

Kinetics of the Esterification of Potassium *p*-Nitrobenzoate by Benzyl Bromide using Dicyclohexyl-18-crown-6 as Phase-transfer Agent

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Summary Both S_N1 and S_N2 rate constants for the formation of ester between benzyl bromide and potassium *p*-nitrobenzoate using dicyclohexyl-18-crown-6 as a phase transfer agent have been determined simultaneously.

We report the kinetic behaviour of the reaction between benzyl bromide ($[BB]=0.50$ M) in CH_2Cl_2 and potassium *p*-nitrobenzoate ($[KNB]=1.0$ M) in water, in the presence of dicyclohexyl-18-crown-6 (2,5,8,15,18,21-hexaoxatricyclo-[20.4.0.0^{9,14}]hexacosane). Without the crown ether benzyl *p*-nitrobenzoate (BNB) was not observed even after vigorous stirring for a long time at room temperature.

However, in the presence of the crown ether (0.01 M), the expected product could be detected by high pressure liquid chromatography (h.p.l.c.) after stirring for 30 min at 25 °C. After stirring for 24 h BNB was isolated, purified, and characterized (m.p. 83.5—84 °C).

A few cases of the use of crown ethers as phase transfer catalysts to bring together reactants from different phases have been reported.^{1,2} However, in all these cases, one of the reactants served as one phase in the reaction system, and this could be a limitation of this technique. In our system, the reactants were dissolved separately in immiscible liquids and the crown ether acted as the transfer agent enabling reaction to occur in a homogeneous phase.

Here, the nucleophile, *i.e.* the *p*-nitrobenzoate was extracted from the aqueous layer into the CH_2Cl_2 layer by dicyclohexyl-18-crown-6. By the same method used in the transfer of potassium picrate into CHCl_3 ,³ the equilibrium constant for the transfer reaction: $\text{KNB}(\text{in } \text{H}_2\text{O}) + \text{crown}$

ether (in CH_2Cl_2) \rightleftharpoons $\text{KNB-crown ether complex}(\text{in } \text{CH}_2\text{Cl}_2)$ was found to be 1.81 mol^{-1} where $[\text{KNB}] = 0.87 \text{ M}$, $[\text{KOH}] = 0.44 \text{ M}$,[†] and [dicyclohexyl-18-crown-6] was varied between 2.0×10^{-3} and $1.0 \times 10^{-2} \text{ M}$. Since the salt concentration in our system was much higher than the initial crown ether concentration, the concentration of the complex in CH_2Cl_2 can be expressed as equation (1), where

$$[\text{KNB-crown ether complex}] = \frac{\{K_{\text{eq}}[\text{KNB}]_0/\{1 + K_{\text{eq}}[\text{KNB}]_0\}\}[\text{C}]_0}{(1)} \quad (1)$$

$[\text{KNB}]_0$ is the potassium salt concentration in water and $[\text{C}]_0$ is the initial crown ether concentration in CH_2Cl_2 . For up to 30% conversion into BNB during kinetic measurements, $[\text{KNB-crown ether complex}]$ varied from 3.2×10^{-2} to $3.0 \times 10^{-2} \text{ M}$ with $[\text{C}]_0 = 5.0 \times 10^{-2} \text{ M}$, $[\text{KNB}]_0 = 1.0 \text{ M}$, and $[\text{BB}]_0 = 0.5 \text{ M}$. Thus $[\text{KNB-crown ether complex}]$ in CH_2Cl_2 may be considered as being constant. The reaction kinetics can then be regarded as pseudo first-order (equations 2 and 3), where $[\text{BB}]_0$ is the initial concentration

$$d[\text{BNB}]/dt = k_{\text{obs}}[\text{BB}] \quad (2)$$

$$\log \{1/([\text{BB}]_0 - [\text{BNB}])\} = (k_{\text{obs}}/2.3)t + \text{constant} \quad (3)$$

of benzyl bromide and k_{obs} is the observed first order kinetic rate constant.

Plots of $\log\{1/([\text{BB}]_0 - [\text{BNB}])\}$ vs. time for different concentrations of dicyclohexyl-18-crown-6 in CH_2Cl_2 were straight lines with the intercept at $\log(1/[\text{BB}]_0)$ for up to 30% reaction at 25 °C. At the end of the kinetic run, the organic layer was checked using i.r. spectroscopy to ensure that no benzyl alcohol had been formed. The absence of benzyl alcohol, shown by h.p.l.c., during the kinetic measurements also agreed with the i.r. spectral data.

The nucleophilic substitution of benzyl bromide by methoxide is known to follow an $\text{S}_{\text{N}}2$ mechanism at a concentration of 1.0 M in methanol⁴ while solvolysis with water in formic acid⁵ and the reaction with carboxylic salts in protic solvents are both $\text{S}_{\text{N}}1$ mechanisms.⁶ The $\text{S}_{\text{N}}1$ mechanism can be accounted for by the formation of a benzyl carbonium ion stabilized by resonance. Assuming that both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms are operating in our reaction system, the overall rate of the ester formation can be expressed as equation (4), where the first term is associated with an $\text{S}_{\text{N}}1$ mechanism and the second term with an

$$d[\text{BNB}]/dt = fk_1[\text{BB}] + k_2[\text{BB}][\text{KNB-crown ether complex}] \quad (4)$$

$\text{S}_{\text{N}}2$ mechanism. Because there is a possibility that the carbonium ion intermediate could react with water present in the CH_2Cl_2 to form benzyl alcohol, a factor *f* was introduced to represent the percentage of benzyl *p*-nitrobenzoate

formed from the carbonium ion intermediate in the $\text{S}_{\text{N}}1$ mechanism. However, absence of benzyl alcohol implies that *f* is unity. Therefore, equation (4) can be written as equation (5). If the equilibrium constant k_{eq} is known and $d[\text{BNB}]/dt = k_1[\text{BB}] + k_2[\text{BB}][\text{KNB-crown ether complex}] \quad (5)$

if $[\text{KNB}]_0 \gg [\text{crown ether}]_0$, $[\text{KNB-crown ether complex}]$ can be substituted into equation (5). The overall reaction rate can then be represented as equation (6). Comparing $d[\text{BNB}]/dt = [\text{BB}]\{k_1 + k_2K_{\text{eq}}[\text{KNB}]_0[\text{C}]_0/(1 + K_{\text{eq}}[\text{KNB}]_0)\} \quad (6)$

equations (2) and (6), the observed rate constant for the pseudo first order reaction can be represented as equation (7).

$$k_{\text{obs}} = k_1 + k_2K_{\text{eq}}[\text{KNB}]_0[\text{C}]_0/(1 + K_{\text{eq}}[\text{KNB}]_0) \quad (7)$$

By plotting k_{obs} vs. initial crown ether concentration while keeping $[\text{KNB}]_0$ constant, the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ rate constants can be obtained. This plot was a straight line with a non-zero intercept at $1.0 \times 10^{-5} \text{ min}^{-1}$. Knowing the value of K_{eq} , the $\text{S}_{\text{N}}2$ rate constant was found to be $8.2 \times 10^{-3} \text{ l mol}^{-1} \text{ min}^{-1}$ at 25 °C.

These two rate constants show that $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms are indeed competing in the reaction. We found that the rates for the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms were $1.0 \times 10^{-5} [\text{BB}]$ and $6.9 \times 10^{-3} [\text{C}]_0[\text{BB}]$, respectively. For low crown ether concentrations *e.g.* $5.0 \times 10^{-3} \text{ M}$ (the concentration of the nucleophile, *i.e.* the *p*-nitrobenzoate, was accordingly low), *ca.* 22% of the product was due to the $\text{S}_{\text{N}}1$ mechanism, 78% being due to the $\text{S}_{\text{N}}2$ mechanism. However, with higher crown ether concentrations, <3% of the product would be due to the $\text{S}_{\text{N}}1$ mechanism. Thus, an $\text{S}_{\text{N}}2$ mechanism is the predominant reaction pathway when using phase transfer reagents such as crown ethers.

We found that when the concentration of the nucleophile was high, the reaction mainly followed an $\text{S}_{\text{N}}2$ mechanism with no benzyl alcohol being formed. When the nucleophile concentration was low, the product from the $\text{S}_{\text{N}}1$ mechanism should become significant and thus benzyl alcohol should be detectable in the products, formed by reaction of the benzyl carbonium ion intermediate with the water dissolved in the CH_2Cl_2 . However, the fact that benzyl alcohol was not detected does not rule out the $\text{S}_{\text{N}}1$ mechanism. As in the solvolysis of benzyl tosylate in methanol, benzyl methyl ether was obtained. If a more powerful nucleophile such as bromide was added, the $\text{S}_{\text{N}}1$ rate was unchanged but the product was benzyl bromide.⁷ As the nucleophilicity of water in our case was much lower than that of the *p*-nitrobenzoate and the solubility of water in CH_2Cl_2 is only 0.17% at 20 °C,⁸ coupled with the fact that there is only 22% $\text{S}_{\text{N}}1$ product and a low concentration of the nucleophile, it is not surprising therefore that benzyl alcohol was absent in the reaction product.

(Received, 6th October 1977; Com. 1045.)

† The presence of KOH is to prevent the extraction of *p*-nitrobenzoic acid into the organic layer. See also reference 3.

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