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Conversion of Pollutants in Dilute Aqueous Waste Streams to Useful Products: a Potential Method Based on Phase-Transfer Catalysis

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Abstract:

Many waste streams contain anions at low concentration in water. This paper describes results obtained when aqueous solutions of various anions at 1 wt % were subjected to reactions with alkyl and acyl halides without solvent. High yields of valuable products such as phenylacetonitrile, alkyl phenyl ethers, alkyl acrylate, and benzoyl cyanide were obtained at moderate temperatures and reaction times. The formation of byproducts deriving from reactions with large amounts of water was easily controlled. The method was successfully applied to selectively react and extract a target anion out of a mixture of anions.

Liquid−liquid phase-transfer catalysis (PTC) has been successfully applied to economically viable synthesis of many important and valuable chemicals. For reactions following the Starks'mechanism,[1] the reaction rates depend on the concentration of reactants in the organic phase and concentrations of anions in the aqueous phase should have no effect on the reactions kinetics. Nevertheless, researchers invariably minimize water use, and consequently the concentration of water soluble reactants is relatively high.[2] The possible rationale is that when large amounts of water are present in the reaction mixture, even relatively slow processes involving water can become dominant and undesired products may result.[3] However, there have been no systematic studies on liquid−liquid PTC reactions employed to mixtures that contain relatively low concentrations of water soluble reactants. The specific findings of this paper suggest that such systematic studies would be very fruitful.

The reasons to perform PTC-enhanced reactions using the low concentration of reactants in an aqueous phase include the following:

Availability. There is a plurality of aqueous waste streams containing various reactive anions at low concentrations. Some of these anions such as cyanide or phenolate are hazardous pollutants. Successful application of PTC-assisted reactions to these streams to produce useful chemicals would offer an economic and environmental benefit.

Catalyst Stability. Many PTC reactions must be performed at high pH to ensure proton removal. However, it has been well established that most catalysts belonging to onium salts decompose rapidly in highly alkaline solutions,[4,5] and their decomposition rates increase with increased pH. Thus, it would be important for catalyst stability if nucleophilic substitution reactions that require base were performed at lower concentrations of the anion (and subsequently of the hydroxide). For such reactions, the "life expectancy" of a catalyst would dramatically increase.

Solubility. Certain anions of interest may show low solubility in water. It should not preclude them from participating in PTC-assisted reactions.

We wish to report some of our results of reactions performed at concentrations of 1.0% w/w of anions dissolved in water. While PTC has been applied to water systems containing anions at this or similar concentrations, the number of such reports is very limited.[6−8] To maximize the concentration of reactants in the organic phase, no solvents were used. Recently, Eyende and Mailleux[9] described the synthesis of phenyl ethers using alkylating agents such as iodomethane or 1-bromoheptane as an organic solvent with high anionic concentrations in the aqueous phase. Conversely, we are not aware of any attempts to react anions at low concentrations in the aqueous phase with alkyl halides acting as reactants and solvents.

The yields, reaction times, temperatures, and products are presented in Table 1, and the equations are presented in the Scheme 1. Reactions conditions reported here were not optimized. Yields are reported as GC yields against an internal standard. The general procedure was as follows: 250 g of 1.0% w/w aqueous solution containing the anion, between 10 and 20% molar excess of sodium hydroxide (if needed since some anions were already in salt form) and, in some reactions, a small quantity of sodium iodide,[10] were transferred to a three-necked 500 mL flask and stirred (600 rpm) continuously at a controlled temperature. The organic phase consisting of the alkyl (acyl) halide (usually 3 mol of halide based on 1 mol of anion), PTC catalyst (methyltrioctylammonium chloride in all cases with the exception of example three where tetrabutylammonium bromide was used; between 0.1 [example six] and 10 mol % based on 1 mole of anion), and gas chromatographic internal standard (durene,

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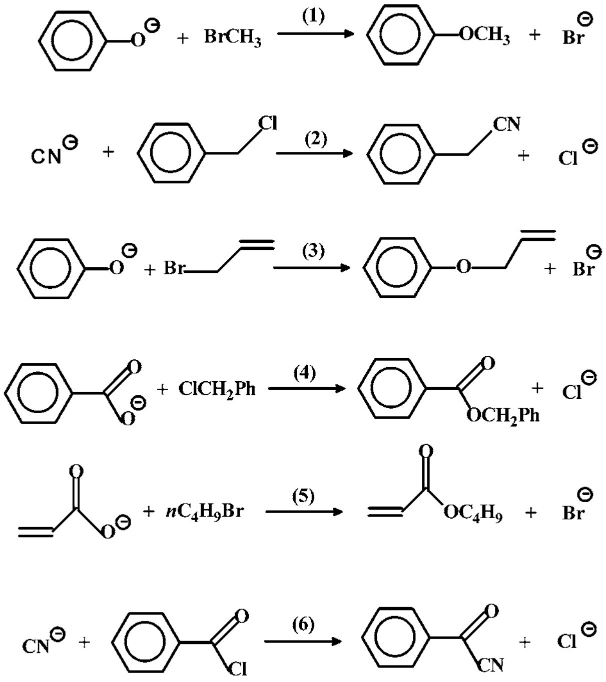
Table 1. **Conditions and Yields of Reactions with Anions at 1.0 wt % in the Aqueous Phase**

no.	anion (aqueous phase)	organic phase reactant	temp (°C)	time (min)	product	yield (%)
1	sodium phenolate	methyl bromide	40	15	anisole	95
2	sodium cyanide	benzyl chloride	40	60	phenylacetonitrile	92
3	sodium phenolate	allyl bromide	33	15	allyl phenyl ether	90
4	sodium benzoate	benzyl chloride	45	180	benzyl benzoate	87
5	sodium acrylate	butyl bromide	69	180	butyl acrylate	>60
6	sodium cyanide	benzoyl chloride	7	5	benzoyl cyanide	95

Scheme 1



few hundred milligrams) was introduced to the reactor during stirring. Aliquots of the organic phase were taken every few minutes. When methyl bromide was the reacting alkyl halide, it was fed from a regulated gas cylinder. All reactions were preceded by blank experiments that did not contain either one of the reactants or a catalyst. In particular, it was shown that the rate of benzoyl chloride reaction with water was essentially negligible as compared with the rate of the benzoyl chloride reaction with cyanide anion. It is worth noting that no “dimer” was detected in the reaction mixture.

Yields are higher than expected, even though no optimization of the reaction conditions was attempted. In particular, the rate of alkyl halide hydrolysis to produce the corresponding alcohol was negligible. However, we observed that hydrolysis becomes important at moderately elevated temperatures. For example, when benzyl chloride was reacted with aqueous sodium acetate to form benzyl acetate, the yield of the product depends strongly on the reaction temperature. For the reaction performed at 40 °C for 335 min, the yield of benzyl acetate based on the limiting reactant (sodium acetate) was 50%, the conversion of sodium acetate was 58%, and the byproducts present in the reaction mixture were benzyl alcohol (3%) and benzyl iodide (trace, some sodium iodide was added to the reaction mixture). For the same reaction performed for 240 min at 60 °C, the yield of benzyl acetate based on sodium acetate was 57%, the conversion of sodium acetate was 89%, and the reaction mixture contained a significant quantity of benzyl alcohol (above 10%).

Additionally, the method can be applied to the separation of anions. When a mixture of sodium salts of benzoic and *p*-hydroxybenzoic acids (1.0 wt % in water) was reacted with benzyl chloride, benzyl benzoate was isolated as the only product. The result is not surprising, since benzoate is expected to react faster. However, it is likely that a small percent of benzyl *p*-hydroxybenzoate was also formed and overlooked due to its non-negligible water solubility. Similarly, when an authentic sample of phenolic waste (containing resorcinol, cresols, and phenol; dissolved in the aqueous phase at the level of about 5 wt %) was reacted with allyl bromide, only phenol derived products (allyl phenyl ether and C-alkylation products) were detected in the reaction mixture.

In conclusion, we believe that this approach opens a new area of phase-transfer catalysis applications, that is, to diluted aqueous solutions. The importance lies in the fact that many wastes, including hazardous wastes, contain reactive anions that can be transferred to the organic phase and reacted to form saleable products. The economic benefits are obvious: no cost for starting materials that are waste components plus avoidance of hazardous treatment costs due to the need for high temperature incineration of the alkyl halide. Additionally, as a result of the hydrophobic character of most potential products, they can be effectively removed from the aqueous phase. In those cases where the coreactant is toxic (e.g., allyl bromide, methyl bromide), this eliminates their influence on the system toxicity.

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