmitted to the process vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers stainless steel body. The sonochemical reactor configuration used in the present work is basically an ultrasonic bath. The internal dimension of the ultrasonic cleaner tank is 48 cm × 28 cm × 20 cm with liquid holding capacity of 5 L. Two types of frequencies of ultrasound were used in these experiments, which are 28 kHz and 40 kHz with each output as 300 W. Both ultrasounds separately produces through a flat transducer mounted at the bottom of the sonicator. The reactor was a 250 mL three-necked Pyrex round-bottom flask. This reaction vessel was supported at the center of the ultrasonic cleaning bath 2 cm above from the position of the transducer to get the maximum ultrasound energy. All the experimental parameters were done at 40 kHz with output power of 300 W.

4. Synthesis of a new MPTC

A mixture of 2.5 mL of N-ethyl-N-isopropylpropan-2-amine, 2.0 mL of 1,6-dichlorohexane, and 60 mL of ethanol was placed in a 250 mL three necked round – bottomed Pyrex flask. The reaction mixture was refluxed in the nitrogen atmosphere for 15 h. The solvent and excess 1,6-dichlorohexane were completely removed under vacuum and onium salt, i.e. N^1,N^6-diethyl-N^1,N^1,N^6,N^6-tetraisopropylhexane-1,6-diaminium dichloride (MPTC, Scheme 1) was washed with n-hexane (3 × 20 mL). The white solid MPTC (hygroscopic) was stored in a $CaCl_2$ desiccator. m.pt. 192 °C; Yield: 93%; FT-IR: 1181 cm^{-1} (C–N^+ stretching); ^{1}H NMR (400 MHz, $CDCl_3$); δ.1.41–1.43 (m, 30H–**C**H_3), 1.51–1.56 (s, 4H, CH_2),1.68–1.99 (s, 4H, C**H$_2$**), 3.07–3.14 (m, 8H, N^+–C**H$_2$**) 3.63–3.71 (heptuplet, 4H, C**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ. 12.19 (**C**H_3), 17.40 (**C**H_3), 18.68 (**C**H_2), 26.26(**C**H_2), 42.51 (N^+–**C**H_2), 54.25 (N^+–**C**H).

5. Synthesis of 1-(4-nitrophenyl) imidazole under mechanical stirring

To the mixture of NaOH (20 g) in water (15 mL) and the newly synthesized MPTC (0.3 g, 1.45×10^{-3} mol), imidazole (1.0 g, .0147 mol) was added under overhead stirring to generate the imidazole anion. Then 1-chloro-4-nitrobenzene (2.77 g, 0.0177 mol) in chlorobenzene (40 mL) was added slowly. The reaction mixture was heated at 60 °C for 6 h with vigorous stirring. The crude product was isolated by simple extraction with diethyl ether (3 × 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was chromatography (SiO_2) employing hexane: ethyl acetate (9:1) as an eluent to obtain a pure monoderivative. The identity of the product was confirmed by ^{1}H NMR and ^{13}C NMR spectra of the product. m.pt. 203 °C; Yield: 92%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.32 (s, 1H), 7.36–7.39 (s, 1H), 7.86 m–7.99 (s, 1H), (Imidazole-**H**). 7.58–7.61 (q, 2H, Ar–C**H**), 8.37–8.40 (q, 2H, Ar–C**H**). ^{13}C NMR (75 MHz, $CDCl_3$): δ. 117.65, 131.75, 135.41, (Imidazole-**C**H). 117.65, 121.07, 142.00, 146.30 (Ar–**C**H).

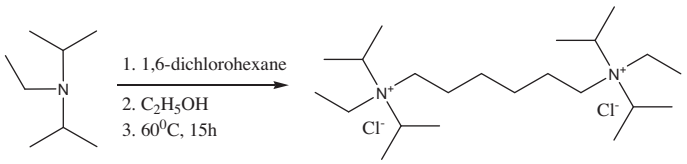
6. Reaction mechanism and kinetic model

For synthesizing 1-(4-nitrophenyl) imidazole compound, the overall reaction of imidazole and 1-chloro-4-nitrobenzene (CNB) was catalyzed by the newly prepared MPTC (Q^+Cl^-) in the aqueous alkaline (NaOH) bi-phase medium and is represented in Scheme 2. The reaction is carried out under MPTC assisted ultrasonic irradiation condition (40 kHz, 300 W) under pseudo first-order condition. In the current investigation the kinetics was followed in the presence of an excess amount of imidazole and by fixing 1-chloro-4-nitrobenzene as limiting agent. The main reason for investigating this reaction is, the effect of low frequency ultrasound irradiation (40 kHz, 300 W) along with agitation speed (300 rpm) to find out the effect of change of k_{app} value of this system.

6.1. Definition

The conversion (X) of 1-chloro-4-nitrobenzene (CNB) is defines as follows:

$$X = 1 - \{[CNB]_0/[CNB]_{.o,i}\} \quad (1)$$



N-ethyl-*N*-isopropylpropan-2-amine N^1,N^6-diethyl-N^1,N^1,N^6,N^6-tetraisopropylhexane-1,6-diaminium dichloride

Scheme 1. Preparation of MPTC.