

TRIPHASE VS. TWO-PHASE TRANSFER CATALYSIS; AN ECLECTIC APPROACH

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A new and effective way of eliminating phase transfer catalysts from an organic phase involves treatment with an ion exchange resin in a triphase system.

The difficulty in separating and recovering the catalyst in classical two phase transfer catalysis reactions has spurred considerable research to develop insoluble catalysts consisting of active groups bound to an insoluble matrix, usually a styrene/DVB copolymer. These phase transfer catalysts (PTCs) make work-up and recovery very simple, its potential industrial use having been emphasized (1, 2). Even the new concept of triphase catalysis is being developed (3).

The main disadvantages associated with such PTCs are the lower reaction rates generally obtained and its being not readily available and expensive, while conventional PTCs are in industrial production and very cheap. Also the physical stability of solid catalysts can be endangered under the high stirring rates required (2) or when used in severe conditions.

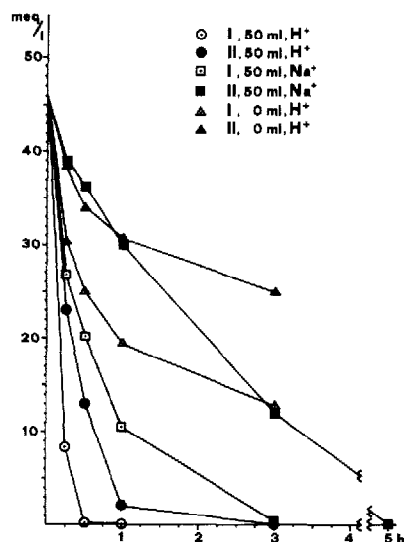
We suggest as an alternative approach running the reaction in a two phase system and separating the PTC in a triphase system from which it can be easily filtered off and recovered. In our view this procedure has the advantages of both two phase and triphase methods and none of its disadvantages, being even semicontinuous industrial operation easily envisaged.

Although some work has been published on the absorption of quaternary ammonium compounds by ion exchange resins from water or homogeneous water/solvent mixtures (4, 5, 6), no paper is known to us dealing with the absorption from a two-phase mixture.

In our experiments, the ion exchanger was converted to the desired ionic form by conventional methods and thoroughly rinsed with water; in the "no added water" experiments it was additionally carefully rinsed with ethanol and toluene in succession. As PTCs, a slightly water soluble catalyst Adogen 464 (7) (catalyst I), and water insoluble (8) hexadecyl tributyl phosphonium bromide (catalyst II) were used. In each run, the specified amount of water was added to 150 ml of a toluene solution containing 6,9 mmol of catalyst and then 38 mmol of Dowex 50 W - X4 resin, 50-100 mesh, prepared as described before. The mixture was magnetically stirred

at room temperature and 25 ml samples of clear toluene phase were periodically withdrawn and titrated with 0,02 N sodium lauryl sulphate solution in a two phase system using disulphine blue/dimidium bromide as indicator.

The results are plotted in the graph as found concentration of catalyst in toluene vs. time; for each curve it is indicated catalyst, ml of water added and counterion in the resin. It is shown that both catalysts can be completely absorbed in a reasonable time if a water phase is present, behaviour that probably reflects solvation of the ion pair. Also  $H^+$  is more effective than  $Na^+$  as a counterion, as expected. In the absence of a water phase the absorption is very slow, and could not be driven to completion.



In additional single-sampling experiments run under identical triphase conditions with resin in  $H^+$  form we have determined that for a degree of absorption of more than 99,9 %, catalyst I needs 1 hr and catalyst II 3 hrs. More than 95 % of the catalyst can be recovered from the resin treating it with a homogeneous acid/solvent solution such as aq HCl/THF or aq HCl/EtOH. The catalyst could not be recovered in a triphase system apparently because the lipophylic catalyst prevents the water phase from penetrating the resin pores.

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