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THE EFFECT OF POLYMER SWELLING ON ALKYLATION OF PHENYLACETONITRILE BY POLYMER-SUPPORTED PHASE TRANSFER CATALYSIS

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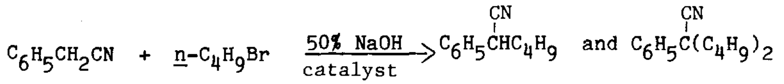
Abstract. Alkylation of phenylacetonitrile by 1-bromobutane with 50% sodium hydroxide and a polymer-supported phase transfer catalyst proceeds fastest when the phenylacetonitrile is added to the mixture before the 1-bromobutane.

Alkylation of phenylacetonitrile (PAN) promoted by aqueous sodium hydroxide and quaternary ammonium salts is one of the most widely studied examples of phase transfer catalysis (PTC).[1] When the catalyst is bound covalently to an insoluble polymer, it can be separated easily by filtration from the liquid organic and aqueous phases. However, in many cases the activities of polymer-supported catalysts are lower than those of soluble phase transfer catalysts.[2] Our investigations of the mechanisms of polymer-supported PTC are aimed at understanding the role of the polymer in controlling catalytic activity.[3] We report here remarkable rate differences in the alkylation of PAN with 1-bromobutane (eq 1) obtained simply by changing the order of addition of reagents to the triphase reaction mixture.



$$C_6H_5CH_2CN + \underline{n}\text{-}C_4H_9Br \xrightarrow[\text{catalyst}]{50\%\ NaOH} C_6H_5\overset{CN}{\overset{|}{C}}HC_4H_9 \text{ and } C_6H_5\overset{CN}{\overset{|}{C}}(C_4H_9)_2 \qquad (1)$$

The kinetic experiments employed 25.0 mL of 1-bromobutane (0.233 mol), 2.00 mL of PAN (0.0175 mol), and 45.0 mL of 50% w/w aqueous sodium hydroxide stirred mechanically in a 100 mL

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flask at 80.0 ± 0.2 °C. The catalyst was a polystyrene-bound benzyltrimethylammonium chloride containing 1.40 mequiv/g of active sites prepared from a suspension copolymer of styrene, 2 wt % divinylbenzene, and 25 wt % chloromethylstyrenes. Reaction rates depended upon stirring speed and particle size of the catalyst. The 60/100 mesh fraction of the copolymer was sieved in catalyst form before use to insure particle uniformity. The rate constants[4] were linearly dependent on the weight of catalyst up to 0.6 g, with zero rate observed in the absence of polymer beads and in the presence of unfunctionalized 2% crosslinked polystyrene beads.

In the direct addition method the aqueous phase, 1-bromobutane, and catalyst were stirred at 100 rpm for 60 min at 80°C to condition the catalyst, PAN was added, and the stirring speed was increased. In the reverse addition method aqueous phase and catalyst were conditioned 50 min at 80°C before PAN was added. After another 10 min the stirring speed was increased and 1-bromobutane (preheated to 80°C) was added. The Figure shows that the rate constants depend on stirring speed, and maximum rate is reached in the reverse addition method only at > 500 rpm. More vigorous vibromixing gave the same rate as 500-700 rpm mechanical stirring. The reverse addition method gives a rate constant 8 times greater than the direct addition method with 500 rpm stirring. Similar results have been obtained with catalysts of smaller particle size, catalysts with a higher degree of ring substitution, and catalysts with benzyltri-*n*-butylammonium or benzylquinuclidinium active sites.

We attribute the rate dependence on order of addition of reagents to the greatly different abilities of PAN and 1-bromobutane to swell the catalysts. When 1.0 mL of the dry 60/100 mesh benzyltrimethylammonium catalyst at 80°C is treated successively with 25 mL of 1-bromobutane and 2 mL of PAN, the catalyst swells slowly to 1.4 mL over 12 h. When 1.0 mL of dry catalyst is treated with 2 mL of PAN at 80°C, it swells to 3.0 mL in 5 min. Addition of 25 mL of 1-bromobutane causes a decrease in volume to 2.0 mL over a period of 30 min and no further change in volume over 12 h. Catalytic activity requires that PAN, 1-bromobutane, and hydroxide ion all diffuse into the polymer to reach active sites. When the catalyst is highly swollen, intraparticle diffusion is rapid. When the catalyst is only slightly swollen, slow intraparticle diffusion severely limits the reaction rates.

By the faster reverse addition method these reactions of PAN with 1-bromobutane proceed much faster at 80°C than the same reaction using commercial ion exchange resins as catalysts at 70°C in an earlier study.[5] Even with a thirteen-fold excess of 1-bromobutane over PAN we

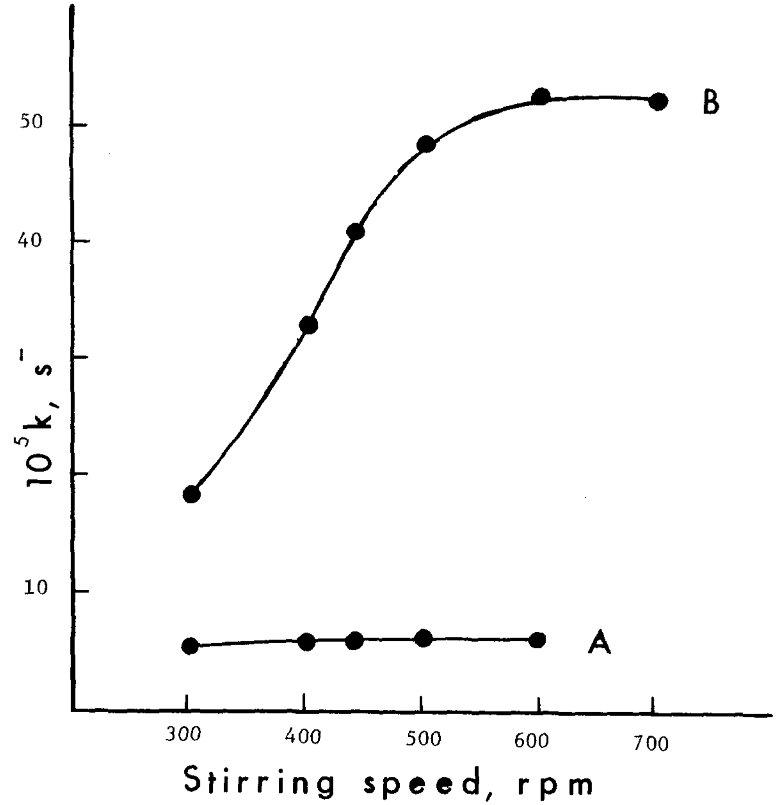

FIGURE. Effect of stirring speed and method of addition on rate of butylation of phenylacetonitrile. A, phenylacetonitrile added to mixture after 1-bromobutane. B, 1-bromobutane added to mixture after catalyst swelling in phenylacetonitrile.

obtained 80.3% monobutyl PAN, only 3.3% dibutyl PAN and 16.4% unreacted PAN after 80 min. The reaction is fast and reasonably selective for monoalkylation, and the catalyst is easily separated from the reaction mixture by filtration. Recovered catalyst was over 90% as active as the original catalyst in a recycle experiment.

Correlations between activity of polymer supported phase transfer catalysts and degree of swelling of the polymer have been observed also in nucleophilic displacements on 1-haloalkanes,[3,6] where rates increase with increasing ability of solvent to swell the polymer, and rates decrease as the degree of crosslinking of the polymer increases. The rate dependence on swelling for alkylation of phenylacetonitrile is the most dramatic observed so far. Many more examples likely will be found as polymer-supported phase transfer catalysts become more widely used.

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[4] Six 0.2 mL aliquots of the organic phase were removed from the reaction mixture and analyzed in duplicate for disappearance of PAN on a 6 ft. x 0.125 in. o.d. column of 20% SE-30 on 80/100 mesh Gas Chrom Q at 170°C. The last data point corresponded to 15-29% conversion in direct addition experiments and 24-79% conversion in reverse addition experiments. In all cases mono- and dibutyl PAN accounted for all PAN consumed. Rate constants were evaluated as slopes of $\ln([\mathrm{PAN}]_o/\{[\mathrm{PAN}]_o - [\mathrm{PAN}]_t\})$ *vs.* t graphs. In duplicate runs rate constants differed by an average of 3%.

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