Bull. Chem. Soc. Jpn., **68**, 2417—2423(1995)

Phase-Transfer Nucleophilic Reactions Using Water-Insoluble Alcohols as Organic Solvents

Noritaka Ohtani,* Yukihiko Inoue, Noriyuki Shinoki, and Katsuhiro Nakayama

Department of Materials Engineering and Applied Chemistry, Akita University, Akita 010

(Received April 3, 1995)

Simple nucleophilic substitutions were done under liquid–liquid phase-transfer reaction conditions using water-insoluble alcohols as organic solvents. The reactions proceeded at considerable rates even in the absence of any catalysts, depending on the alcohol, inorganic salt, and the aqueous concentration of the salts. An addition of single- or double-chained onium salts enhanced the reaction rate almost linearly with the amount of the onium salts. The concentrations of inorgainc salts and water in the alcohol phase were analyzed and the relationship between these concentrations and the observed rate constant was discussed. An interfacial reaction mechanism explains the kinetics of this reaction system better than the conventional ion-pair mechanism assumed by most research using hydrocarbon solvents.

Phase-transfer catalysis by low-molecular-weight or polymer-supported onium salts has been used for many synthetic reactions.[1—11] The early studies on its reaction mechanism conclude that, as an organic solvent for liquid–liquid phase-transfer catalysis, a nonpolar aprotic solvent is preferrable for simple nucleophilic substitutions. This is based on the assumption that lipophilic quaternary salts, extracted into the organic solvent, are present in the form of ion pairs and that the activity of the ion pairs depends on the degree of hydration due to the water coextracted from the aqueous phase.[1,3,8,12—14] Therefore, protic solvents have been seldom used because of their hydrophilic nature and strong solvation to anions.

In such studies, the aggregation of onium salts was neglected and the organic solvent phase was assumed to consist of an isotropic solution with no molecular assemblies of onium salts. On the other hand, one of us has proposed an inverted micelle model for polymer-supported phase-transfer catalysis, based on the amounts of mutually immiscible solvents, which were simultaneously imbibed by the cross-linked catalyst polymers.[15,16] Recent studies on the solution behavior and reactivity of linear polymer-supported onium salts (cationic ionomers) have shown that the state of the onium salts is greatly dependent on the solvent system.[17—20] The solubility of the cationic ionomers in a water/toluene two-liquid system is quite different from that in water/tetrahydrofuran or methanol/toluene one-liquid systems.[21]

Water-insoluble aliphatic alcohols function as a cosolvent to form microemulsions in surfactant-oil-water systems. According to the theory of Ninham et al.,[22] alcohols enlarge the volume of surfactant tails and, thus, make it advantageous to form inverted water-in-oil structures. This suggests that water-insoluble alcohols make it possible for single- or double-chained low-molecular-weight onium salts to form inverted microemulsions in the organic phase of liquid–liquid phase-transfer catalytic reaction systems.

In this article, we demonstrate that water-insoluble alcohols are efficient solvents for phase-transfer catalysis of simple nucleophilic substitution reactions using several quaternary salt catalysts including single- and double-chained cationic surfactants. Furthermore, we show that the phase-transfer reactions proceed at considerable rates even in the absence of catalysts. A possible participation of an interfacial reaction step in these phase-transfer reactions is discussed.

Experimental

General Procedures. All of the solvents, quaternary ammonium salts, and inorganic reagents are commercially available guaranteed reagent grade. Deionized water was used throughout the experiment. Reaction mixtures were analyzed by GLC on a Hitachi Model 163 FID instrument with a 1 m column of SE-30 or PEG-20M at 170 °C. The concentration of anions in alcohol phase was measured by GLC in the following way. A sample of the alcohol layer was withdrawn, to which a prescribed amount of pentadecane and excess decyl methanesulfonate were added. The mixture was allowed to react at 90 °C. The final amount of 1-substituted-decane, which was formed through the reaction of the anion with decyl methanesulfonate, was analyzed. The concentration of water in the alcohol phase was measured by Karl–Fischer titration of a sample of the alcohol layer, using a Mitsubishi Kasei Automatic Titrator GT-06. Electric conductivity was measured with a Toa Denpa conductometer CM-15A.

Kinetics Run of the Phase-Transfer Reaction. The general procedure is as follows. A 50-ml culture tube with a Teflon®-lined screw cap was filled with 50 μmol of a catalyst, prescribed amounts of water and an inorganic reagent, and 2 ml of an alcohol containing pentadecane as an internal standard. The tube was placed in an oil bath maintained at 90 °C and the mixture was stirred for 30 min with a Teflon®-coated magnetic stirring bar, followed by injection of 70 μl of an organic substrate via a micropipette. Samples of the organic layer were withdrawn periodically with a microsyringe and the concentrations of the substrate and an yielding product were measured by GLC. The semilogarithmic plot of the fraction of unreacted substrate against time gave a straight line with a slope, from which the first-order rate constant was calculated. A control reaction without catalyst was done in the same way.

Results and Discussion

Phase-Transfer Reactions in the Absence of Catalysts. Water-insoluble alcohols were very good organic solvents for liquid–liquid phase transfer reactions. Some substitution reactions of 1-bromodecane with aqueous inorganic salts proceeded at considerable rates even in the absence of catalysts. In Table 1 are summarized the results for the reactions of 1-bromodecane with several aqueous potassium salts using cyclohexanol as a solvent. The decrease in 1-bromodecane followed psuedo first-order kinetics for all the reactions. The mass balance of the substrate and a product was excellent. Very fast reactions were observed particularly for iodide and thiocyanate ions. It was found that the cyclohexanol phase contained considerable amounts of reagent salts and water. Those concentrations, $[\mathrm{MX}]_{\mathrm{org}}$ and $[\mathrm{H_2O}]_{\mathrm{org}}$, are also listed in Table 1.

The rate of nucleophilic substitution reactions depended strongly on the structure of the solvent alcohol. Table 2 shows the influence of alcohol on the rate of the reaction between 1-bromodecane and aqueous potassium iodide. In cyclohexanol or benzyl alcohol, the rate of the reaction was very fast and the half-life of the reaction was only 7 min in benzyl alcohol, while nonpolar solvents such as toluene or octane had negligibly small rates. The first-order rate constant, k_{obsd}, was independent of the dielectric constant of the alcohol. Each alcohol contained some potassium iodide, which was extracted from the aqueous phase. The observed first-order rate constant, k_{obsd}, was approximately proportional to this iodide concentration, $[\mathrm{KI}]_{\mathrm{org}}$. This indicates that all the alcohols give a similar apparent second-order rate constant, k_2, if one calculates it from the first-order rate constant divided by the concentration of potassium iodide in the alcohol phase; $k_2=k_{\mathrm{obsd}}/[\mathrm{KI}]_{\mathrm{org}}$. The amount of water that was detected in the alcohol

Table 1. Phase-Transfer Nucleophilic Substitution Reactions of 1-Bromodecane with Inorganic Salts in Cyclohexanol[a)]

Inorganic Reagent MX	$\times 10^5 k_{\mathrm{obsd}}$ $\mathrm{s^{-1}}$	$[\mathrm{MX}]_{\mathrm{org}}$ $\mathrm{mmol\,dm^{-3}}$	$[\mathrm{H_2O}]_{\mathrm{org}}$ $\mathrm{mol\,dm^{-3}}$	$\times 10^3 k_2$ $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$
KCl	0.8	27	3.4	0.31
KOAc	5.0	560	1.7	0.089
KCN	12	24	3.5	5.1
KSCN	170	840	0.54	2.0
KI	150	240	3.2	6.6
NaCN	21	36	2.0	5.6

a) Reaction conditions: 1-bromodecane, 70 μl; inorganic reagent, 10 mmol for KCl, KSCN, and KI, 25 mmol for KOAc, KCN, and NaCN; cyclohexanol, 2 ml; water, 1.7 ml for KCl, 1.3 ml for KOAc, 2.0 ml for KCN, 1.5 ml for KSCN and NaCN, and 1.2 ml for KI; reaction temperature, 90 °C.

Table 2. The Effect of Alcohol on the Phase-Transfer Reaction of 1-Bromodecane with Potassium Iodide[a)]

Organic solvent	(ϵ_r[b)])	$\times 10^5 k_{\mathrm{obsd}}$ $\mathrm{s^{-1}}$	$[\mathrm{KI}]_{\mathrm{org}}$ $\mathrm{mmol\,dm^{-3}}$	$[\mathrm{H_2O}]_{\mathrm{org}}$ $\mathrm{mol\,dm^{-3}}$	$\times 10^3 k_2$ $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$
Benzyl alcohol	(13.1)	180	260	3.5	6.8
Cyclohexanol	(15.0)	170	240	3.2	6.6
2-Methyl-2-butanol	(5.82)	21	54	2.8	3.9
1-Octanol	(10.3)	17	39	1.5	4.3
2-Ethyl-1-hexanol	(4.41)	3.1	6.6	0.36	4.7
2,6-Dimethyl-4-heptanol	(—)	0.43	1.1	4.7	3.9
Chlorobenzene	(5.65)	≈0	—	—	—
Toluene	(2.24)	≈0	—	—	—
Octane	(1.95)	≈0	—	—	—

a) Reaction conditions: 1-bromodecane, 70 μl; KI, 10 mmol; organic solvent, 2 ml; water, 1.2 ml; reaction temperature, 90 °C. b) Dielectric constant of organic solvents.

phase did not correlate directly to the first-order rate constant. However, the molar ratio of water to potassium iodide in the alcohol phase, n_W/n_{KI}, was closely related to $[KI]_{org}$ as shown in Fig. 1.

With an increasing concentration of potasium iodide in the bulk aqueous phase, $[KI]_{aq}$, $[KI]_{org}$ was increased, accompanying an increase in the rate constant. On the other hand, the water concentration and n_W/n_{KI} were decreased with $[KI]_{aq}$ (Fig. 2). A similar tendency was observed for the reaction between 1-bromooctane and aqueous sodium cyanide (Fig. 3). With an increase in $[NaCN]_{aq}$, $[NaCN]_{org}$ and k_{obsd} increased while n_W/n_{NaCN} decreased, but the extent of the $[MX]_{aq}$ influence on $[MX]_{org}$ and k_{obsd} was different between the two reactions. It is noted that the ratio of n_W/n_{MX} is larger than the corresponding $(n_W/n_{MX})_{aq}$ of the bulk aqueous solution; the ratio is particularly high for sodium cyanide.

Phase-Transfer Reactions in the Presence of Onium Catalysts. Catalytic activities of cetyltrimethylammonium bromide (CTAB) for several phase-transfer nucleophilic substitutions are given in Table 3. The reactions were done using cyclohexanol as an organic solvent. All the reactions proceeded under clear two-phase conditions without an occurrence of emulsification. This is distinctly different from the cases using nonpolar aprotic solvents, which often form stable emulsions in the presence of CTAB. The pseudo first-order rate constant of the catalytic reaction, $(k_{obsd})_{cat}$, was considerably enlarged. This is obvious from the comparison with the results in Table 1. The difference between $(k_{obsd})_{cat}$ and k_{obsd} was divided by the concentration of CTAB in the alcohol phase and the apparent catalytic second-order rate constant, $(k_2)_{cat}$ was calculated. The $(k_2)_{cat}/k_2$ ratios are also given in Table 3. The harder the anion, the larger the ratio. This means that the catalytic efficiency of CTAB is larger for hard anions than for soft anions.

The first-order rate constant was increased almost linearly with an increasing amount of CTAB (Fig. 4).

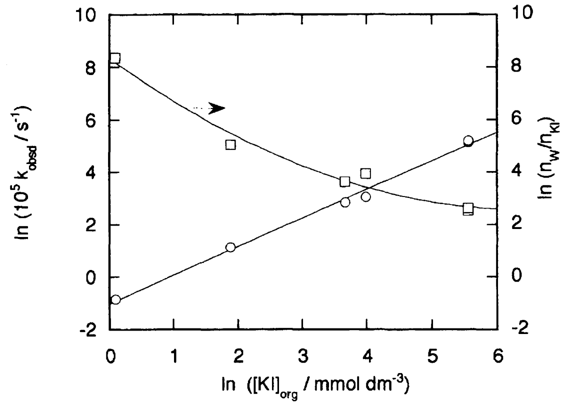

Fig. 1. The influences of $[KI]_{org}$ on k_{obsd} and n_W/n_{KI} for the reaction between 1-bromodecane and aqueous KI using various alcohols. (○), k_{obsd}; (□), n_W/n_{KI}.

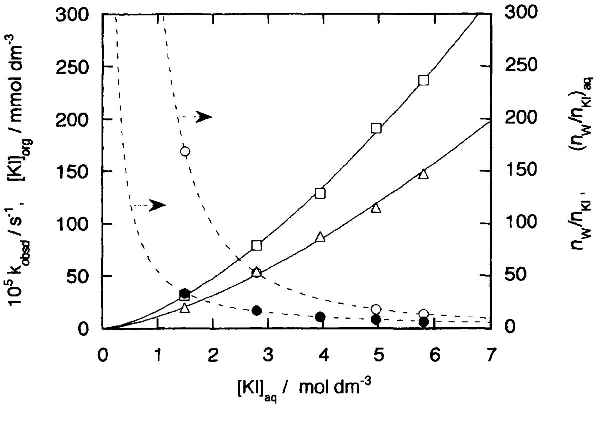

Fig. 2. The influences of $[KI]_{aq}$ on $[KI]_{org}$, k_{obsd}, and n_W/n_{KI} for the reaction between 1-bromodecane and aqueous KI using cyclohexanol as an organic solvent. (△), k_{obsd}; (□), $[KI]_{org}$; (○), n_W/n_{KI}; (●), $(n_W/n_{KI})_{aq}$, the molar ratio of water to KI in the bulk aqueous phase.

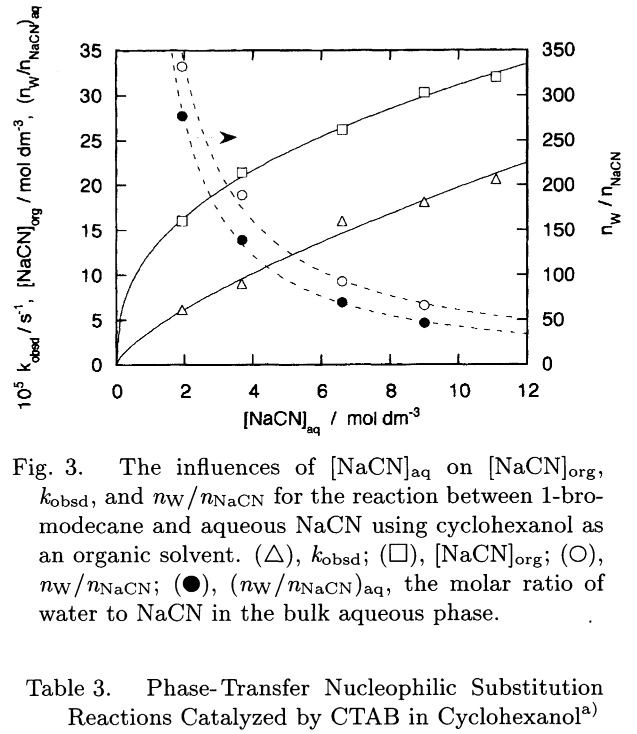

Fig. 3. The influences of $[NaCN]_{aq}$ on $[NaCN]_{org}$, k_{obsd}, and n_W/n_{NaCN} for the reaction between 1-bromodecane and aqueous NaCN using cyclohexanol as an organic solvent. (△), k_{obsd}; (□), $[NaCN]_{org}$; (○), n_W/n_{NaCN}; (●), $(n_W/n_{NaCN})_{aq}$, the molar ratio of water to NaCN in the bulk aqueous phase.

Table 3. Phase-Transfer Nucleophilic Substitution Reactions Catalyzed by CTAB in Cyclohexanol[a]

Inorganic reagent MX	$\times 10^5 (k_{obsd})_{cat}$ s^{-1}	$(k_2)_{cat}/k_2$
KCl	2.6	2.3
KOAc	11	29
KCN	43	2.4
KSCN	180	1.5
KI	200	1.8

a) Reaction conditions: CTAB, 50 μmol; 1-bromodecane, 70 μl; inorganic reagent, 10 mmol for KCl, KSCN, and KI, 25 mmol for KOAc, KCN, and NaCN; cyclohexanol, 2 ml; water, 1.7 ml for KCl, 1.3 ml for KOAc, 2.0 ml for KCN, 1.5 ml for KSCN and NaCN, and 1.2 ml for KI; reaction temperature, 90 °C.

This indicates the second-order rate constant, $(k_2)_{\mathrm{cat}}$, being independent of the CTAB concentration. This is also shown in Fig. 4. Those tendencies were quite the same as conventional phase-transfer catalysis using nonpolar solvents. On the addition of CTAB, the gain of the total concentration of anions in the alcohol phase was approximately equal to or slightly larger than the amount of added CTAB (Fig. 4). Within the experimental error, the concentration of water in the alcohol phase, $[H_2O]_{\mathrm{org}}$, was identical with the value that was obtained in the absence of CTAB. A linear increase in the reaction rate was also observed with the amount of benzyltributylphosphonium chloride (BTBPC), which is one of the most common phase-transfer catalysts. Figure 5 shows the results for the reaction between 1-bromodecane and aqueous sodium cyanide in cyclohexanol. The second-order rate constant of the catalytic reactions were identical irrespective of the BTBPC concentration.

Other quaternary salts also catalyzed the reaction of 1-bromodecane with sodium cyanide or potassium iodide, as shown in Tables 4 and 5. The catalytic effects were clearly observed for every onium salt, while anionic surfactants such as sodium dodecyl sulfate and sodium dodecylbenzenesulfonate had very little catalytic activity. It is noted again that, when water-insoluble alcohols were used as organic solvents, all of the reactions proceeded under clear two-phase conditions except a few reactions using catalysts, such as cationic ionomers, which formed a gel-like third phase with aqueous potassium iodide.

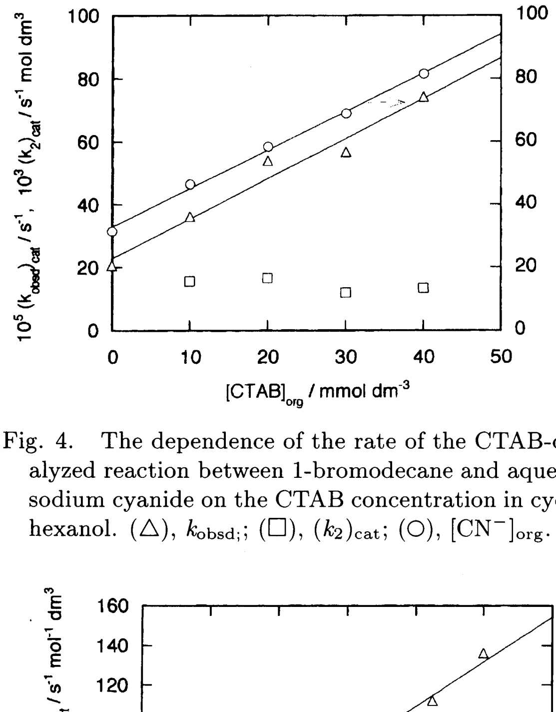

Fig. 4. The dependence of the rate of the CTAB-catalyzed reaction between 1-bromodecane and aqueous sodium cyanide on the CTAB concentration in cyclohexanol. (△), k_{obsd}; (□), $(k_2)_{\mathrm{cat}}$; (○), $[CN^-]_{\mathrm{org}}$.

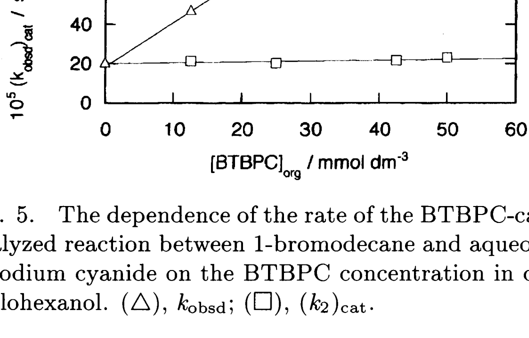

Fig. 5. The dependence of the rate of the BTBPC-catalyzed reaction between 1-bromodecane and aqueous sodium cyanide on the BTBPC concentration in cyclohexanol. (△), k_{obsd}; (□), $(k_2)_{\mathrm{cat}}$.

Reaction Mechanism. The conventional explanation of phase-transfer catalysis was an ion pair mechanism. The basic idea of this mechanism is that the lipophilic ion pairs, which are molecularly isolated from each other in the isotropic organic layer, are so little hydrated that they may easily react with organic substrate. All the results mentioned above might be explained even by this mechanism. (1) The rate of catalytic reactions was linearly proportional to the amount of catalyst: this linearity was the most fundamental basis of the ion pair mechanism. (2) The reactivity of anions and the catalytic efficiency depended on the kind and the structure of cationic counter parts, that is, onium ions and metal ions. (3) The apparent reactivity of an anion depended on the aqueous salt concentration. (4) The rate enhancement in the presence of catalysts tended to increase with the hardness of the reagent anion. All these results coincide accurately with those reported for many phase-transfer catalytic reactions using hydrocarbon solvents.

The distinct difference of our system from the conventional ones is the concentration of water in the organic phase. The weight percentage of water in the organic phase sometimes amounts to 10 wt% and the ratio of n_W/n_X is larger than that of the coexisting bulk aqueous phase, as already shown in Figs. 2 and 3. Furthermore, the organic phase is electrically conductive. Potassium bromide is sparingly soluble in cyclohexanol in the absence of water but an addition of water yields a homogeneous solution, which affords a moderate electric conductivity, as shown in Table 6. The presence of water also leads to a large increase in conductivity of the CTAB solution in cyclohexanol. Interestingly, further addition of potassium bromide to this solution did not increase the electric conductivity much. These results indicate the presence of free ions in the alcohol phase and, therefore, make the definition of ion pair ambiguous. If free ions were to take part in the catalysis, the reactivities of ion pairs and free ions should be equal because the rate constant was linearly proportional to the concentration of onium salts. However this is contradictory to the results (2); the rate constant of catalytic reactions is dependent on the onium structure. Furthermore it is unaccountable that anions are more reactive in the presence of CTAB, because cetyltrimethylammonium salts should dissociate more easily than

Table 4. Catalytic Efficiency of Amphiphiles for Nucleophilic Substitution Reactions of 1-Bromodecane with Sodium Cyanide in Cyclohexanol[a)]

Catalyst	$\times 10^5 (k_{\text{obsd}})_{\text{cat}}$	$\times 10^3 [(k_{\text{obsd}})_{\text{cat}} - k_{\text{obsd}}]/[\text{Amphiphile}]_{\text{org}}$
	s^{-1}	$\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$
None	21	—
DBSS	23	0.80
SDS	26	2.3
LA7.5DoCl	48	11
CTAB	57	15
TOMAC	63	17
LA20DoCl	67	19
BTBPC	71	20

a) Reaction conditions: amphiphile, 50 µmol; 1-bromodecane, 70 µl; NaCN 25 mmol; cyclohexanol, 2 ml; water, 1.5 ml; reaction temperature, 90 °C. DBSS, sodium dodecylbenzenesulfonate; SDS, sodium dodecylsulfate; LAxDoCl, linear polystyrene which contains benzyldimethyldodecylammonium chloride groups with x % of ring substitution; TOMAC, trioctylmethylammonium chloride.

Table 5. Catalytic Efficiency of Amphiphiles for Nucleophilic Substitution Reactions of 1-Bromodecane with Potassium Iodide in 2,6-Dimethyl-4-heptanol[a)]

Catalyst	$\times 10^5 (k_{\text{obsd}})_{\text{cat}}$	$\times 10^3 [(k_{\text{obsd}})_{\text{cat}} - k_{\text{obsd}}]/[\text{Amphiphile}]_{\text{org}}$
	s^{-1}	$\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$
None	0.43	—
LA10DoCl	12	
BMBAC	15	6.0
CTAB	30	12
CP17BuCl	32	13
BTBPC	46	18
DDAB	51	20
TOMAC	52	21

a) Reaction conditions: amphiphile, 50 µmol; 1-bromodecane, 70 µl; KI, 10 mmol; 2,6-dimethyl-4-heptanol, 2 ml; water, 1.2 ml; reaction temperature, 90 °C. BMBAC, benzylbutyldimethylammonium chloride; CP17BuCl, 1%-divinylbenzene-crosslinked polystyrene which contains benzyltributylphosphonium chloride groups with 17% ring substitution; DDAB, didodecyldimethylammonium bromide.

Table 6. Electric Conductance of Cyclohexanol/CTAB/NaBr aq System

System				Electric conductivity	Molar conductivity
Cyclohexanol	H_2O	NaBr	CTAB		
ml	ml	mmol	mmol	$\text{m}\Omega^{-1}\,\text{cm}^{-1}$	$\text{m}\Omega^{-1}\,\text{cm}^{-1}\text{M}^{-1}$
50	—	—	—	0.33	
50	5.0	—	—	0.12	
50	5.0	0.146	—	7.53	2.84
50	—		1.25	3.84	0.154
50	5.0	—	1.25	25.7	1.13
50	5.0	0.146	1.25	28.6	1.13
—	50	—	—	2.40	

metal salts in a medium owing to the larger size of the ammonium cations.

All the results may be explained more reasonably if we presume an interfacial reaction mechanism. It is known that alcohol/water interfacial tension is very low. In fact, the hexanol/CTAB/water system affords a one-phase region of water-in-oil microemulsion in the hexanol-rich region of the phase diagram,[23)] although the form of aggregation of CTAB has not been identified. Water microdroplets may be formed in the alcohol phase of our systems. When all the metal salts solubilized in the microemulsion are adsorbed selectively on

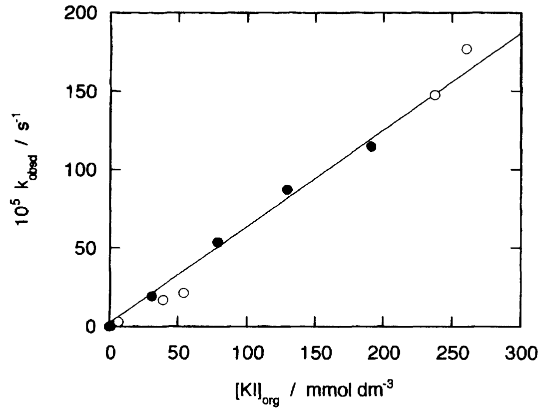

Fig. 6. The dependence of pseudo first-order rate constant on the concentration of inorganic salts in alcohol phase for the reaction between 1-bromodecane and aqueous potassium iodide. (○), k_{obsd} for various alcohol at the constant aqueous KI concentration of 5.8 mol dm^{-3}; (●), k_{obsd} in cyclohexanol at several aqueous KI concentrations.

the interface or when the adsorption sites are enough to accommodate all the solubilized metal salts, the rate of reaction depends linearly on the concentration of metal salts in the alcohol phase, $[MX]_{org}$. This may be the case for the reaction between 1-bromodecane and aqueous potassium iodide as shown in Fig. 6. The psuedo first-order rate constants were linearly dependent on the concentration of potassium iodide in the alcohol phase irrespective of n_W/n_X and the kind of the alcohols. Surface active onium salts may all be present at the interface in the form of ion pairs, leading to a linear increase in the rate constant with an increasing amount of the salts. But the rate constant should depend on the kind of counter cations. In fact, onium salts are more reactive than metal salts: $(k_2)_{cat}$ is larger than k_2. The reactivity of an anion also depends on the onium structure.

When metal salts are non-surface active and prefer to reside inside the water droplets, active species must be the ion pairs that are adsorbed on the interface. Since the number of the adsorbed ion pairs is assumed to be dependent on the MX concentration in the water droplets, the psuedo first-order rate constant is dependent not only on the concentration of metal salts in the alcohol phase but also on n_W/n_X in the alcohol phase. With an increasing concentration of metal salts in the bulk aqueous phase, $[MX]_{org}$ was increased accompanied by a decrease in n_W/n_X, leading to an increase in the first-order rate constant, as shown for the reaction between 1-bromodecane and sodium cyanide (Fig. 3). On the other hand, surface active cetyltrimethylammonium ions are selectively adsorbed on the interface irrespective of counter anions and, then, considerable amounts of the ammonium ions may be present in the form of ion pairs at the interface. Thus, the catalytic efficiency of CTAB is high for hard anions rather than soft anions and the rate enhancement is approximately proportional to the amount of the added CTAB. In this case, a moderate electric conductivity may be observed since the water pools may exchange their constituents with each other.

Our interfacial reaction mechanism may not always be applicable to all phase-transfer catalytic reactions. The importance of this work is the implication that molecularly-isolated ion pairs are not necessarily a definite active species of phase-transfer catalysis. The interfacial nucleophilic substitution has been proposed for other reaction systems.[24] The observed rate constant should be precisely proportional to the onium salt concentration in the organic phase, as far as the ratio of supposed active species remains constant regardless of the onium salt concentration. The linear dependence of the rate constant on the concentration of onium salts does not guarantee the ion pair mechanism. Dissociated ions, ion pairs, and aggregated forms of onium salts may all be candidates for the active species of the catalysis if the organic substrate is able to come into contact physically with these species. The real active species may be different from system to system that comprises organic solvent, amphiphilic onium catalyst, and aqueous inorganic salt. The extensive research to find other reaction systems that can be explained by the interfacial reaction mechanism is now in progress.

References

1) C. M. Starks and C. Liotta, "Phase Transfer Catalysis Principles and Techniques," Academic Press, New York (1978).

2) W. P. Weber and G. W. Gokel, "Phase Transfer Catalysis in Organic Synthesis," Springer-Verlag, Berlin (1977).

3) E. V. Dehmlow and S. S. Dehmlow, "Phase Transfer Catalysis," 2nd ed, Verlag Chemie, Weinheim (1983).

4) M. Makosza, *Pure Appl. Chem.*, **43**, 439 (1975).

5) A. Brandstrom, "Principles of Phase Transfer Catalysis by Quaternary Ammonium Salts," in "Adv. Phys. Org. Chem.," ed by V. Gold, Academic Press, New York (1977).

6) S. L. Regen, *Angew. Chem.*, **91**, 464 (1979).

7) P. Hodge and D. C. Sherrington, "Polymer-Supported Reactions in Organic Synthesis," John Wiley & Sons, New York (1980).

8) F. Montanari, D. Landini, and F. Rolla, *Top. Curr. Chem.*, **101**, 147 (1982).

9) N. K. Mathur, C. K. Narang, and R. E. Williams, "Polymers as Aids in Organic Chemistry," Academic Press, New York (1980).

10) W. T. Ford and M. Tomoi, *Adv. Polym. Sci.*, **55**, 49 (1984).

11) N. Ohtani, *J. Synth. Org. Chem., Jpn.*, **43**, 313 (1985).

12) C. M. Starks and R. M. Owens, *J. Am. Chem. Soc.*, **95**, 3613 (1973).

13) D. Landini, A. Maia, and F. Montanari, *J. Am. Chem. Soc.*, **100**, 2796 (1978); D. Landini, A. Maia, F. Montanari, and P. Tundo, *J. Am. Chem. Soc.*, **101**, 2526

(1979).

14) H. Molinari, F. Montanari, S. Quici, and P. Tundo, *J. Am. Chem. Soc.*, **101**, 3920 (1979).

15) N. Ohtani, C. A. Wilkie, A. Nigam, and S. L. Regen, *Macromolecules*, **14**, 516 (1981).

16) N. Ohtani and S. L. Regen, *Macromolecules*, **14**, 1594 (1981).

17) N. Ohtani, K. Chida, H. Serita, T. Matsunaga, and C. Kimura, *Bull. Chem. Soc. Jpn.*, **61**, 4371 (1988).

18) N. Ohtani, Y. Inoue, H. Mizouka, and K. Itoh, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 2589 (1994).

19) N. Ohtani, M. Nakaya, K. Shirahata, and T. Yamashita, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 2677 (1994).

20) N. Ohtani, Y. Inoue, A. Nomoto, and S. Ohta, *React. Polym.*, **24**, 73 (1994).

21) N. Ohtani, J. Mukudai, H. Mizuoka, and M. Kudo, "The Abstracts of the 5th International Conference on Polymer Supported Reactions in Organic Chemistry," Kyoto (1990), p.73.

22) D. F. Evans, D. J. Mitchell, and B. W. Ninham, *J. Phys. Chem.*, **90**, 2817 (1986).

23) G. Lindblom, B. Lindman, and L. Mandell, *J. Colloid Interface Sci.*, **34**, 262 (1970).

24) N. Tanaka, K. Hosoya, K. Iwaguchi, and M. Araki, *J. Am. Chem. Soc.*, **106**, 3057 (1984).