Selective *para*-Bromination of Toluene catalysed by Na-Y Zeolite in the Presence of an Epoxide

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Propylene oxide, serving as an HBr scavenger, dramatically improved the selectivity of zeolite-catalysed toluene bromination to yield almost pure *p*-bromotoluene.

The selectivity of electrophilic halogenation of alkyl and halogenobenzenes, particularly chlorination and bromination, can be altered by the presence of various zeolites.[1] The mechanism of this reaction and the parameters influencing the isomer ratio have barely been studied. Furthermore, the selectivity for formation of the usually more useful *p*-isomer is relatively low.[1] This is particularly true in the case of toluene where the highest reported *p*-selectivity obtained is 80% for zeolite-catalysed bromination[2] and 77% for the corresponding chlorination.[3] We observed that cation exchange only slightly improved selectivity.[4]

The relatively low shape selectivity of zeolites during halogenation compared with, *e.g.*, alkylation or isomerisation was attributed to the presence of hydrogen halides released during the reaction.[1] Attempts to neutralise these acids by addition of hydrogen carbonate combined with removal of the water released, resulted in only minor improvements in selectivity.[1] It was suggested that deposition of solid salts on zeolite cavities also affected the catalytic activity.[5]

While searching for an additive that would effectively remove hydrobromic acid from the catalytic system without the formation of water or solid salts, we examined, among other materials, the effect of propylene oxide. In the presence of this additive a highly selective bromination was achieved which was developed into an effective synthetic method for the preparation of *p*-bromotoluene in 98% purity.

In a typical procedure, 25 ml of a 2.17 M solution of toluene in tetrachloromethane was mixed with 5 g of commercial Na-Y zeolite (1/16″ pellets containing 5% moisture without any pretreatment) and 20 mmol of propylene oxide. While keeping the mixture at 25 °C, 20 mmol of bromine was added. Mixing was continued for 30 min before quenching the reaction with 2 M aqueous thiosulphate solution, 50 ml of tetrachloromethane was then added and the catalyst was removed by filtration. The organic phase was separated and dried over $MgSO_4$. Gas chromatographic analysis indicated 10% conversion of toluene to bromotoluene with 98% and 2% selectivity for formation of the *p*- and *o*-isomers respectively. This was confirmed by fractional distillation which gave a 90% yield of 98% pure *p*-bromotoluene.

In the presence of propylene oxide, the initial bromination rate was 1.3×10^{-3} mol dm^{-3} s^{-1} but the process stopped completely after 13% conversion of toluene. Addition of bromine with or without propylene oxide did not resume the reaction. The reaction was, however, resumed with the same selectivity upon the addition of a fresh batch of catalyst. After filtration of the catalyst, its activity was regained simply by washing with dilute aqueous sodium hydroxide. The mechanism of the catalyst deactivation has still to be clarified.

In the absence of propylene oxide the initial rate of bromination was approximately double (3×10^{-3} mol dm^{-3} s^{-1}) but the *p*-selectivity was only 81%. Upon the addition of solid potassium hydrogen carbonate or sodium carbonate to the system, instead of propylene oxide, the *p*-selectivity decreased to 74 and 76% respectively and the rate decreased to 2.3×10^{-3} and 1.6×10^{-3} mol dm^{-3} s^{-1} respectively. In all three experiments, however, the reaction proceeded to completion with a final *p*-selectivity of 67%. Mechanistic studies of this system are now underway.

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