The Effect of Phase-transfer Catalysis on Ammonolysis of Alkyl and Aryl Halides

Gabriela Barak and Yoel Sasson*

Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Quaternary ammonium salts improve the solubility of ammonia in organic media and accelerate its reactions with some alkyl and aryl halides.

Phase-transfer catalysis (P.T.C.) is known to lead to an excellent improvement in reactions of charged species (particularly anions) with organic substrates in two-phase and, sometimes, three-phase systems.[1,2] The method is based on extraction of anions into the organic phase mainly by lipophilic quaternary ammonium salts acting as liquid anion exchangers according to equation (1), where Q is a quarternary cation, X^- is a leaving group, and Y^- is an attacking nucleophile applied directly or generated *in situ* in the system.

$$\mathrm{QX(org.)} + \mathrm{Y^-(aq.\ or\ solid)} \rightleftharpoons \mathrm{QY(org.)} + \mathrm{X^-(aq.\ or\ solid)} \quad (1)$$

Another type of mechanism in P.T.C. which is used much less frequently is based on the non-stoicheiometric extraction of protonic compounds *via* hydrogen bonding. For example, acids with the general structure HY can be extracted from the aqueous to an organic phase according to equation (2).

$$\mathrm{QX(org.)} + \mathrm{HY(aq.)} \rightarrow \mathrm{QX(HY)}_n\mathrm{(org.)} \quad (2)$$

Where typical extractable species are strong acids like hydrochloric, hydrobromic,[3] and formic acid, and also with weak acids like phenol,[4] hydrogen peroxide[5] and hypochloric[6] acid were effectively transferred to organic phases, where they reacted with various substrates. The most common protic compound used in conjunction with phase-transfer catalysts and an organic phase is water. Various degrees of hydration were reported for different quaternary salts in different systems[7] which strongly alter the reactions rate. It was proposed that the mechanism of this extraction is based on hydrogen bonding.[1]

We have now found that even the very weak acid ammonia is extracted from aqueous or gaseous phase into various organic solvents where it is activated and reacts in substitution reactions.

In a typical example ammonia gas was passed at a rate of 10 ml/min through a solution of 2,4-dinitrochlorobenzene (10 mmol) in toluene (5 ml) at ambient temperature and pressure. G.c. analysis of the mixture after 3 h indicated that only 0.6% of the substrate had been converted into 2,4-dinitroaniline. When the same operation was repeated with the addition of tetra-n-butylammonium bromide (TBAB) (1 mmol) the amination process was significantly faster yielding 16% of the same product. The reaction was practically complete after 24 h.

Similar amination of benzyl chloride (no solvent) did not proceed at all in the absence of a catalyst while upon addition of TBAB (0.05 mol. equiv.) 52% conversion had taken place after 4 h (mainly into di- and tri-benzylamine).

The catalytic effect was lower when aqueous ammonia (5 mol. equiv.; 25% w/w) was used as the amination agent. 95% conversion of 2,4-dinitrochlorobenzene took place at 70 °C in the presence of TBAB (0.05 mol. equiv.) and only 69% conversion in its absence (both after 20 h). Under the same conditions n-octyl chloride yielded 33% of amines with the catalyst and 13% without catalyst. Benzyl chloride gave at 45 °C after 1 h 55% of benzylamines compared with 20% in the absence of the catalyst.

To our surprise, TBAB had a dramatic catalytic effect also with ammonium carbonate as the source for ammonia. When, for example, equimolar amounts of benzyl chloride and 60% aqueous ammonium carbonate were mixed at 60 °C for 24 h, 6% conversion of benzyl chloride took place, 2% into amines, and 4% into various carbonation products.[8] Upon addition of TBAB (0.04 mol. equiv.) the conversion, under the same conditions, increased to 50% with 75% selectivity for formation of amines (mainly tribenzylamine). Removal of water from these experiments altered the rate and the selectivity only slightly.

We believe that the function of the catalyst in these systems is dual: (a) extraction of ammonia from the aqueous or gas phase to the organic phase and (b) activation of the N–H bond in the ammonia resulting in higher nucleophilicity. Both functions are apparently achieved *via* hydrogen bonding between the bromide anion of the TBAB and an ammonia molecule. Water competes with ammonia for complexation with the catalyst and thus reduces the efficiency.

A similar activation of the N–H bond by hydrogen bonding was reported by us earlier in the alkylation of aniline by alkyl halides which is strongly affected by the presence of quaternary ammonium salts.[9]

Received, 23rd March 1987; Com. 365

References

1 E. V. Dehmlow and S. S. Dehmlow 'Phase Transfer Catalysis,' 2nd edn., Verlag Chemie, Weinheim, 1983.
2 C. M. Starks and C. Liotta, 'Phase Transfer Catalysis,' Academic Press, New York, 1978.
3 D. Landini, F. Montanari, and F. Rolla, *Synthesis*, 1974, 37.
4 H. A. Zahalka and Y. Sasson, *J. Chem. Soc., Chem. Commun.*, 1984, 581.
5 E. V. Dehmlow and M. Slopianka, *Chem. Ber.*, 1979, **112**, 2768.
6 S. Abramovici, R. Neumann, and Y. Sasson, *J. Mol. Catal.*, 1985, **29**, 291.
7 D. Landini, A. Maia, F. Montanari, and F. M. Pirisi, *J. Chem. Soc., Perkin Trans. 2*, 1980, 45.
8 M. Lissel and E. V. Dehmlow, *Chem. Ber.*, 1981, **114**, 1210.
9 E. V. Dehmlow, R. Thieser, H. A. Zahalka, and Y. Sasson, *Tetrahedron Lett.*, 1985, **26**, 297.