

Anion Activation in Quaternary Salts, Crown Ethers, Cryptates, and Related Systems

Anion Activation in Quaternary Salts, Crown Ethers, Cryptates and Related Systems. An Introduction.

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Relevant anionic activation can be achieved with lipophilic systems able to dissolve salts in an organic medium of low polarity, imposing at the same time a large separation between the anion and the cationic center. The most common examples are appropriate quaternary 'onium' salts, but also cyclic, bicyclic and open chain polyethers, together with their aza, thia, etc., analogues.

These systems can also catalyze anion transfer from an aqueous to a mutually insoluble organic phase (phase-transfer catalysis). Furthermore, the same effect can be obtained not only through liquid–liquid phases, but also with solid–solid, solid–gas, liquid–gas and solid–solid phases. Related aspects are immobilization of phase-transfer catalysts on polymeric matrices and the micelle-catalyzed reactions.

A survey of the results obtained will give a deep insight into the possibilities and further developments.

The Recirculation of Q^+ used to Activate Anions

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Phase transfer catalysis is one method to activate anions. In this method the amount of catalyst used is usually equivalent to one percent of the anion to be activated. In almost every case a better yield is obtained by increasing the amount of catalyst to a full equivalent. One example of this is found in the process extractive alkylation which I have presented on several occasions. Another example can be found in reactions performed in the absence of an aqueous layer. In such a process as well as in the extractive alkylations process it is often essential for the economy of the method that the catalyst can be readily

recovered and recirculated. Due to the outstanding selectivity and simplicity of ion pair extraction methods this recovery is very simple and complete in most cases. The principle used will be demonstrated by reductions with diborane generated from a tetraalkylammonium boranate and an alkyl halide in dichloromethane.

Sodium boranate is a versatile reducing agent which has taken an important step towards a big scale use by its introduction as a bleaching agent in the pulp industry. The big scale use of sodium boranate for the generation of diborane has been limited since expensive ether solvents such as tetrahydrofuran have been needed. This problem is however readily circumvented by the use of tetra-alkylammonium boranates in dichloromethane. Solutions of tetrabutylammonium or tributylethylammonium boranate in dichloromethane ready for direct preparation of diborane solutions are prepared from sodium boranate by extractions in a practically quantitative yield. With acetonitrile as the extracting solvent it is even possible to extract tetraethylammonium boranate in an excellent yield.

A solution of tetraalkylammonium boranate in dichloromethane gives diborane on the addition of an alkyl halide. These solutions of diborane in dichloromethane can be used in the same way as a solution of diborane in an ether. In fact it is in some cases still more reactive and useful. A tetraalkylammonium halide is obtained as a byproduct which is readily recovered and reconverted to the tetraalkylammonium boranate. Several examples will be given.

Anion Activation by Catalysts Used in Phase Transfer Catalysis

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The chemical kinetics of phase transfer catalyzed reactions depend primarily on several inter-related parameters:

- (a) catalyst structure,
- (b) reaction conditions and concentrations,
- (c) type of reaction being catalyzed.