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

---

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

FERNANDO MONTANARI

Istituto di Chimica Industriale, Università di Milano, Milan, Italy

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

ARNE BRÄNDSTRÖM

AB Hässle, S-431 83 Mölndal, Sweden

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 tetrahydrofurane 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

CHARLES M. STARKS

Conoco Inc., Ponca City, Okla. U.S.A.

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

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

From the kinetics one may often assess the relative importance of these parameters. Of particular interest is the effect of the molecular structure of the catalyst on its effectiveness. Molecular structure in anion transfer catalysts affects not only the ability of the catalyst to transfer anions from solid or aqueous phases into organic phases, but it also affects the ability of the catalyst to activate the anion for its reaction with the organic phase reactant. The lecture to be presented is a summary of work dealing with the dependence of the kinetics of some phase transfer catalyzed reaction systems on catalyst structure, and of how these structures influence anion activation.

Structures and Ambident Reactivity of β-keto Enolates Ion-Pairs

G. BRAM

Groupe de Recherches No 12, CNRS, 2 - 8, rue Henri-Dunant, F 94320 Thiais, France

Relationships between conformations [1] and ambident reactivity [2] of enolates of β-dicarbonyl compounds will be discussed. Some structural features of these enolates will be presented: X-ray diffractions [3–6], ^{1}H NMR [4, 7, 8], ^{13}C NMR [9–11], ^{23}Na HMR [12], ^{7}Li NMR [4], U.V. [1, 11] and I.R. spectroscopies [4–6, 11, 13]. The discussion will be mainly focused on the structure and the reactivity of 'crowned' and 'cryptated' β-keto enolates ion-pairs.

References

1 H. E. Zaugg and A. D. Schaefer, *J. Am. Chem. Soc., 87,* 1858 (1965).
2 L. M. Jackman and B. C. Lange, *Tetrahedron, 33,* 2737 (1977).
3 F. A. Schroeder and H. P. Weber, *Acta Cryst., B31,* 1745 (1975).
4 C. Cambillau, *Thèse de Doctorat d'Etat,* Orsay, 1978.
5 C. Cambillau, G. Bram, J. Corset, C. Riche and C. Pascard-Billy, *Tetrahedron, 34,* 2675 (1978).
6 C. Cambillau, G. Bram, J. Corset and C. Riche, *Nouv. J. Chim., 3,* 9 (1979).
7 M. Raban, E. Noe and G. Yamamoto, *J. Am. Chem. Soc., 99,* 6527 (1977).
8 A. A. Petrov, S. M. Esakov and B. A. Ershov, *J. Org. Chem. SSSR, 12,* 774 (1976).
9 A. A. Petrov and B. A. Ershov, *J. Org. Chem. SSSR, 14,* 867 (1978).
10 M. Raban and D. P. Haritos, *J. Am. Chem. Soc., 101,* 5178 (1979).
11 V. M. De Palma and E. M. Arnett, *J. Am. Chem. Soc., 100,* 3514 (1978).
12 A. Cornelis, P. Laszlo and C. Cambillau, *J. Chem. Research (S),* 462 (1978).
13 P. Sarthou, G. Bram, F. Guibe and J. Corset, *Tetrahedron,* in the press.