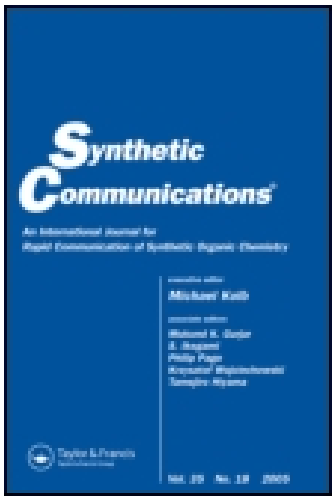

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ULTRASOUND ENHANCED PTC CONVERSION OF BENZAMIDE TO BENZONITRILE

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ULTRASOUND ENHANCED PTC CONVERSION OF BENZAMIDE TO BENZONITRILE

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ABSTRACT

Enhancement of the reaction rate by combining the beneficial effects of PTC and ultrasound has been explored in the present study by taking the transformation of benzamide by dehydration to give benzonitrile as a model system. It was found that there is a substantial reduction in the reaction time when ultrasound was coupled with PTC.

INTRODUCTION

Liquid-liquid heterogeneous systems form an important place in the domain of chemical reactions. The major limitation is the generation of sufficient interfacial area especially for mass transfer controlled reactions.

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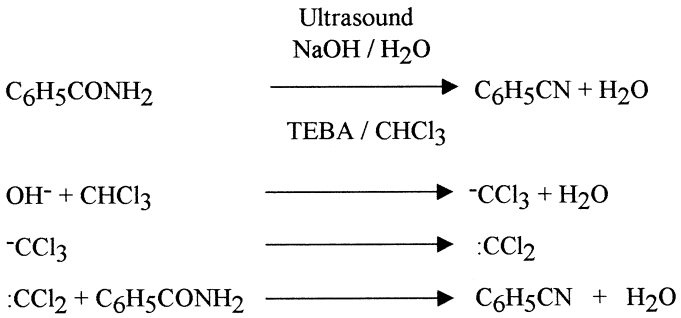
The role of PTC in enhancing the rate of the reaction under these conditions is a well known phenomenon.[1] Application of ultrasound for substantial improvement of rate and product yields of variety of reactions is also an area studied widely.[2] Most of the reactions initiated by ultrasound proceeds via free radical mechanism (true and direct chemical effect). In case of liquid-liquid immiscible systems it causes homogenisation or generates extremely fine emulsions/dispersions resulting in higher interfacial area, which then leads to the desired chemical effect (indirect chemical effect). This is an unique property of ultrasound since conventional methods of mixing cannot produce such a high interfacial area, especially when one of the phase used is highly viscous.[3–5] Thus, ultrasound can play a dual role of creating higher interfacial area as well as facilitating the process of interfacial transport. Such useful effects which led to the use of ultrasound to enhance the efficacy or even to replace PTC's (solid/liquid) in some of the chemical reactions.

SELECTION OF REACTION

The two-phase reaction, which has been selected under the study, is the dehydration of benzamide to give benzonitrile. This reaction is of practical importance, since many of the cyano compounds are useful as drug as well as agrochemical intermediates. Generally this reaction is carried out by means of dehydration with the application of a number of acid catalysts such as aluminium chloride, phosphorous pentoxide, phosphorous oxy chloride, thionyl chloride and trimethylsilylpolyphosphate.[6] The use of these catalysts presents many difficulties in practice. Most of these are required in large excess and many get destroyed during recovery of the product. Also, the catalysts often render the medium corrosive which, can result into a product contamination. Mildly acidic catalysts have also been used in the reaction. Temperatures in the range of 280 to 380°C have to be employed for these acidic catalysts.[7] Although high yields of nitriles have been reported by vapour phase dehydration over zeolite catalysts,[8–9] this method also requires a high reaction temperature, say 400°C and again it is restricted to volatile amides. PTC's or quaternary ammonium salts like Benzyltriethyl ammonium chloride (TEBA) have also been employed in this conversion, by carrying out the reaction in a two-phase mode.[10] The main advantage of this reaction is that it proceeds at room temperature with good yields in 2 hrs of time. In order to enhance the reaction rates further, ultrasound was coupled with PTC in the above transformation. The possible reaction scheme under the application of

ultrasound and PTC can be shown as,



EXPERIMENTAL

All Ultrasonically mediated dehydrations were carried out using a variable amplitude/intensity type ultrasonic probe (Ace Glass Inc., New York, USA) having a driving frequency of 22.5 kHz, with a rated power of 600 W. This horn has the provision for tuning, which is used to overcome the drop in performance due to the continuous erosion at the horn tip. In the present study, the horn was tuned prior to the study, in order to obtain maximum performance. In all the studies, it was operated at 20% amplitude i.e., at an electrical output of 120 Watts. All the chemicals used were of analytical grade (S. D. Finechem, India) and were used without further purification.

General Procedure: Dehydration of Benzamide by Ultrasound and PTC

Mixture of 0.5042 g benzamide (4.17 mmol), 0.023 g TEBA (0.1 mmol), 10.1 ml chloroform and 3.3 g of NaOH (83.25 mmol, as 50% aqueous solution) were taken in a 25 ml reactor and irradiated by keeping the horn at the interface for a given period of time at 25°C with different conditions like stirring with ultrasound and with only ultrasound irradiation. The reaction mixture, including the white precipitate was then extracted with chloroform (2×10 ml), then washed with 10 ml water. Finally the obtained organic layer was dried over Na_2SO_4 and the product was then distilled under reduced pressure to afford oily residue, benzonitrile (b.p. 78–79°C/20 mmHg). Isolated benzonitrile was identified by direct comparison with an authentic

sample. A standard reaction with PTC was also carried out for 2 hrs by taking the same quantities of the reactants as those taken for the corresponding sonochemical reactions, as explained before.

RESULTS AND DISCUSSION

It can be seen from the above mechanism that the transfer of OH^- (from NaOH) from the aqueous phase to the organic phase ($CHCl_3$) is the rate controlling step. This transfer is mediated with the help of PTC and the application of ultrasound along with PTC enhances the transfer rate significantly. The experimental results obtained at different conditions are as shown in the table and are discussed below.

From the table, it can be seen that in the absence of PTC, there was no reaction even if sonication is carried out for 1 hr. But, once a combination of sonication and PTC was applied to the system, it resulted in a better overall effect. This clearly confirms that larger interfacial area generated by the ultrasound is not the controlling factor in the reaction. Thus, the ultrasonic acceleration was ascribed to efficient mixing, enabling better mass transfer between the two phases, providing the transfer of PTC through this interface.

When irradiation was applied to the reaction without stirring, the results obtained were similar as it was obtained with the combination of stirring and sonication. This confirms that stirring doesn't have any effect in

Table. Experimental Results of Ultrasonic Dehydration of Benzamide to Give Benzonitrile Under Different Conditions

Conditions	Time (min)	Yield of Benzonitrile (%)
(A) With PTC		
Only Stirring	120	84.76
Stirring + Ultrasound	5	29.43
Stirring + Ultrasound	10	45.9
Stirring + Ultrasound	15	52.85
Stirring + Ultrasound	20	80.12
Only Ultrasound	10	45.22
Only Ultrasound	20	84.61
(B) Without PTC		
Stirring + Ultrasound	60	0

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the presence of sonication. In other way, again this reflects that only the interfacial mass transfer controls the overall reaction rate, which is substantially (6 fold), enhanced by the use of ultrasound. Thus, there is a tremendous potential for combining PTC and ultrasound to get the desired synergistic effects.

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