Importance of small amount of water in solid-liquid phase transfer catalysis: Reaction of benzyl chloride with solid sodium sulphide

Narayan C Pradhan*
Department of Chemical Engineering, Indian Institute of Technology, Kharagpur 721 302, India

Received 5 September 2000; accepted 19 March 2001

The reactions of benzyl chloride with solid sodium sulphide were carried out in the presence of two different phase transfer catalysts. The rate of reaction was found to vary non-linearly with catalyst concentration in both the cases. This was explained in terms of phase transfer catalyst-promoted dehydration of the solid reactant. The phenomenon was also explained theoretically which proved the importance of small amount of water in solid-liquid phase transfer catalysis.

The role of minute quantity of water is reported to be very important in solid-liquid phase transfer catalysis. Several workers have recommended that in order to achieve best results with phase transfer catalysts, the nucleophilic substitution reaction should be carried out in solid-liquid mode, i.e., in the absence of water. Some others report that the presence of a small amount of water is essential in the solid-liquid phase transfer catalysis, for the exchange process to take place, and that the quaternary ammonium salts cannot directly exchange anions with the solid but only with an aqueous solution of the salt. The water present in the system coats the solid surface and thus a thin aqueous film is formed around the solid surface where solid dissolution takes place rapidly. This thin aqueous film around the solid salt is conveniently called as "Omega Phase." The present work is concerned with the establishment of the importance of small amount of water in solid-liquid phase transfer catalysis.

The reactions of organic halides like benzyl chloride with sulphide ions result in the formation of diaryl sulphides. These diaryl sulphides find many applications as additives for extreme pressure lubricants, anti-wear additives for motor oils, stabilisers for photographic emulsions, in recovery and refining of precious metals and in different anticorrosive formulations. Phase transfer catalysed preparation of these compounds is considered the best over other alternatives. Pradhan and Sharma have made a detailed study of the reaction system in the presence of both soluble and triphasic catalysts. However, they have not reported the effect of catalyst concentration on this commercially important reaction in solid-liquid mode. It was, therefore, thought desirable to study the effect of catalyst concentration on solid-liquid phase transfer catalysed reaction and to find out a suitable mechanism for the transfer process.

In the present work, the effect of catalyst concentration on the reaction of benzyl chloride and solid sodium sulphide has been studied and the role of a minute amount of water has been examined for this solid-liquid phase transfer catalysed reaction. Two different types of catalyst have been used, namely hydrophilic tetrabutyl ammonium bromide (TBAB) and hydrophobic tricaprylyl methyl ammonium chloride (Aliquat 336). A theoretical analysis of the experimental observations has also been presented.

Experimental Procedure

Materials

Benzyl chloride and solid sodium sulphide (extra pure) were obtained from Loba Chemie Pvt Ltd, India. p-Chlorobenzyl chloride and catalysts (TBAB and Aliquat 336) were obtained from Fluka Chemica. Solvent toluene (AR grade) was obtained from S D Fine Chemicals Pvt Ltd, India.

Method

The reaction of benzyl chloride with solid sodium sulphide was carried out in a 9.2 cm I.D., mechanically agitated, fully baffled glass reactor provided with a stainless steel cooling coil and a glass thermowell. A 2.5 cm diameter glass disc turbine impeller, located at a height of 1.5 cm from the bottom was used for stirring the reaction mixture.

*E-mail: ncp@che.iitkgp.ernet.in; Fax: (03222)-55303
Water was used as coolant to control the temperature of the reaction mixture. The whole reactor assembly was kept in a constant temperature polyethylene glycol-400 (PEG-400) bath whose temperature could be controlled within ±0.5°C. In all experiments, toluene was used as the solvent.

In a typical run, 300 cm³ of the organic phase consisting of 1.25x10⁻³ mol/cm³ of benzyl chloride and 1.25x10⁻⁵ mol/cm³ of catalyst TBAB (or Aliquat 336), dissolved in toluene, was kept in the reactor at a predetermined reactor temperature. Then the solid sodium sulphide (Na₂S·3.5H₂O) particles of a particular average size was added in one lot and the mixture was stirred at a fixed speed of agitation. Samples from the organic phase were withdrawn at regular intervals after stopping the agitation and separation of the phases within the reactor.

All samples from the organic phase were analysed by gas-liquid chromatography (GLC) using a 2x3mm stainless steel column packed with 10% OV-17 on Chromosorb W (80/100) and flame ionization detector (FID). The rates of reaction of organic reactants were calculated knowing the time required for a fixed conversion from the concentration versus time plot. The sodium sulphide content of the solid salt was determined by the standard iodometric titration procedure.

Theoretical Analysis

Pradhan and Sharma have found that the reaction of sodium sulphide (Na₂S·2.5H₂O) with benzyl chloride in the presence of phase transfer catalyst is mass transfer controlled conforming to Regime 2 of mass transfer with chemical reaction. It is also widely accepted that the presence of a small amount of water is essential for the exchange process in solid-liquid phase transfer catalysis (S-LPTC) to take place, and that the quaternary ammonium salt cannot directly exchange anions with the solid but only with an aqueous solution of the salt. If it is assumed that the water associated with the solid sulphide forms a thin aqueous layer around the solid, as shown in Fig. 1, then the whole process can be depicted as

\[
\text{Na}_2\text{S (s)} \rightarrow \text{Na}^+ \text{Na}^+ \text{S}^{-\text{(aq)}} + (\text{M}^+ \text{X}^-)_{\text{(aq)}} \quad \text{(1)} \\
(\text{M}^+ \text{X}^-)_{\text{(aq)}} + (\text{Q}^- \text{Y}^+)_{\text{(org)}} \leftrightarrow (\text{Q}^- \text{Y}^+)_{\text{(org)}} + (\text{M}^+ \text{X}^-)_{\text{(aq)}} \quad \text{(2)} \\
(\text{Q}^- \text{Y}^+)_{\text{(org)}} + \text{RX}_{\text{(org)}} \rightarrow \text{RSR}^+ + (\text{Q}^- \text{X}^-)_{\text{(org)}} + (\text{M}^+ \text{X}^-)_{\text{(org)}} \quad \text{(3)}
\]

As the reaction is mass transfer controlled, the rate of reaction can be written as

\[ R_A = k_0 a [Q^-Y^+]_{\text{(org)}} \quad \text{(5)} \]

Quaternary ammonium compounds have strong affinity for water and they become hydrated by taking up water. In the course of reaction, a part of the catalyst is used in extracting water from the solid surface as water of hydration of the quaternary ammonium ion. Moreover, as the catalyst extracts water from the surface, the aqueous-organic interface (which is important for the exchange process) shrinks and, in the extreme case, the solid-organic interface appears ('dry' spots). Since the exchange rate at the solid organic interface is negligibly slow, it can be neglected, with the result that the effective interfacial area, \( a \), in Eq. (5), decreases with the extraction of water. Therefore, a proportionality relationship between \( a \) and the concentration of water in the solid may be written as

\[ a \propto [W] \]

or,

\[ a = C_1 [W][C_1 \text{ is the proportionality constant}] \quad \text{(6)} \]

Let \([Q_o]\) be the total catalyst (per unit volume of organic phase) present in the system, where a fraction \(\alpha\) of it is used for the extraction of water from the surface at any time, which means that the remaining...
Table 1—Effect of TBAB concentration on the reaction of benzyl chloride with solid sodium sulphide

<table>
<thead>
<tr>
<th>Catalyst concentration x10^5 (mol/cm^3)</th>
<th>Rate of reaction (mol/cm^3 s)</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.08 x 10^{-9}</td>
<td>—</td>
</tr>
<tr>
<td>0.625</td>
<td>8.33 x 10^{-8}</td>
<td>77</td>
</tr>
<tr>
<td>1.25</td>
<td>2.70 x 10^{-7}</td>
<td>250</td>
</tr>
<tr>
<td>2.50</td>
<td>6.94 x 10^{-7}</td>
<td>643</td>
</tr>
<tr>
<td>3.75</td>
<td>8.77 x 10^{-7}</td>
<td>812</td>
</tr>
<tr>
<td>5.00</td>
<td>9.85 x 10^{-7}</td>
<td>912</td>
</tr>
</tbody>
</table>

*Reaction conditions: Volume of organic phase \( v = 300 \text{ cm}^3 \); concentration of benzyl chloride in organic phase = \( 1.25 \times 10^{-3} \text{ mol/cm}^3 \); solid sodium sulphide loading = 10% (w/v); \( d_{sulphide} \) of sulphide particles = 1200 \( \mu \text{m} \); speed of agitation = 2000 rev/min; temperature = 40°C; matching conversion = 25%.

(1 - \( \alpha \)) fraction is in the hydrated state at that instant. If it is assumed that the hydration of the catalyst does not change its activity significantly then all of the catalyst will participate in the exchange process [Eq. (2)]. This assumption is justified as the catalysts work well in liquid-liquid (organic-aqueous) mode. If \( [Q_h] \) be the amount of catalyst involved at any instant for water extraction, then the rate at which water will be removed from the surface can be expressed as

\[
-d[W]/dt = k_h [Q_h][W] = \alpha k_h [Q_o][W]
\]  

where \( k_h \) is the hydration constant for the catalyst.

Eq. (7) on integration gives

\[
[W] = [W_o] \exp(-\alpha k_h [Q_o] t)
\]  

where \([W_o]\) is the initial water concentration in the solid and \( \alpha \) and \( k_h \) are assumed to be constants.

From Eqs (6) and (8),

\[
a = C_1 [W_o] \exp(-\alpha k_h [Q_o] t)
\]

or,

\[
a = a_o \exp(-\alpha k_h [Q_o] t)
\]

where \( a_o \) is the initial aqueous-organic interfacial area (at \( t = 0 \)).

Since all the catalyst participates in the anion exchange process, from equilibrium (2) it can be shown that

\[
[Q^*Y^-]_{(org)} = \frac{[Q_o]}{1 + \frac{r}{K_{eq}}}
\]  

where, \( r = [X]_{eq} [Y]_{eq} \).

As the concentration of the leaving anion in the aqueous phase is very low compared to that of the nucleophile, Eq. (10) can be simplified as

\[
[Q^*Y^-]_{(org)} = [Q_o]
\]  

Eq. (5), therefore, takes the following form

\[
R_A = a_o k_L [Q_o] \exp(-\alpha k_h [Q_o] t).
\]

The average value of \( R_A \) may now be calculated as follows.

\[
-dC/dr = R_A = a_o k_L [Q_o] \exp(-\alpha k_h [Q_o] t)
\]

which on integration gives

\[
C_i - C = (a_o k_L \alpha k_h) \left[1 - \exp(-\alpha k_h [Q_o] t)\right].
\]  

From Eq. (14), the average rate may be expressed as
least square fit, are shown in Table 3.

The values of these different parameters, thus obtained by minimization of the square of the differences in experimental and theoretical rates and that calculated from Eq. (15) at different catalyst concentrations, are shown in Table 3.

Table 2—Effect of Aliquat 336 concentration on the reaction of benzyl chloride with solid sodium sulphide

<table>
<thead>
<tr>
<th>Catalyst concentration (mol/cm³)</th>
<th>Rate of reaction (mol/cm³ s)</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.08×10⁻⁹</td>
<td></td>
</tr>
<tr>
<td>0.625</td>
<td>4.25×10⁻⁸</td>
<td>39</td>
</tr>
<tr>
<td>1.25</td>
<td>1.38×10⁻⁷</td>
<td>128</td>
</tr>
<tr>
<td>2.50</td>
<td>1.66×10⁻⁷</td>
<td>154</td>
</tr>
<tr>
<td>3.75</td>
<td>2.25×10⁻⁷</td>
<td>208</td>
</tr>
<tr>
<td>5.00</td>
<td>2.67×10⁻⁷</td>
<td>247</td>
</tr>
</tbody>
</table>

*Reaction conditions: Volume of organic phase V = 300 cm³; concentration of benzyl chloride in organic phase = 1.25×10⁻³ mol/cm³; solid sodium sulphide loading = 10% (w/v); d_{av} of sulphide particles = 1200 μm; speed of agitation = 2000 rpm/min; temperature = 40°C; matching conversion = 25%.

From this figure that, for certain values of the parameters, k_{h}, k_{L} and α , the experimental rates match very well with that obtained theoretically. The values of these different parameters, thus obtained by least square fit, are shown in Table 3.

It can be seen from Table 3 that the values of k_{h} and k_{L} are higher for TBAB than that of Aliquat 336. Since TBAB is a hydrophilic catalyst, it is expected that the rate constant for hydration of this catalyst should be higher than that of Aliquat 336 which is a hydrophobic catalyst. Moreover, as the size of Aliquat 336 is much larger than that of TBAB, its diffusivity will be low compared to TBAB. Thus a lower mass transfer coefficient value was obtained with Aliquat 336 compared to TBAB.

It is also evident from Table 3 that the value of the parameter α is higher for hydrophobic catalyst than that for hydrophilic one. If the hydration reaction is viewed as a fast reversible reaction, then α [Q_{0}] represents the equilibrium concentration of unhydrated catalyst which will be higher for a hydrophobic catalyst. A higher value of α for Aliquat 336 compared to TBAB, is, therefore, quite expected.

The above discussion clearly indicates the validity of the theoretical analysis presented here. The non-linear variation in rate with solid-liquid phase transfer catalysed reaction under investigation is, therefore, due to extraction of water by the catalyst from the solid reactant disfavouring anion exchange at the solid surface. The linear variation could have been observed with no extraction of water by the catalyst. As more and more amount of water is extracted with increasing catalyst concentration, the rate of reaction does not vary proportionately with the catalyst concentration and a non-linear variation is thus observed.

Conclusions

The effect of catalyst concentration on solid-liquid phase transfer catalysed reaction of benzyl chloride with solid sodium sulphide was studied. It was found that the rate of reaction varied non-linearly with catalyst concentration. The rate data were interpreted theoretically in terms of PTC assisted 'dehydration' of the solid reactant. Thus it may be concluded that the small amount of water plays an important role in solid-liquid phase transfer catalysis.

Nomenclature

- R_{A} = (C_{1} - C_{2})/t = (a_{0}k_{L}/α k_{h}t_{0})[1-exp(-α k_{h}[Q_{0}t_{0}])]
- \( k_{L} \) = mass transfer coefficient, cm/s
- \( k_{h} \) = hydration constant, cm³/mol s
- \( A \) = benzyl chloride
- \( K_{eq} \) = equilibrium constant for reaction (2)
- \( a_{0} \) = initial aqueous-organic interfacial area, cm²/cm³
- \( A_{o} \) = initial aqueous-organic interfacial area, cm²/cm³
- \( \alpha \) = aqueous-organic interfacial area, cm²/cm³
- \( \alpha = \) aqueous-organic interfacial area, cm²/cm³
- \( A = \) benzyl chloride
- \( K_{eq} = \) equilibrium constant for reaction (2)
- \( k_{h} = \) hydration constant, cm³/mol s
- \( k_{L} = \) mass transfer coefficient, cm/s
- \( [Q_{0}] = \) initial catalyst concentration in the organic phase, mol/cm³
- \( [Q_{0}] = \) concentration of unhydrated catalyst at any instant, mol/cm³
- \( t_{0} = \) initial aqueous-organic interfacial area, cm²/cm³
$R_A$ = rate of reaction of benzyl chloride, mol/cm$^3$/s
$R_{AV}$ = average rate of reaction of benzyl chloride, mol/cm$^3$/s
$[W]$ = water concentration in the solid reactant, mol/cm$^3$
$[W_0]$ = initial water concentration in the solid reactant, mol/cm$^3$

References