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Study of Phase Transfer Catalysis by Layered Scintillation Method

Taketoshi Hideshima,* Misao Morinaga,† and Hideo Kimizuka††
College of Arts and Sciences, Chiba University, Yayoi-cho, Chiba 260
† *Otsuka Chemical Co. Ltd., Naruto, Tokushima 772*
†† *Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812*
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The static and kinetic feature of the reaction of sodium cyanide with 1-bromoalkanes in the presence of various phase transfer catalysts was investigated in the oil/water system by using a layered scintillation method and the mechanism of catalytic action was discussed. From the measurement of equilibrium constants for both reactions of hexadecyltrimethylammonium cyanide with 1-bromooctane and of sodium cyanide with hexadecyltrimethylammonium bromide in organic phase, it was pointed out that the latter reaction was responsible for the advance of overall reaction. It was also found that majority of the phase transfer catalysts exist in the oil phase. It was suggested that an uptake reaction of cyanide ion from the aqueous phase at the interface is essential and that the reaction process does not follow a simple model proposed by Starks *et al.*

It is well known that the presence of a small quantity of phase transfer catalyst such as hexadecyltrimethylammonium bromide remarkably promotes the reaction of 1-bromooctane in the organic phase with sodium cyanide in the aqueous solution, although the reaction does not take place even after two weeks boiling in the absence of the catalyst. The mechanism of this reaction has been considered by Starks *et al.* as follows:[1)]

$$\begin{array}{lccccccc} \text{oil phase} & RCN & + & QBr & \rightleftarrows & RBr & + & QCN \\ & & & \downarrow & & & & \uparrow \\ \hline \text{aqueous phase} & NaCN & + & QBr & \rightleftarrows & NaBr & + & QCN \end{array}$$

where QBr denotes quaternary ammonium bromide. It has been postulated that the circulation of the catalyst between the two phases dominates. On the other hand, a few papers against this simple model have also been presented.[2—4)]

In the preceding papers,[5—8)] a new technique using liquid scintillation counter has been devised for the study of the interaction in the oil/water system. This method has been proved to be very useful for the direct measurement of the dynamic and static interaction including the interfacial accumulation as well as the oil-water partitioning of radioactive species.

In this paper, the application of this method to the reaction of various 1-bromoalkanes with sodium cyanide in the presence of the phase transfer catalysts is described from both views of kinetics and statics and the mechanisms of catalytic action is briefly discussed.

Experimental

The procedure for measurement was described elsewhere.[5,6)] The pH of the aqueous solution was adjusted at 9.0 with Menzel's buffer solution. The experiments were carried out at 20±1.5 °C except for the case otherwise described.

Materials. In this study, 1-bromobutane, 1-bromohexane, 1-bromooctane, 1-bromodecane, 1-bromododecane, 1-bromohexadecane, bromobenzene, and 1-bromonaphthalene were used as reagents in organic phase. In these, 1-bromooctane was purified by fractional distillation. Quaternary ammonium bromides used here as the phase transfer catalysts were tetramethylammonium bromide(Me_4NBr), tetraethylammonium bromide(Et_4NBr), tetraprorylammonium bromide(Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), trimethylvinylammonium bromide(Me_3VNBr), benzyltriethylammonium bromide($BeEt_3NBr$), hexadecyltrimethylammonium bromide(CTAB), ethyldimethylhexadecylammonium bromide($CEtMe_2NBr$), and hexadecylpyridinium bromide(CPydBr). Most of these reagents were commercial ones and were used without further purification unless otherwise stated. Radioactive sodium cyanide-^{14}C obtained from New England Nuclear was used as a nucleophilic agent for the displacement reaction, and it was diluted to a suitable specific activity 9.16 Ci/mol with nonradioactive sodium cyanide of guaranteed grade. Radioactive and nonradioactive hexadecyltrimethylammonium cyanide(CTACN) were prepared from CTAB by using anion exchange resin in the CN form. Radioactive [methyl-^{14}C] hexadecyltrimethylammonium bromide(CTAB-^{14}C) was purchased from The Radiochemical Center, England. 2,5-Diphenyloxazole (PPO) and 1,4-bis-(5-phenyloxazolyl)benzene (POPOP) obtained Packed Instrument Co., Ltd. were used as scintillators.

Procedure. *Layered Scintillation Method*: The scintillator solution without a reactant (ST) was prepared by dissolving 2 g PPO and 0.125 g POPOP into 1000 cm³ of a toluene solution containing 10 vol% 1-butanol. The scintillator solution with a reactant(ST(R)) was prepared by dissolving a given amount of bromoalkanes in ST.

First, 10 cm³ of ST(R) or ST was layered on 10 cm³ of the aqueous solution of cyanide ion labeled with ^{14}C, and the time course of increase in the amount of radioactive substance entering into the scintillator phase was measured by a liquid scintillation counter, Beckman LS-100.

After the reaction reached equilibrium, 0.5 cm³ of the aqueous solution and 5 cm³ of the scintillator solution were taken from each phase. The concentration of the radioactive substance in each phase was determined by the standardization procedure as follows; 0.5 cm³ of the radioactive aqueous solution was mixed with 5 cm³ of ST, 5 cm³ of ST(R) (or ST) and 10 cm³ of methanol. 5 cm³ of the scintillator solution was mixed with 0.5 cm³ of nonradioactive solution of cyanide ion having the same composition as the radioactive one, 5 cm³ of ST and 10 cm³ of methanol. Since the quenching efficiencies are the same for these standardized solutions, we can determine the partition coefficient of the total radioactive cyanide from the ratio of the counts of the two standardized solutions. The partition coefficients measured in this study were as follows:

$$1)\quad K_{CN} = \frac{[CN]_o}{[CN]_w} = \frac{[NaCN]_o + [QCN]_o}{[NaCN]_w + [QCN]_w}$$

(Partition coefficient of cyanide ions in the absence of a 1-bromoalkane and in the presence of the catalyst)

2) $$K^{\mathrm{R}}_{\mathrm{CN}} = \frac{[\mathrm{CN}]_{\mathrm{o}}+[\mathrm{RCN}]_{\mathrm{o}}}{[\mathrm{CN}]_{\mathrm{w}}} = \frac{[\mathrm{NaCN}]_{\mathrm{o}}+[\mathrm{QCN}]_{\mathrm{o}}+[\mathrm{RCN}]_{\mathrm{o}}}{[\mathrm{NaCN}]_{\mathrm{w}}+[\mathrm{QCN}]_{\mathrm{w}}}$$

(Partition coefficient of cyanide ions in the presence of a 1-bromoalkane and catalyst)

3) $$K^{\mathrm{R}}_{\mathrm{NaCN}} = \frac{[\mathrm{NaCN}]^{\mathrm{R}}_{\mathrm{o}}}{[\mathrm{NaCN}]_{\mathrm{w}}}$$

(Partition coefficient of sodium cyanide in the absence of catalyst and in the presence of a 1-bromoalkane)

4) $$K_{\mathrm{NaCN}} = \frac{[\mathrm{NaCN}]_{\mathrm{o}}}{[\mathrm{NaCN}]_{\mathrm{w}}}$$

(Partition coefficient of sodium cyanide in the absence of both the catalyst and a 1-bromoalkane)

5) $$K_{\mathrm{QCN}} = \frac{[\mathrm{QCN}]_{\mathrm{o}}}{[\mathrm{QCN}]_{\mathrm{w}}}$$

(Partition coefficient of CTACN in the absence of a 1-bromoalkane when QCN is used in place of the mixture of NaCN and QBr)

6) $$K^{\mathrm{R}}_{\mathrm{QCN}} = \frac{[\mathrm{QCN}]_{\mathrm{o}}+[\mathrm{RCN}]_{\mathrm{o}}}{[\mathrm{QCN}]_{\mathrm{w}}}$$

(Partition coefficient of CN in the presence of a 1-bromoalkane when QCN is used in place of the mixture of NaCN and QBr)

7) $$K_{\mathrm{Q}} = \frac{[\mathrm{Q}]_{\mathrm{o}}}{[\mathrm{Q}]_{\mathrm{w}}} = \frac{[\mathrm{QCN}]_{\mathrm{o}}+[\mathrm{QBr}]_{\mathrm{o}}}{[\mathrm{QCN}]_{\mathrm{w}}+[\mathrm{QBr}]_{\mathrm{w}}}$$

(Partition coefficient of Q^{+}-^{14}C)

In these equations the subscripts o and w, and superscript R refer to oil and aqueous phase and the reactant, respectively.

Potentiometric Measurement: The concentrations of bromide and sodium ions in the aqueous phase were potentiometrically measured by Horiba N-7 Ion Meter with the aid of the specific ion electrode for bromide and sodium ions of Activion Halstead and Horiba Ltd., respectively. In some instances, the concentration of cyanide ion was also measured with the cyanide ion electrode of Orion Research Inc.. The experimental conditions were the same as those in the layered scintillation method.

Results

Time Courses of Permeation of Hexadecyltrimethylammonium Ions and Cyanide Ions. The time course of the permeation of hexadecyltrimethylammonium ions from aqueous to organic phase without agitation is shown in Fig. 1. This figure indicates that the time courses of hexadecyltrimethylammonium entering into the organic phase of the systems with and without 1-bromooctane are almost the same and reach equilibrium within 2 h.

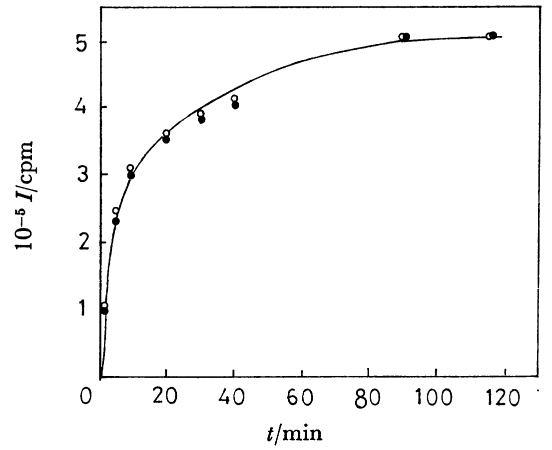

Fig. 1. Time courses of permeations of hexadecyltrimethylammonium ions into scintillator phase. ○: In the absence of 1-bromooctane, ●: in the presence of 115 mM 1-bromooctane. Initial concentration of CTAB is 0.1 mM.

On the other hand, the permeation of cyanide ions is much slower than that of hexadecyltrimethylammonium ions and it takes 20—30 h to reach equilibrium. The time course of increasing counting rate can be expressed by

$$I_\infty - I = I_\infty \exp(-kt) \qquad (1)$$

for the system without the displacement reaction of 1-bromoalkane and cyanide ion in the organic phase, while it becomes

$$I_\infty - I = I_{1\infty}\exp(-k_1t) + I_{2\infty}\exp(-k_2t) \qquad (2)$$

for the system with the displacement reaction, where I denotes the counting rate at a time t, I_∞, $I_{1\infty}$, and $I_{2\infty}$, those at an infinite time and k, k_1, and k_2, the rate constants.

The estimated values of rate constants are summarized in Table 1. In these rate constants, k_1 is thought to be the rate constant for the permeation of cyanide ion into the organic phase, since the value of k_1 is near to that of k for the system without the displacement reaction of 1-bromooctane and cyanide ion. Hence, k_2 may be refered to the rate constant for the displacement reaction in the organic phase. An agitation may cause the increase in k_1.

Partition Coefficients for Various Systems. Table 1 also shows the partition coefficients of cyanide ions

TABLE 1. PARTITION COEFFICIENTS OF CYANIDE IONS AND RATE CONSTANTS

Aqueous phase	NaCN* a)	NaCN*	NaCN* + CTAB	NaCN* + CTAB	CTACN*	CTACN*
Organic phase	—	$C_8H_{17}Br$	—	$C_8H_{17}Br$	—	$C_8H_{17}Br$
Partition coefficient	0.206 (K_{NaCN})	0.205 ($K^{\mathrm{R}}_{\mathrm{NaCN}}$)	0.207 (K_{CN})	0.478 ($K^{\mathrm{R}}_{\mathrm{CN}}$)	0.196 (K_{QCN})	0.568 ($K^{\mathrm{R}}_{\mathrm{QCN}}$)
Rate constant						
k or k_1/h^{-1}	0.360	0.350	0.358	0.304	0.336	0.308
k_2/h^{-1}	—	—	—	0.162	—	0.0240

a) The asterisk denotes the labeled compound with ^{14}C and initial concentrations of NaCN, CTAB, CTACN, and $C_8H_{17}Br$ are 0.1, 0.1, 0.11, and 115 mM, respectively.

in various systems. The partition coefficients of cyanide ions are small and independent of counter ions since $K_{CN} \simeq K_{NaCN} \simeq K_{QCN}$. It is also found that the direct displacement reaction of NaCN with 1-bromooctane does not take place in the absence of phase transfer catalyst since $K^R_{NaCN} = K_{CN}$. The occurrence of displacement reaction is indicated by the result, $K^R_{CN} > K_{CN}$, when the phase transfer catalyst CTAB is present. The use of CTACN in the place of the mixture of CTAB and NaCN in the aqueous phase leads to the advance of the displacement reaction in the organic phase to more extent ($K^R_{QCN} > K^R_{CN}$).

The partition coefficients of hexadecyltrimethylammonium ions, K_Q, are shown in Table 2. Since the partition coefficient of CTA$^+$ is larger than that of CN$^-$, it is evident that most of CTA$^+$ exist in the organic phase. The increase in the concentration of 1-bromooctane leads to the slight decrease of the partition of CTA$^+$, but in the lower concentration of 1-bromooctane the partition coefficients are the same as that in the absence of 1-bromooctane.

Tables 3 and 4 show the partition coefficients in the systems other than that of 1-bromooctane and CTAB. From these tables, it is found that alkyl bromide with carbon number less than 6 or more than 8, and aryl bromides were not catalyzed by the phase transfer catalysts used in this experiment. Table 3 also indicates that Me_4NBr, Me_3VNBr, $BeEt_3NBr$, and Bu_4NBr are not effective or almost noneffective in the catalytic action. As shown in Table 4, CTAB is effective only in the case of $C_8H_{17}Br$ while $CEtMe_2NBr$ and CPydBr cause the displacement reaction of cyanide with $C_6H_{13}Br$ and $C_8H_{17}Br$ and Et_4NBr, with $C_6H_{13}Br$. The rate constants for these systems are summarized in Table 5. As shown in this table, the time course obey the Eq. 2 except the systems of $C_6H_{13}Br$ with $CEtMe_2NBr$ or Et_4NBr which have smaller partition coefficients than other systems in this table.

Table 2. Partition coefficient of hexadecyltrimethylammonium ions

$[C_8H_{17}Br]$/mM	0	57.5	115	287	574
Partition coefficient	15.4	15.3	15.9	14.0	12.4

Initial consentration of CTAB-^{14}C is 0.1 mM.

Formation Constant. The partition coefficient of cyanide ions increases with the increase in the initial concentration of 1-bromooctane as shown in Fig. 2. Let us define the formation constant of alkanenitrile in the organic phase as

$$K^{\circ}_{f(RCN)} = \frac{[QBr]_o[RCN]_o}{[QCN]_o[RBr]_o}. \tag{3}$$

Rearranging Eq. 3 we have

$$\begin{aligned}[RCN]_o &= K^{\circ}_{f(RCN)}[RBr]_o[QCN]_o/[QBr]_o \\ &= K^{\circ}_{f(RCN)}([R]_T-[RCN]_o)[QCN]_o/[QBr]_o,\end{aligned} \tag{4}$$

where $[R]_T$ is the total concentration of alkyl group.

In the system using CTACN in place of the mixture of NaCN and CTAB, the total concentration of Q, $[Q]_T$, is given as follows:

$$[Q]_T = [QCN]_o(1+K^{-1}_{QCN})+[QBr]_o(1+K^{-1}_{QBr}). \tag{5}$$

Then,

$$\begin{aligned}[QBr]_o &= \{[Q]_T - [QCN]_o(1+K^{-1}_{QCN})\}/(1+K^{-1}_{QBr}) \\ &= \{[CN]_T - [QCN]_o(1+K^{-1}_{QCN})\}/(1+K^{-1}_{QBr})\end{aligned} \tag{6}$$

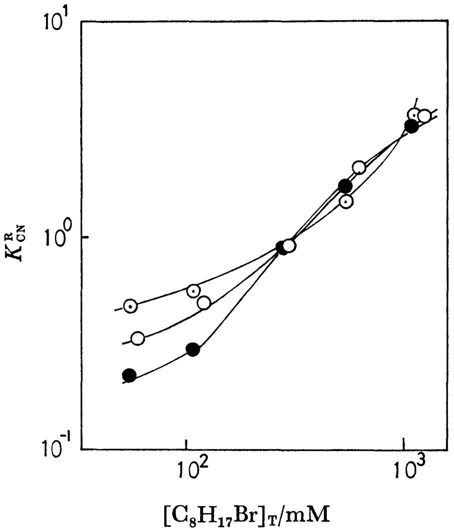

Fig. 2. Plot of partition coefficient *vs.* concentration of 1-bromooctane in the presence of QBr.
○: CTAB, ●: $CEtMe_2NBr$, ⊙: CPydBr. Initial concentrations of NaCN and QBr are all 0.1 mM.

Table 3. Partition coefficients of CN in various systems (1)

R	[RBr]/mM	Partition coefficient				
		Pr_4NBr	Bu_4NBr	Me_4NBr	Me_3VNBr	$BeEt_3NBr$
	0	0.164	0.172	0.190	0.180	0.207
C_4H_9	234	0.155	0.186	0.178	0.155	0.172
C_6H_{13}	236	0.128	0.189	0.190	0.177	0.192
C_8H_{17}	287	0.233	0.277	0.235	0.157	0.174
$C_{10}H_{21}$	242	0.127	0.153	0.167	0.177	0.180
$C_{12}H_{25}$	200	0.135	0.192	0.184	0.169	0.184
$C_{16}H_{33}$	218	0.150	0.278	0.181	0.209	0.214
C_6H_5	239	0.143	0.190	0.200	0.210	0.204
$C_{10}H_7$	238	0.129	0.196	0.182	0.208	0.208

Initial concentrations of NaCN and QBr are all 0.1 mM.

Table 4. Partition coefficients of CN in various systems (2)

R	[RBr]/mM	Partition coefficient			
		CTAB	$CEtMe_2NBr$	CPydBr	Et_4NBr
	0	0.207	0.204	0.293	0.143
C_4H_9	234	0.144	0.196	0.360	0.153
C_6H_{13}	236	0.166	0.716	0.872	0.663
C_8H_{17}	287	0.892	0.870	0.889	0.153
$C_{10}H_{21}$	242	0.138	0.223	0.357	0.155
$C_{12}H_{25}$	200	0.205	0.201	0.362	0.143
$C_{16}H_{33}$	218	0.240	0.301	0.396	0.158
C_6H_5	239	0.139	0.214	0.347	0.233
$C_{10}H_7$	238	0.139	0.214	0.347	0.250

Initial concentrations of NaCN and QBr are all 0.1 mM.

Table 5. The rate constants for systems with the displacement reaction

RBr	Catalyst	k_1/h^{-1}	k_2/h^{-1}
$C_6H_{13}Br$	$CEtMe_2NBr$	0.116	—
$C_8H_{17}Br$	$CEtMe_2NBr$	0.086	0.0082
$C_6H_{13}Br$	CPydBr	0.120	0.0104
$C_8H_{17}Br$	CpydBr	0.141	0.0097
$C_6H_{13}Br$	Et_4NBr	0.128	—

The experimental conditions are the same as those of Table 4.

where $[CN]_T$ is the total concentration of CN. In obtaining Eq. 6 the initial condition, $[CN]_T = [Q]_T$, is used. On the other hand, we derive from the equations for K_{QCN} and K^R_{QCN}

$$[RCN]_o = \frac{K^R_{QCN} - K_{QCN}}{K_{QCN}}[QCN]_o = \frac{K^R_{QCN} - K_{QCN}}{1 + K^R_{QCN}}[CN]_T \tag{7}$$

and hence, from Eqs. 6 and 7, we obtain

$$(1 + K^{-1}_{QBr})[QBr]_o = [QCN]_o(K^R_{QCN} - K_{QCN})/K_{QCN}. \tag{8}$$

Combining Eqs. 4, 7, and 8 gives

$$\frac{[R]_T}{[CN]_T} \cdot \frac{1 + K^R_{QCN}}{K^R_{QCN} - K_{QCN}} - 1 = \frac{K^R_{QCN} - K_{QCN}}{K^\circ_{f(RCN)} K_{QCN}(1 + K^{-1}_{QBr})}. \tag{9}$$

Figure 3 shows the plots for the system of CTACN and 1-bromooctane according to Eq. 9, from which the values of $K^\circ_{f(RCN)}$ are found to be 9.34×10^{-4} at 20 °C and 1.46×10^{-1} at 28 °C, and corresponding free energy, ΔG, 17.0 and 0.48 K J/mol, respectively.

We also estimated an equilibrium constant for the formation of QCN in the organic phase defined as

$$K^\circ_{f(QCN)} = \frac{[NaBr]_o[QCN]_o}{[NaCN]_o[QBr]_o}. \tag{10}$$

This value can be estimated with the aid of following equations by measuring the concentrations of cyanide, bromide and sodium ion in each phase for the system of NaCN and CTAB without RBr

$$[CN]_o = [NaCN]_o + [QCN]_o \tag{11}$$

$$[Br]_o = [NaBr]_o + [QBr]_o \tag{12}$$

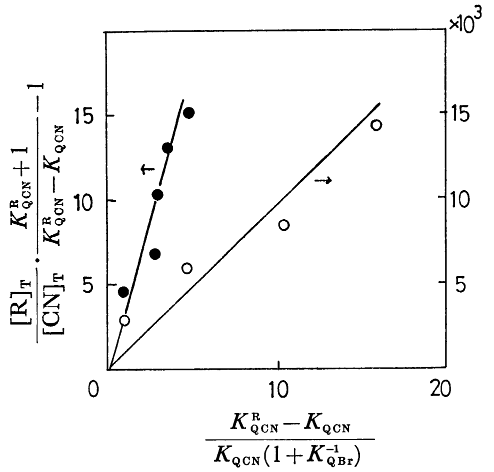

Fig. 3. Plot of Eq. 9 for the system of CTACN and 1-bromooctane.
○: 20 °C, ●: 28 °C. Initial concentration of CTACN is 0.1 mM at 20 °C and 1 mM at 28 °C.

$$[Na]_o = [NaCN]_o + [NaBr]_o \tag{13}$$

and

$$[NaCN]_o(1 + K^{-1}_{NaCN}) = [QBr]_o(1 + K^{-1}_{QBr}). \tag{14}$$

From the results of potentiometric measurement, the value of $K^\circ_{f(QCN)}$ for hexadecyltrimethylammonium cyanide was found to be 75 at 28 °C ($\Delta G = -10.8$ K J/mol).

Discussion

Consider the displacement reaction of sodium cyanide with 1-bromooctane occurring in the presence of CTAB. There are four species in the aqueous phase, NaCN, NaBr, QCN, and QBr, which permeate into the organic phase. Majority of CTA^+ ions exists in the organic phase at the equilibrium (Table 3), while the partition coefficient of cyanide ions is small compared to K_Q (Tables 1 and 2). Consequently it is thought that CTA^+ in the aqueous phase permeate into the organic phase mainly in the form of CTAB. Furthermore, as shown in Fig. 1, the permeation rate of CTA^+ into the organic phase is so large that the amount of CTA^+ in the organic phase are saturated rapidly. The mode of permeation does not change even in the presence of 1-bromooctane in the organic phase. On the other hand, the permeation of cyanide ions into the organic phase is much slower than that of CTA^+ and hence we may consider the ionic exchange reaction of CN^- by Br^- at the interface as the counter ion of CTA^+ as was suggested by Makosza *et al.*[2] We have two rate constants for the system with the displacement reaction of 1-bromooctane and CN^- and they are attributed to the permeation of CN^- into the organic phase and the displacement reaction in the organic phase respectively. From these facts, we may conclude that the catalytic action of CTA^+ would proceed rather in the organic phase and not by the circulation between the aqueous and organic phase.

The free energy change for the displacement reaction of 1-bromooctane and CTACN is positive, and hence it is thermodynamically impossible that this reaction proceed independently. But this reaction may proceed by utilyzing the negative free energy for the displacement reaction between NaCN and CTAB at normal temperature. The free energy change for the overall reaction of NaCN and 1-bromooctane in the presence of CTAB is estimated to be −10.3 kJ/mol at 28 °C, which shows the possibility of the advance of the overall reaction. However, we may consider that the increase in temperature puts forward the displacement reaction of CTACN with 1-bromooctane from the fact that the value of $K^{\circ}_{f(RCN)}$ at 28 °C is larger than that at 20 °C.

The direct reaction of NaCN and 1-bromooctane seems not to advance because of very small reaction rate (Table 1). According to Starks *et al.*, the increase in the ionic radius of cation lowers the activation energy for the displacement reaction.$^{9)}$ Changing Na^+ to CTA^+ may be essential for the acceleration of displacement reaction.

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