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ROLE OF WATER IN ALUMINA-ASSISTED SOLID-LIQUID INTERFACIAL REACTION

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Heterogeneous reaction between octyl bromide and alkali acetate solid in toluene is facilitated in the presence of alumina *and* a trace of water. The reactivity shows a maximum for a certain amount of water, and this optimum amount varies depending on the alkali metal cation. Role of water in the interfacial reaction is discussed.

The use of inorganic solid support for organic synthesis has been a growing concept in recent years.$^{1)}$ Various types of inorganic reagents adsorbed on or in the presence of supports show much enhanced reactivity compared to those reagents without supports. On the other hand, the importance of the presence of water in a trace amount has been recognized in several solid-liquid interfacial reactions.$^{2-6)}$ In the absence of water, high reactivity has not been observed at all in some cases,$^{3-5)}$ and completely different products have been obtained in other case.$^{2)}$ Menger and Lee have even proposed the idea that a primary function of a support is to supply a trace of water.$^{3)}$ We now report the results of our research on the role of water in a typical solid-liquid interfacial reaction promoted in the presence of a support.

Nucleophilic substitution of octyl bromide with acetate anion was chosen as a reference reaction (Eq. 1). The reaction has been reported to be promoted in the presence of alumina.$^{7,8)}$ A heterogeneous mixture of octyl bromide and

$$n\text{-}C_8H_{17}Br \; + \; MOAc \xrightarrow[90\ °C]{toluene} n\text{-}C_8H_{17}OAc \; + \; MBr \qquad (1)$$

potassium acetate (M = K) in toluene with or without added alumina and water was vigorously agitated at 90 °C in a test tube with a Teflon-coated screw cap. The results are summarized in Table 1.

In the absence of a support, no reaction was observed; addition of water did not accelerate the reaction at all. In contrast to the literature,$^{7,8)}$ the reaction proceeded only very slowly when dry alumina (Merck, neutral, Type 90 for column chromatography, activity I, 70-230 mesh) was added into the mixture; the production of dioctyl ether was rather the main reaction. However, when a small quantity of water (n : molar ratio of H_2O to KOAc = 0.1) was added together with alumina, the reaction was promoted to a remarkable extent. Interestingly, the reaction was further accelerated with an increase in water up to n = 0.4 and then retarded or almost inhibited with a further increase in water. These results are illustrated in Fig. 1.

Table 1. Reaction of Octyl Bromide with Potassium Acetate[a]

Support	H_2O/n[b]	Time/h	Yield/%[c]		
			Acetate	Alcohol	Ether
None	0	91	0.3	0.1	0.0
"	0.1	91	0.0	0.1	0.0
"	0.23	91	0.1	0.1	0.0
Al_2O_3[d]	0	91	1.8	0.1	16
"	0.1	92	26	6.2	2.5
"	0.23	91	49	5.1	1.1
"	0.4	91	66	2.8	0.6
"	0.7	96	13	1.7	0.3
"	1.0	91	2.3	1.9	0.1

a) To a toluene solution (5 cm^3) containing octyl bromide (0.62 g, 3.2 mmol) were added KOAc (pulverized and dried in vacuo at 145 °C, 1.57 g, 16 mmol) and alumina (1.6 g), and the mixture was vigorously agitated at 90 °C. Water was added to the mixture with a syringe. b) Molar ratio of H_2O to KOAc. c) Determined by GLPC using tetradecane as an internal standard. d) See text.

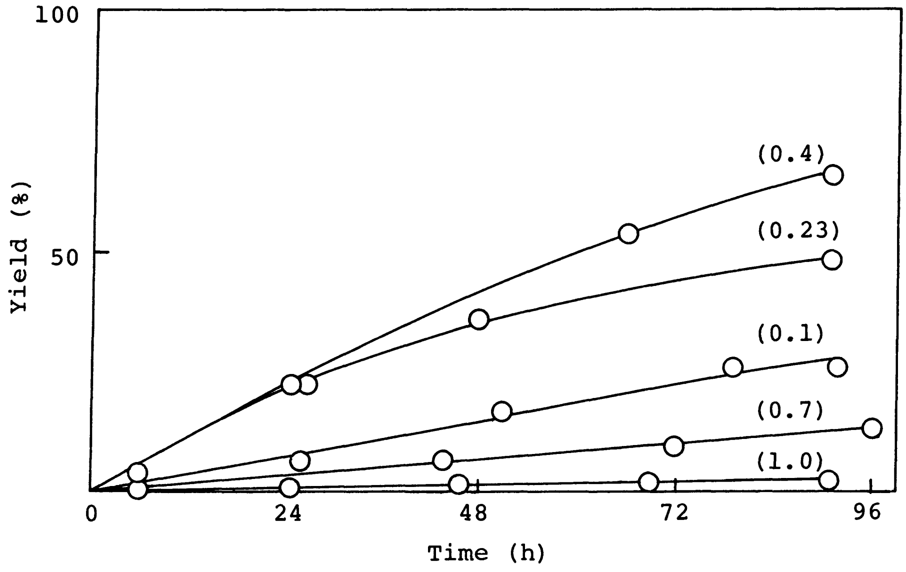

Fig. 1. Plots of octyl acetate yields vs. reaction time. Figures in parentheses show the molar ratio (n) of the added H_2O to KOAc.

The yield of dioctyl ether, a by-product, greatly decreased when water was added, and another by-product, octanol, was obtained instead. Interestingly, a further increase in water decreased the yield of octanol. Thus, the nucleophilic substitution with acetate anion was almost exclusively facilitated when the optimum amount of water ($n = 0.4$) was present in the reaction. These observations indicate that the combination of the high surface area of alumina and a trace of water is essential for promoting the reaction.

It is generally accepted that adsorption of substrates is an important factor for promoting inorganic solid-supported reactions. Although this may also be valid in the present reaction, the enhanced reactivity in the presence of water suggests the importance of another factor, i. e., the interaction among the inorganic salt, alumina, and water.

In order to look into further detail of the role of water and to clarify the cause of the maximum observed for the amount of water, the reaction was carried out for a series of alkali acetate salts (Eq. 1; $M = Cs$, Na, Li). The results are quite noteworthy: the amount of water giving the maximum acceleration varied depending on the cation (Fig. 2). The most reactive caesium salt showed a sharp maximum for the smallest amount of water ($n = 0.23$), while the least reactive lithium salt showed a broad maximum for the largest amount of water ($n \sim 1.0$).

Weber and Gokel, having pointed out the important role of water in solid-liquid phase-transfer processes, have proposed the idea that the hydration of an

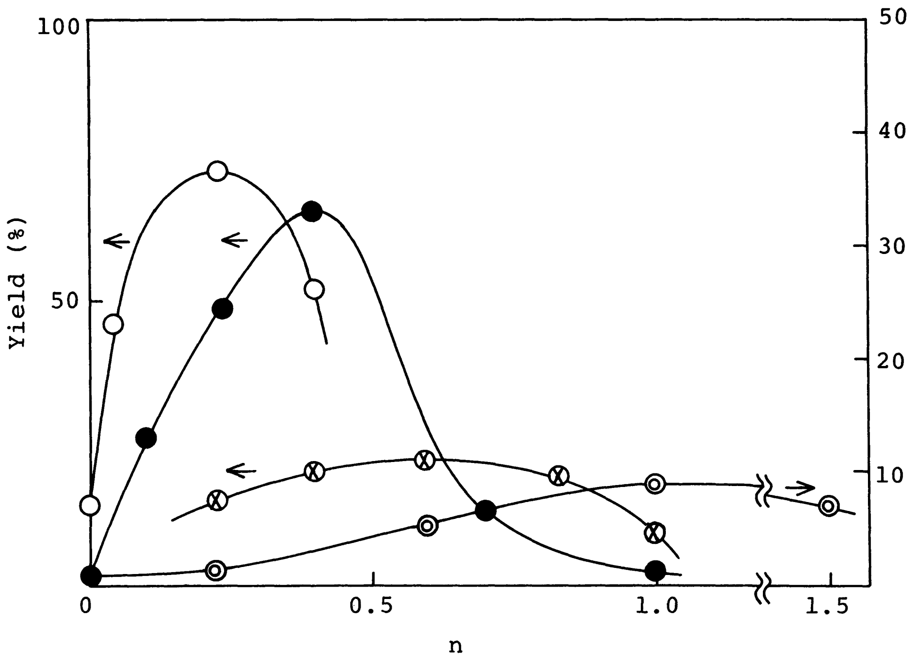

Fig. 2. Plots of octyl acetate yields vs. the molar ratio (n) of the added H_2O to MOAc. Yields were determined at a definite reaction time for each salt: ○ CsOAc, 51 h; ● KOAc, 91 h; ⊗ NaOAc, 144 h; ◎ LiOAc, 164 h. For LiOAc the scale at the right ordinate is used.

ion pair must overcome the lattice energy before normal phase-transfer processes occur.[9)] A similar idea has been adopted by Tanaka and Koyanagi in their recent study on the heterogeneous preparation of aroyl cyanides.[6)]

The present observations in the alumina-assisted solid-liquid interfacial reaction can also be rationalized by a similar idea that the added water molecule attacks the crystal lattice of the acetate salt to produce partially hydrated and rather active acetate ion on the polar surface of alumina and thus accelerate the reaction. A smaller amount of water is enough to activate an acetate salt with a smaller lattice energy, while a larger amount of water is required for the salt with a larger lattice energy.[10)] Although an increase of the added water increases the acetate ion released from the crystal lattice and accessible for the reaction, a simultaneous increase in hydration to the acatate ion results in a decrease of its nucleophilicity and thus produces the maximum. Microscopic evolution of the water layer on the surface of the support may also contribute to the decreased reactivity when a large amount of water was added.

The reactivity order of the acetate salts was actually not held constant and varied depending on the amount of the added water; e. g., KOAc is more reactive than CsOAc for $n = 0.4$. This variable reactivity order may be interpreted by the competitive hydration to the cation and anion; potassium ion requires more water than caesium ion and thus produces a more naked acetate nucleophile for a fixed amount of water.

In conclusion, the present investigation presented the strong pieces of evidence in support of the idea that a trace of water is required in order to destroy the crystal lattice of an inorganic reagent and to produce active ions or ion-pairs for promoting a solid-liquid interfacial reaction. Further study along this line is now in progress.

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10) Lattice energy: CsOAc, 682; KOAc, 686; NaOAc, 761; LiOAc, 881 kJ mol^{-1}. Data from "CRC Handbook of Chemistry and Physics", CRC Press, Cleveland (1979).

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