Catalyst Poisoning Phenomenon in Phase Transfer Catalysis: Effect of Aqueous Phase Concentration

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Catalyst poisoning was studied in the phase transfer-catalysed esterification of alkyl chlorides by sodium formate; the poisoning effect is minimized by use of highly concentrated formate solutions where high conversion and first order kinetics are observed.

Simple two-phase displacement reactions where the substrate, usually an alkyl halide, is in an organic phase and the nucleophile is in an aqueous solution are effectively accelerated in the presence of various quaternary ammonium and phosphonium salts acting as phase transfer catalysts; see the general equation (1). The kinetics and mechanism of this

$$RX(\text{org.}) + Y^-(\text{aq.}) \rightarrow RY(\text{org.}) + X^-(\text{aq.}) \tag{1}$$

process as well as its wide synthetic applications have been discussed.[1-3]

Reactions of type (1) result in high conversions only when the extraction coefficient[1] of Y^- in the particular system is
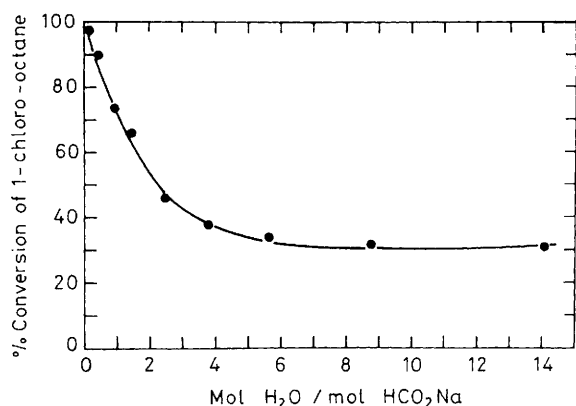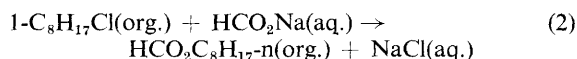
Figure 1. Effect of H_2O/HCO_2Na ratio on the maximum conversion in reaction (2).

larger than the corresponding coefficient of X^-, or, using the term introduced by Gordon and Kutina,[5] when $K_{Y/X}^{sel.} > 1$. In other examples, namely when $K_{Y/X}^{sel.} < 1$ and particularly when $K_{Y/X}^{sel.} < 0.1$ the exchange reaction stops after a certain degree of conversion. This phenomenon, catalyst poisoning,[6] was attributed to the saturation of the catalyst with the anion X^- which reduces the ion-pair extraction of Y^- practically to zero. Quantitative conversions of RX into RY under these conditions can be obtained only by application of large excesses of Y^- (usually with replacement of the aqueous phase with fresh batches of Y^- several times).[7]

In this article we present a new solution to the catalyst poisoning problem based on the dramatic variation in the behaviour of the systems as a function of the amount of water in the reaction mixtures.

We have studied the substitution of alkyl bromides and alkyl chlorides with hydrophilic anions, e.g. fluoride, formate, and ethoxide. None of these exchange reactions is reversible and the fact that they all stop at a certain conversion is attributed to the poisoning of the catalyst. It was found that the particular point at which the reaction stops is a function of the anions involved, the nature of the catalyst, the solvent, and the temperature. The most significant effect was the amount of water in the system. As a general rule higher conversions were observed when smaller quantities of water were present.

A typical example is the reaction of 1-chloro-octane with aqueous sodium formate in the presence of 5 mole % of tetra-n-butylammonium hydrogen sulphate at 90 °C [reaction (2)].

$$1\text{-}C_8H_{17}Cl(\text{org.}) + HCO_2Na(\text{aq.}) \rightarrow \\ HCO_2C_8H_{17}\text{-}n(\text{org.}) + NaCl(\text{aq.}) \qquad (2)$$

The reaction was carried out several times with a $1:1$ mole ratio of formate salt to 1-chloro-octane with different quantities of water in each run. The mixtures were kept in sealed tubes with magnetic stirrers in a thermostatic bath at 90 °C for two weeks.

The final conversion in each run was determined by g.l.c., and the results are shown in Figure 1, where the maximum conversions are plotted as a function of the amount of water employed.

It is apparent from Figure 1 that the conversion is practically constant in the region where the amount of water added is in excess of the HCO_2Na saturation level; in this region the system contains two pure liquid phases. However, maximum conversions increase sharply with decreasing water concentration; thus the aqueous phase becomes saturated with HCO_2Na. In this region a solid starts to precipitate.
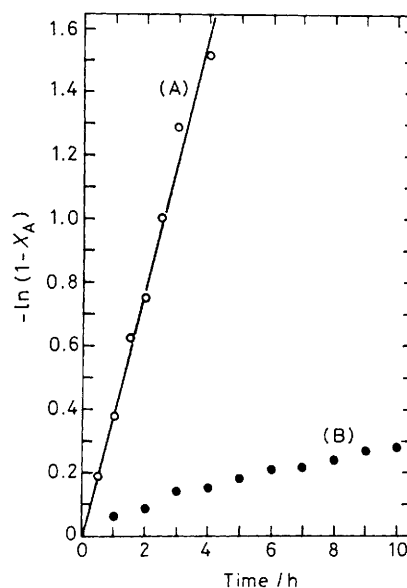
Figure 2. Effect of the amount of water on the kinetics of reaction (2). (A), 98% w/w HCO_2Na; (B) 50% w/w HCO_2Na.

Analysis of the solid precipitate in the mixtures using saturated solutions of sodium formate showed that it was almost entirely composed of sodium chloride. It was separately observed that saturated sodium formate solutions do not dissolve sodium chloride. It was also shown that the quaternary salt cannot exchange anions with salts in the solid phase. Thus, the salts precipitated from the system do not participate in the phase-transfer system, and cannot poison the catalyst.

The concentration of the aqueous phase has a marked effect on the kinetic behaviour of reaction (2) also. Figure 2 presents kinetic profiles of reaction (2) plotted as a first-order reaction. The reaction mixtures were stirred at 1000 r.p.m., the rates remaining independent of stirring speed. It is clear that curve (A) (98% w/w sodium formate) is in excellent agreement with first-order kinetics while curve (B) (50%) suggests a different mechanism. Curve (B) did not show second-order behaviour either. If we assume that the substitution follows an S_N2 mechanism then the rate equation is given by equation (3). In curve (A) the composition of the

$$-d[RCl]/dt = k[RCl]_{\text{org}}[HCO_2^-]_{\text{org}} \qquad (3)$$

aqueous phase does not change with conversion and thus the concentration of the formate ion as an ion-pair in the organic phase is constant; thus the reaction follows pseudo-first-order kinetics [equation (4)] up to at least 90%. In curve (B) the

$$\text{Rate} = k_{\text{obs}}[RCl]_{\text{org}} \qquad (4)$$

composition of the aqueous phase varies with the conversion and the chloride ion in the solution competes for the quaternary cation. The concentration of formate ion pair in the organic phase therefore changes with time and the kinetic behaviour of the reaction is quite complicated. It should be noted that under the same conditions, but in the absence of catalyst, no appreciable conversion was detected after 5 days.

Similar behaviour was found in related substitutions of alkyl chlorides or bromides by acetate, fluoride, methoxide, or ethoxide ions, and details will be published elsewhere.

We conclude that since anions of higher lipophilicity are usually less soluble in water than anions of lower lipo-

philicity, the use of a saturated aqueous phase of the attacking hydrophilic nucleophile which precipitates the salt of the leaving group provides a simple solution to catalyst poisoning.

Received, 15th July 1983; Com. 947

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