

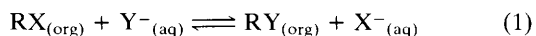
## Inhibition of the Solid-Liquid Phase Transfer Substitution Process by Excess of Quaternary Ammonium Catalyst

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Whereas in phase transfer catalysis increasing catalyst concentrations usually result in higher reaction rates, in solid-liquid reactions an excess of catalyst has been found to lead to deactivation, owing to complete dehydration of the solid salt by the quaternary onium catalyst.

Heterogeneous liquid-liquid reactions of the general type (1) are known to be effectively catalysed by lipophilic quaternary onium salts acting as phase transfer catalysts.<sup>1</sup> It has been shown that these substitution reactions are advantageously carried out in a solid-liquid system,<sup>2</sup> particularly when  $Y^-$  is a highly hydrophilic anion, *e.g.* fluoride,<sup>3</sup> ethoxide,<sup>4</sup> or formate.<sup>5</sup> Under such conditions the problem of catalyst poisoning by the more lipophilic anion  $X^-$  is eliminated and first order reaction profiles are obtained until almost complete conversion.<sup>5</sup>



It has been found that the presence of a small amount of water is essential for the exchange process to take place, and that quaternary ammonium salts cannot directly exchange anions with the solid but only with an aqueous solution of the salt.<sup>6,7</sup> In the case of the substitution reaction of 1-chlorooctane with sodium formate at 100 °C, the highest rate was measured when the salt initially contained 0.2% w/w of water.<sup>5</sup>

We have now observed that in these solid-liquid reactions, where the catalytic behaviour is sensitive to the presence of trace amounts of water, addition of the quaternary ammonium catalyst itself significantly alters the distribution of the water

molecules between the inorganic and organic phases. In extreme cases this might result in complete drying of the solid salt due to the extraction of the water into the organic phase<sup>8</sup> by the catalyst, causing the reaction process to cease. This phenomenon results in a complex dependence of the reaction rates on the concentration of the catalyst. No reaction was observed when potassium formate (27 mmol, containing 0.015 mole % of water) was mixed with 1-chlorodecane (18 mmol) in *o*-dichlorobenzene (10 ml) (75°C, 3 h) in the absence of catalyst. Karl Fischer titration of both the salt and the organic phases indicated that the solid potassium formate had retained over 90% of its original water content throughout the operation. As expected, repeating the experiment with the same total amount of water but in the presence of 1 mmol of Aliquat 336 catalyst resulted in a facile substitution reaction for which we measured a first order rate constant of  $2 \times 10^{-3} \text{ min}^{-1}$ . To our surprise, water analysis of each of the two phases in this system indicated that 88% of the water had drifted during the reaction from the solid to the organic phase. A similar effect was observed when potassium formate with a higher water content was used. Thus with 1% water in the salt 51% of the water was transferred to the organic phase and with 2% water in the salt 30% was transferred to the organic phase during the course of the substitution reactions carried out under the above conditions. This observation suggests that the quaternary ammonium salt has a very high affinity for the water molecules and it extracts them effectively even from the solid, highly hygroscopic potassium formate, thus significantly changing the water balance in the system. Another surprising

result was found when the above reaction was carried out under identical conditions but with 3.5 mmol of Aliquat 336 catalyst. The measured first order rate constant dropped to  $1 \times 10^{-3} \text{ min}^{-1}$ . Increasing the catalyst amount to 7 or 10 mmol resulted in a further drop of the reaction rate.

Based on these, and on results with other salts, we believe that this is a general phenomenon in similar solid-liquid phase transfer catalysed reactions. Namely, since traces of water are critical in these reactions one should be cautious with the amount of quaternary onium catalyst used since the very presence of the catalyst might dry the solid salt slowing down and even completely inhibiting the catalytic process.

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