

The influence of water on cyanide displacement of 1-halobutanes using 18-crown-6 ether as phase transfer catalyst

F. Baudoul, A. Borcy, S. Mommerency, P. Vanderwegen, G. Jannes *

Institut Meurice, Av. E. Gryzon, 1, B-1070 Brussels, Belgium

Abstract

The influence of water on the cyanide displacement reaction of 1-chlorobutane and of 1-bromobutane has been studied. Kinetics of both reactions have been followed under homogeneous and transfer conditions. The influence of water on the reaction rate and on the relative molar conductivity of the 18-crown-6 ether–KCN complex has been measured. In the first reaction, water reduces the reactivity of cyanide anions by solvating them. In the second reaction, this negative effect is overcompensated by the positive influence of water on the transfer steps between solid and liquid phases.

Keywords: Water; Cyanide; Halobutanes; Crown ethers; Phase transfer catalysis

1. Introduction

The hydrogenation of saturated and unsaturated nitriles has already been proposed as a kinetic tool to characterise hydrogenation catalysts [1–3]. Some compounds, such as acetonitrile, butyronitrile, adiponitrile or benzonitrile are used to characterise hydrogenation catalysts through their ability to form primary, secondary and tertiary amines. In another way, unsaturated nitriles like acrylonitrile, 2-butenitrile and 3-butenitrile are well-adapted to characterise hydrogenation catalysts through the study of the C=C double bond reduction.

In the case of 3-butenitrile, the double bond is not conjugated to the nitrile group and a

particular hydrogenation mechanism has been proposed by Dallons et al. [3]. With the aim to determine if this mechanism is also operative in the case of other non-conjugated unsaturated nitriles, it is interesting to verify whether the substitution level and the position of the olefinic bond play any role in the hydrogenation. Hence, the study of the reduction of higher non-conjugated unsaturated nitriles, such as isomeric pentenenitriles and 3,3-dimethyl-3-butenitrile has been envisaged. Whereas 3-pentenenitrile is commercially available, the others must be synthesised.

An easy way to prepare aliphatic nitriles starts from the corresponding acid and proceeds via dehydration of the amide. But the dehydration step generally occurs at high temperature and, if we aim at obtaining a non-conjugated unsaturated nitrile, milder chemistry would be

* Corresponding author.

preferred. A feasible way to prepare these nitriles is the nucleophilic substitution of an halide in halogenoalkenes by a cyanide anion. However, the formation of a homogeneous phase containing an inorganic salt and the organic reactant at high concentration is challenging. Phase transfer catalysis may be the solution. Starks and Liotta [4] describe different cyanide displacements using liquid–liquid phase transfer catalysis or solid–liquid phase transfer catalysis.

Solid–liquid phase transfer catalysis is often preferred to liquid–liquid phase transfer catalysis, because the solvation of the reactive cyanide anion is lower in the first system. But sometimes it is noted that (i) a different order in the halobutane reactivity is observed in comparison with the common order suggested by the literature and that (ii) small amounts of water added to the mixture increases the reaction rate.

Displacement reactions under phase transfer conditions may sometimes be very sensitive to the water present in the organic phase. In some cases, it is suggested to add small amounts of water in order to increase the reaction rate and the name omega phase was given to a new region of the reaction system where water coats the surface of the salt and extracts the crown from the organic phase [5,6].

This study attempts to give a better interpretation of the key role played by water by correlating the reaction rate with the concentration of water in the organic phase and by the study of the influence of water on the relative molar conductivity of the 18-crown-6 ether–KCN complex in an organic solution.

This work also describes the kinetics of cyanide displacement of 1-chlorobutane and 1-bromobutane using 18-crown-6 ether as transfer agent with and without water addition to the reaction mixture.

These halobutanes were chosen as model molecules of the more expensive bromoalkenes and chloroalkenes we intend to use for the synthesis of the desired unsaturated nitriles. We have verified that, as expected, the presence of a

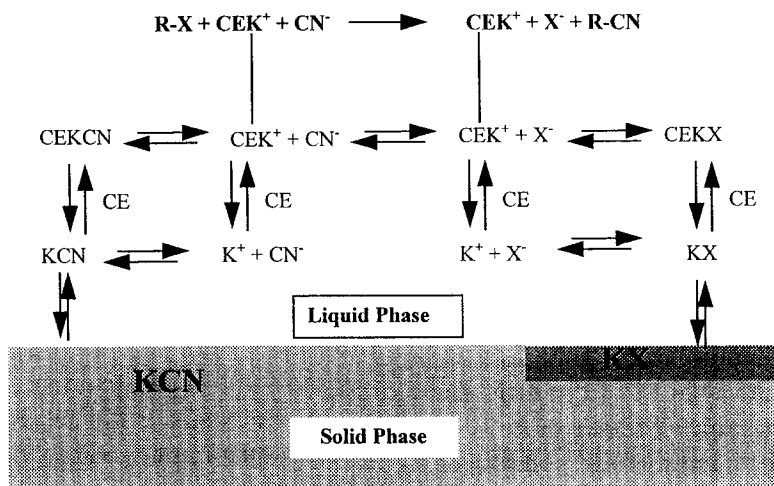
C=C double bond does not influence the reaction kinetics.

2. Experimental

Reaction mixture (halobutane, potassium cyanide, catalyst and acetonitrile as solvent) was refluxed (acetonitrile b.p.: 81.6°C) in a two-necked flask fitted with a condenser and magnetic stirrer. All the reagents were laboratory grade (acetonitrile: Janssen Chimica, 99%; potassium cyanide: Merck p.a., min. 97%; 1-chlorobutane: Aldrich, 99.9%; 1-bromobutane: Aldrich, 99%; 18-crown-6: Aldrich, 99%). Potassium cyanide was dried under vacuum at 80°C, crushed in a planetary mill and dried again before use. The water concentration was measured by the Karl–Fischer method. The concentrations of reactants were determined by gas chromatography (Hewlett Packard 5890, column: CP Wax 52 CB from Chrompack). Atomic absorption measurements were carried out with a Perkin Elmer E360 apparatus with an air/acetylene flame; potassium determination was made according to Vogel's standard method. Metrohm Konduktoskop E365 was used to measure conductimetric data.

Two sets of kinetic experiments were carried out. In the first (phase transfer experiments), an excess of potassium cyanide (10 g) was added to the reaction mixture (4 ml of 1-halobutane, 200 ml of acetonitrile and 1 g crown ether). In a second series (homogeneous experiments), reaction mixtures were derived from a saturated solution prepared in the following way: excess potassium cyanide, 10 g of crown ether and 500 ml of acetonitrile were refluxed for 2 h in a 1-l flask. The solution was stirred overnight at room temperature. After filtering, the volume was adjusted to 500 ml. Starting from this stock solution, dilutions were made to obtain the correct concentration and an equimolar amount of the co-reactant was added.

Potassium concentration and water concentra-



Scheme 1.

tion in the organic phase were determined on samples prepared as in the first set of kinetic experiments but without the halide compound.

3. Results and discussion

3.1. Mechanism

Scheme 1 summarises all the equilibria coexisting during the reaction. First, potassium

cyanide is complexed by the crown ether (CE). The complex $\text{CE} \cdot \text{KCN}$ then dissociates to produce a free cyanide anion which can react with the organic reactant. The same equilibria appear with the potassium halide produced by the synthesis reaction. At equilibrium, the reaction yield depends on the solubility ratio of potassium cyanide to potassium halide.

In a previous study [7], we have shown that at low crown ether concentration (0–0.02 M), all the transfer agent is complexed with cyanide

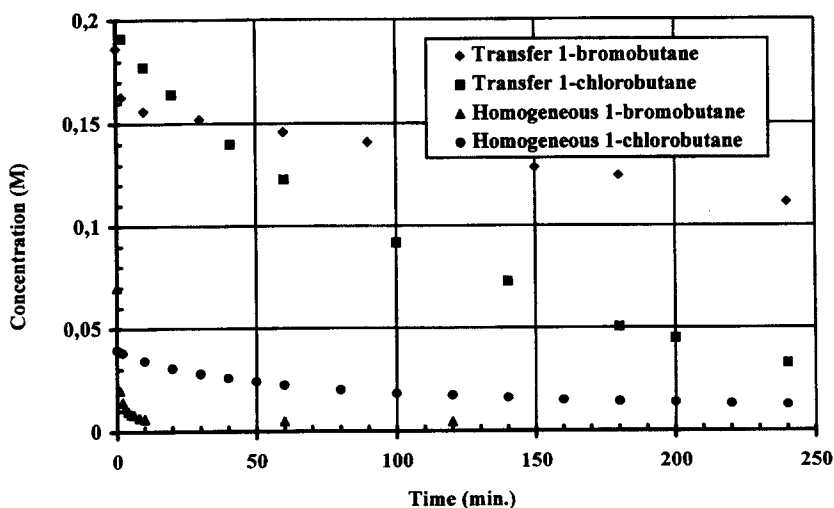


Fig. 1. The comparison of homogeneous and transfer reactions of cyanide displacement of 1-chlorobutane or 1-bromobutane (temperature: 81.6°C, initial concentration of organic reactant: 0.2 M, crown ether concentration: 0.019 M).

anions. It was also demonstrated that the ionisation constant (K) is equal to 0.05.

$$K = \frac{[\text{CE} \cdot \text{K}^+][\text{CN}^-]}{[\text{CE} \cdot \text{KCN}]} \\ = \frac{[\text{CN}^-]^2}{[\text{CE} \cdot \text{KCN}]} = 0.05$$

This value was determined by measuring the limiting molar conductivity. During the same study, we have concluded that the rate determining step of 1-chlorobutane cyanation was the nucleophilic substitution itself. This fact was verified by the comparison of the kinetic constant of reactions conducted under both 'transfer' conditions and 'homogeneous' conditions.

3.2. Kinetic results

3.2.1. Comparison of the cyanation of 1-chlorobutane and 1-bromobutane.

The kinetic results of cyanide displacement of 1-chlorobutane and 1-bromobutane under 'transfer' conditions and 'homogeneous' conditions are given in Fig. 1. For a 'homogeneous' reaction, the rate equation is:

$$r = k[\text{CN}^-][1\text{-halobutane}]$$

We know that under 'transfer' conditions, the cyanide anion concentration in the organic phase is constant, and determined by the crown ether

concentration. Hence, the reaction rate expression reduces to:

$$r = k_{\text{app}}[1\text{-halobutane}]$$

where $k_{\text{app}} = k[\text{CN}^-]$.

In the case of 1-chlorobutane, as previously mentioned [7], the true kinetic constants k are equal under 'homogeneous' and 'transfer' conditions. Hence, we may conclude that the reaction rate is not limited by the transfer of species at the solid-liquid interface.

If we compare the results obtained with 1-bromobutane and 1-chlorobutane, it may be seen that under 'transfer' conditions, the reaction rate of the chloride is higher than that of the bromide. This confirms the observation done by Starks and Liotta in a similar experimental system. However, our experiments show a marked initial drop in the bromobutane concentration. This drop is nearly equal to the value of the crown ether concentration. After this initial drop, the concentration of the reactant linearly decreases in time. This suggests an apparent zero order reaction rate in contrast with the results found in the case of 1-chlorobutane. Under 'homogeneous' conditions, the rate diagram is classical, and 1-bromobutane runs faster than 1-chlorobutane. Actually, the reaction is so fast

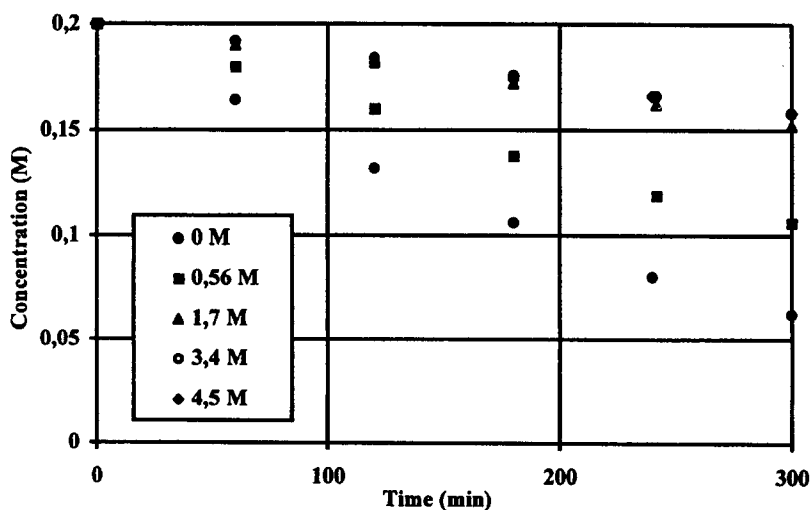


Fig. 2. The influence of the water concentration on the reaction rate of cyanide displacement of 1-chlorobutane (initial concentration of 1-chlorobutane: 0.2 M, crown ether concentration: 0.019 M).

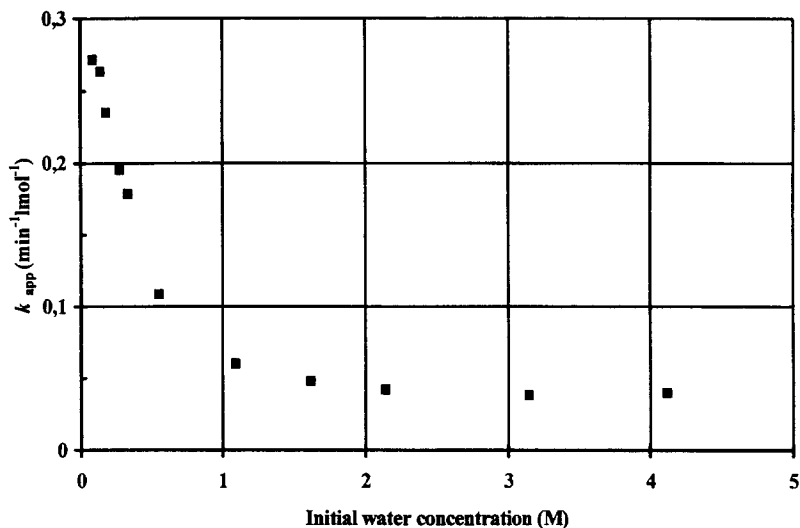


Fig. 3. The kinetic constant dependence of transfer reactions of cyanide displacement of 1-chlorobutane as a function of initial water concentration added to the mixture (initial concentration of 1-chlorobutane: 0.2 M, crown ether concentration: 0.019 M).

that it is not possible to determine the reaction order and the value of the kinetic constant. The comparison with 1-chlorobutane is therefore impossible.

Consequently, in the case of the 1-bromobutane, under transfer conditions, the reaction seems to be limited by the transfer of species through the solid–liquid interface.

3.2.2. The influence of water

Fig. 2 shows the influence of water on the kinetics of cyanide displacement of 1-chlorobutane. The addition of water clearly decreases the reaction rate as demonstrated by the comparison of the concentration–time curves at low or at high amount of added water. We may also observe that the apparent reaction order remains

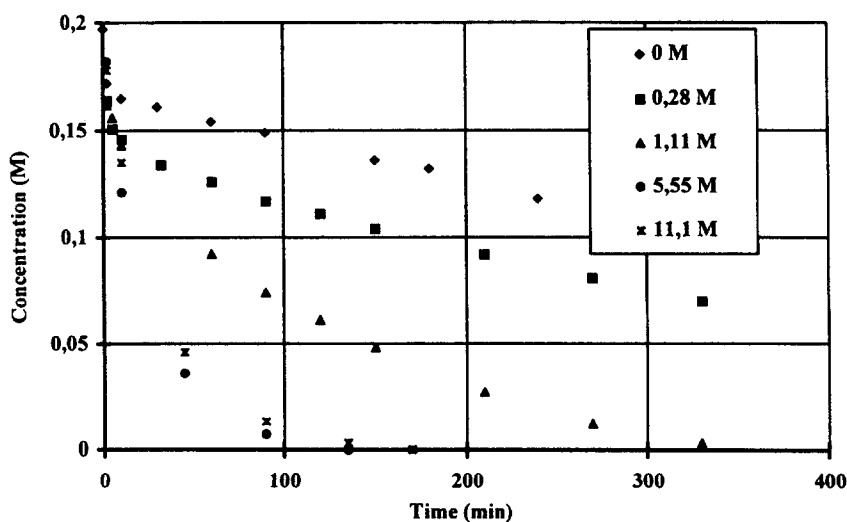


Fig. 4. The influence of water concentration on the kinetic rate of cyanide displacement of 1-bromobutane (initial concentration of 1-bromobutane: 0.19 M, crown ether concentration: 0.019 M).

unchanged and is still equal to 1. However, the effect of water is more important at low concentration than the effect of further water addition.

Fig. 3 shows the dependence of the kinetic constant on the amount of water added to the mixture. In the concentration range of 0 to 1 M of added water, the value of the kinetic constant sharply decreases. At higher concentrations, the changes are much smaller and the value of the apparent rate constant approaches $0.04 \text{ min}^{-1} \text{ mol}^{-1}$.

In the case of 1-bromobutane (Fig. 4), higher water concentrations lead to higher reaction rates in the range of added water from 0 to 5 M. Moreover, the concentration–time curves look more like first order kinetics.

From the above data, it is evident that water has an opposite effect on the two halides undergoing the nucleophilic substitution. However, in both cases, with the same amount of added water, the catalytic system is similar and does not depend on the nature of the halide compound: the solvation level of cyanide anions and their ionisation constant are identical, but the reaction rates vary in opposite ways. Water has a deactivating effect on the reaction of 1-chloro-

butane, and exhibits an activating effect for the bromo compound.

3.3. Water concentration in the organic phase

In a first series of experiments, we have determined by the Karl–Fischer's method the concentration of water in the organic phase. The samples were prepared as for the kinetic experiments under transfer conditions. The results were compared to the results of experiments without crown ether in the system. Fig. 5 shows the concentration of water in the organic phase versus the amount of water added to the mixture. The general behaviour does not depend on the presence of transfer agent and we pointed out that three different zones (A, B, C) may be defined in the evolution of the water concentration. In zone A (0–2 M of water), all the water goes into the organic phase. When the initial water concentration is increased (zone B, 2–5 M), the water concentration in the organic phase remains constant at about 2 M. In this zone, a solubility equilibrium is reached between a new aqueous phase and solid cyanide. The system is then triphasic: solid (KCN)–liquid (water satu-

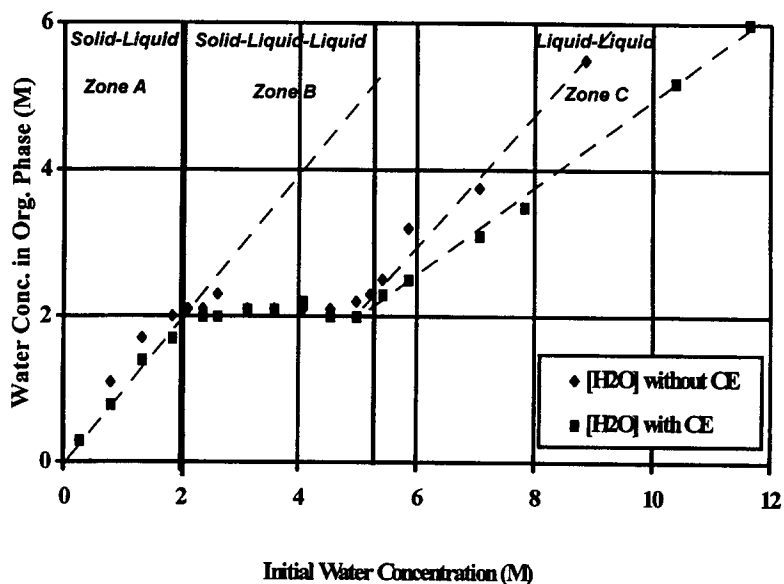


Fig. 5. Water concentration in the organic phase determined by the Karl–Fischer method as a function of the initial water concentration introduced into samples with or without crown ether (crown ether concentration: 0.019 M, room temperature).

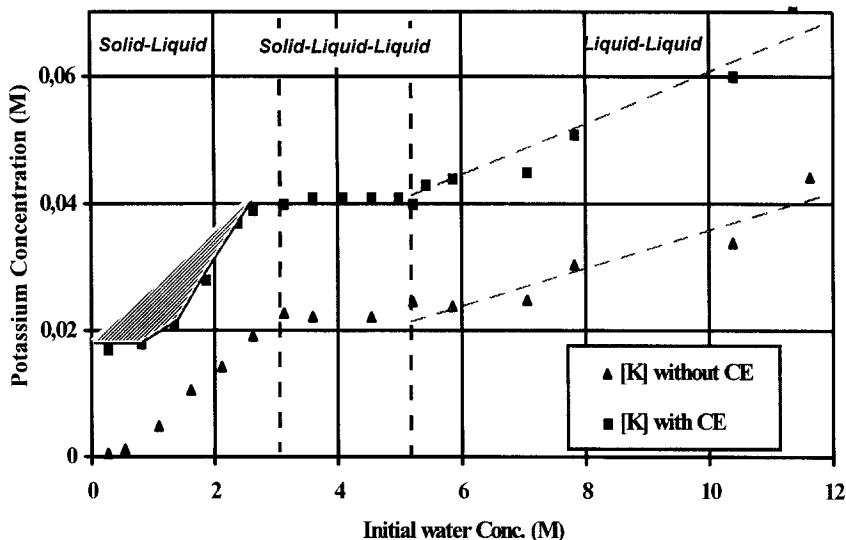


Fig. 6. Potassium concentration in the organic phase as a function of initial water concentration for samples with or without crown ether (crown ether concentration: 0.019 M, room temperature).

rated by KCN)—liquid (acetonitrile with a water concentration equal to 2 M). For an overall water concentration above 5 M (zone C), all the solid is solubilised in the water and the system is formed by two liquid phases only. The calculated KCN concentration in the aqueous phase (45 g/100 ml H₂O) is close to KCN solubility (50 g/100 ml).

In a second series of experiments, we have measured the potassium concentration in the organic phase by flame AA spectroscopy and studied the effect of 18-crown-6 ether addition (Fig. 6). The general behaviour of the curves is similar to what was described above. In zones B and C, the curves are parallel and the increase in potassium solubility is equal to the added

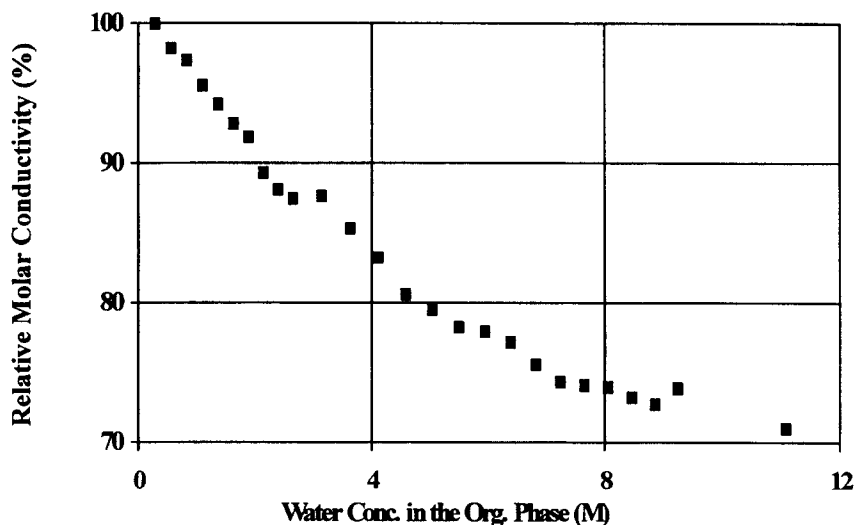


Fig. 7. The dependence of the relative molar conductivity as a function of water concentration in the organic phase (complex concentration: 0.019 M, room temperature).

amount of crown ether. In zone A, the curves are not parallel. Crown ether is less effective probably because the transfer agent (dashed area) coats the surface of solid potassium cyanide.

The last experiment (Fig. 7) shows the molar conductivity of the crown ether–KCN complex versus the concentration of water in the organic phase. The results clearly show a decrease in the molar conductivity on increasing water content. This demonstrates the effect of solvation of the ions by water leading to a reduced mobility, in the same way as it leads to a decreased reactivity.

In zone A, the added water completely goes in the organic phase. In this range (0–2 M), water realises the solvation of the cyanide anions and reduces their reactivity. Consequently, the reaction rate must decrease. This fact is observed using 1-chlorobutane as starting organic compound (see Figs. 2 and 3). The decrease of the value of the apparent rate constant k_{app} as a function of the amount of added water is in good agreement with the variation of the molar conductivity described in Fig. 7.

In the case of the bromo compound, the same effect probably exists, but it is overcompensated by the influence of water on the transfer steps between solid and liquid phase. Work is under progress to distinguish between an effect on cyanide solubilisation or complexation, or an effect on bromide deposition.

4. Conclusions

Synthesis of nitriles by cyanide displacement of chloroalkenes can be envisaged by solid–liquid phase transfer catalysis. Presence of water should be avoided as it reduces the reactivity of cyanide anions by solvation.

When bromoalkanes or bromoalkenes are considered as starting material, 100% conversion will be very difficult to achieve, unless water is added in the system. Addition of suitable amounts of water may realise an optimum between the negative effect of solvation and the positive effect water exerts on phase transfer. This optimum probably lies in using liquid–liquid phase transfer catalysis.

References

- [1] J.L. Dallons, Ph.D. Thesis, Louvain-la-Neuve, Belgium, 1986.
- [2] J.L. Dallons, G. Jannes and B. Delmon, in M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, C. Montassier and G. Perot (Eds.), *Heterogeneous Catalysis and Fine Chemicals, Studies in Surface Science and Catalysis*, Vol. 41, Elsevier, Amsterdam, 1988, p. 115.
- [3] J.L. Dallons, G. Jannes and B. Delmon, *Catal. Today*, 5 (1989) 257.
- [4] C.M. Starks and C.L. Liotta, *Phase Transfer Catalysis, Principles and Techniques*, Academic Press, New York, 1978.
- [5] H.A. Zahalka and Y. Sasson, *J. Chem. Soc., Chem. Commun.*, (1984) 1652.
- [6] S. Dermeik and Y. Sasson, *J. Org. Chem.*, 50 (1985) 879.
- [7] G. Jannes, P. Vanderwegen, L. Elsen and F. Carette, *J. Mol. Catal.*, 62 (1990) 255.