Iodine- or Iodine Monobromide-Catalyzed Alkoxy-Alkoxy Exchange Reactions of Alkylalkoxysilanes: Formation of the Catalyst-Alkoxysilane Complexes and the Reaction Mechanism

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The formation of charge-transfer complexes of iodine and of iodine monobromide with alcohols and alkoxysilanes has been established spectroscopically, and the formation constants of iodine-ethoxytriethylsilane and iodine-diethoxydimethylsilane complexes has been determined as 0.55±0.01 and 0.61±0.02, respectively. On the basis of these observations and the kinetic information recently reported, the previously proposed mechanism for the iodine or iodine monobromide catalyzed alkoxy-alkoxy exchange reactions of alkoxysilanes is discussed afresh. It has been confirmed that a mechanism involving a four-centered transition state containing a CT-complex is most favorable.

In our previous work we disclosed that halogens and interhalogen compounds were extremely favorable catalysts for quantitative studies of the alcoholysis and redistribution reactions of alkoxysilanes.[1,2] These catalysts accelerate the alkoxy-alkoxy exchange reactions at ordinary temperature without any by-products, unlike conventional catalysts such as various acids and bases.

Among these catalysts, iodine and iodine monobromide that are easier to handle than others were preferred for the determination of alcoholysis and redistribution equilibrium constants, and the extensive data at 20 °C and 40 °C could be successfully observed.[1,2]

Since only a few redistribution equilibria have so far been examined at 150 °C[3,4] and 120 °C[5] in the absence of a catalyst and no alcoholysis equilibria have been examined, halogens and interhalogen compounds may be the first catalysts to make it possible to investigate these equilibria quantitatively at ordinary temperature.

A kinetic study on the following iodine-catalyzed alcoholysis was undertaken, in order to ascertain the catalytic activity of iodine quantitatively and to provide information about the mechanism of the reaction, $Et_3SiOBu^n+Bu^sOH \rightleftarrows Et_3SiOBu^s+Bu^nOH$ Both forward and reverse reactions were of first order with respect to butoxysilane, to butanol and also to iodine.[7]

Hologens and interhalogen compounds are expected to form charge-transfer complexes (CT-complexes) with alkoxysilanes as well as alcohols,[6] and the present reactions have been assumed to proceed via four-centered transition states containing such CT-complexes as intermediates.

To confirm the formation of these CT-complexes, we have now made spectrophotometric studies of iodine and iodine monobromide solutions in various alkoxysilanes, and determined the formation constants of iodine complexes with ethoxytriethylsilane and with diethoxydimethylsilane. Based on the results obtained here and of the kinetic studies mentioned above, the reaction mechanism previously proposed has been confirmed.

Results and Discussion

Studies on Alkoxy-Alkoxy Exchange Equilibria of Alkoxysianes. The following two iodine-catalyzed alcoholysis and three iodine monobromide-catalyzed redistribution equilibria of alkylalkoxysilanes were examined at 20 °C, and the equilibrium constants K were evaluated from the equilibrium compositions determined by gas chromatographic analysis.

No. 1

$$Et_3SiOBu^n+Bu^sOH \rightleftarrows Et_3SiOBu^s+Bu^nOH \ (I_2)$$

$$K=\{[Et_3SiOBu^s][Bu^nOH]\}/\{[Et_3SiOBu^n][Bu^sOH]\}$$

No. 2

$$Me_2Si(OPr^n)_2+2Bu^nOH \rightleftarrows Me_2Si(OBu^n)_2+2Pr^nOH \ (I_2)$$

$$K_1=\{[Me_2Si(OPr^n)(OBu^n)][Pr^nOH]\}/\{[Me_2Si(OPr^n)_2][Bu^nOH]\}$$

$$K_2=\{[Me_2Si(OBu^n)_2][Pr^nOH]\}/\{[Me_2Si(OPr^n)(OBu^n)][Bu^nOH]\}$$

No. 3

$$Me_2Si(OEt)_2+Me_2Si(OPr^n)_2 \rightleftarrows 2Me_2Si(OEt)(OPr^n)$$

(IBr, in hexane solution)

$$K=[Me_2Si(OEt)(OPr^n)]^2/\{[Me_2Si(OEt)_2][Me_2Si(OPr^n)_2]\}$$

Nos. 4 and 5

$$R_2Si(OEt)_2+Et_3SiOR' \rightleftarrows R_2Si(OEt)(OR')+Et_3SiOEt$$

$$R_2Si(OEt)(OR')+Et_3SiOR' \rightleftarrows R_2Si(OR')_2+Et_3SiOEt \ (IBr)$$

$$R_2Si(OEt)_2+R_2Si(OR')_2 \rightleftarrows 2R_2Si(OEt)(OR')$$

$$K_1=\{[R_2Si(OEt)(OR')][Et_3SiOEt]\}/\{[R_2Si(OEt)_2][Et_3SiOR']\}$$

$$K_2=\{[R_2Si(OR')_2][Et_3SiOEt]\}/\{[R_2Si(OEt)(OR')][Et_3SiOR']\}$$

$$K_3=[R_2Si(OEt)(OR')]^2/\{[R_2Si(OEt)_2][R_2Si(OR')_2]\}$$

R=Et, R′=Pr^n (No. 4); R=Me, R′=Bu^n (No. 5)

In each of the Nos. 1, 2, and 3 reactions, equilibrium was approached from both directions. As for reaction No. 4 and 5, however, the following four processes were examined (A, B, C, and D-series).

A-series $R_2Si(OEt)_2+Et_3SiOR' \longrightarrow$
B-series $R_2Si(OEt)(OR')+Et_3SiOEt \longrightarrow$
C-series $R_2Si(OEt)(OR')+Et_3SiOR' \longrightarrow$
D-series $R_2Si(OR')_2+Et_3SiOEt \longrightarrow$

The results are summarized in Table 1.

Each reaction reached equilibrium within several hours at 20 °C without formation of any by-products, and equilibrium constants obtained from both directions agreed well with each other.

Catalytic Action of Iodine or Iodine Monobromide and of Conventional Catalysts. Various acids and bases have so far been used to promote alkoxy-alkoxy exchange reactions. As acid catalysts, *p*-toluenesulfonic acid[8,9] and others[10-14] are employed, while base catalysts such as sodium or sodium alkoxides[8,10,15-20] are most frequently utilized.

Catalyses of such acids and bases were examined by tracing the following reaction by means of gas-liquid partition chromatography (GLC). $Et_3SiOBu^n+Bu^sOH \rightleftarrows Et_3SiOBu^s+Bu^nOH$

Sodium exhibited little activity to this alcoholysis at ordinary temperature and reflux was required to cause the reaction to proceed.

A sample of one hour heating indicated little progress of the reaction, while a sample of thirty hours heating contained larger quantities of the products, along with fairly large amounts of impurities, especially the condensate $(Et_3Si)_2O$.

In general, acids promote alcoholysis more significantly than bases, but they also accelerate the condensation of alkoxysilanes markedly, if water coexists even slightly.[21,22] For example, *p*-toluenesulfonic acid (monohydrate) promoted the reaction appreciably at ordinary temperature, but a fair amount of condensed compound and other impurities were always formed. Trifluoroacetic acid[14] accelerated the reaction remarkably, but even in this case the concentration of the condensed compound increased with the lapse of time.

Halogen and interhalogen compounds such as iodine and iodine monobromide are favorable catalysts as mentioned above. Iodine monobromide is more active than iodine, and is well suited for promotion of the redistribution reactions and the alcoholyses associated with tertiary alcohols. Iodine is conveniently used in other alcoholyses.

Consequently, they are especially favorable catalysts for the quantitative work on the alkoxy-alkoxy exchange reactions of alkoxysilanes.

Absorption Spectra of Iodine or Iodine Monobromide Solutions in Alkoxysilanes or Disiloxanes. Since iodine and iodine monobromide exhibit excellent catalytic action in the present reactions, it is expected that specific interactions must occur between these catalysts and the alkoxysilanes.

Iodine and iodine monobromide appear to form CT-complexes with alkoxysilanes, and it can reasonably be assumed that these CT-complexes facilitate the reactions.

However little is known concerning the formation of such molecular complexes, except for the following spectroscopic study on the solvation of iodine. A solution of iodine in octamethylcyclotetrasiloxane $(Me_2SiO)_4$ is reddish violet, and the absorption maximum λ_{max} is observed at 518 nm. A solution in tetraethoxysilane is brown, having the λ_{max} at 475 nm.[23] This blue shift in the absorption spectrum may be attributed to the formation of a CT-complex in the latter solution.[28]

Iodine or iodine monobromide was dissolved in various alkoxysilanes and disiloxanes, and the λ_{max} values of these solutions were determined in order to see if CT-complexes were formed.

Table 1. Alcoholysis and Redistribution Equilibrium Constants of Alkylalkoxysilanes at 20 °C

Reaction system	Equilibrium constant: Forward reaction	Reverse reaction	Mean value
No. 1	K =0.45±0.02	0.44±0.02	0.45±0.02
No. 2	K_1=2.05±0.01	2.04±0.03	2.04±0.02
	K_2=0.48±0.01	0.47±0.01	0.48±0.01
No. 3	K = 4.1±0.1	4.0±0.1	4.0±0.1

Reaction system	Equilibrium constant: A-series	B-series	C-series	D-series	Mean value
No. 4	K_1=1.90±0.02	1.92±0.01	1.90±0.01	1.90±0.01	1.91±0.02
	K_2=0.48±0.01	0.48±0.01	0.49±0.01	0.48±0.01	0.48±0.01
	K_3= 4.0±0.1	4.0±0.1	3.9±0.1	3.9±0.1	4.0±0.1
No. 5	K_1=1.90±0.02	1.91±0.02	1.90±0.06	1.89±0.01	1.90±0.02
	K_2=0.49±0.01	0.50±0.01	0.49±0.01	0.49±0.01	0.49±0.01
	K_3= 3.9±0.1	3.8±0.1	3.9±0.1	3.9±0.1	3.9±0.01

Absorption spectra of four disiloxane solutions of iodine were measured, and the absorption maxima were observed as follows.

$(Me_3Si)_2O$: 517—518 nm

$(Me_2EtSi)_2O$, $(MeEt_2Si)_2O$, $(Et_3Si)_2O$: 520 nm

The solutions are reddish violet and the λ_{max} values are around 520 nm similarly to the value in $(Me_2SiO)_4$ solution. A linear plot passing through the origin was always found between the absorbance at λ_{max} and iodine concentration in each solution, suggesting no interaction between iodine and disiloxane.

The λ_{max} in the visible region of the iodine or iodine monobromide spectrum in non-polar solvents is around 520 nm (I_2) or 490—500 nm (IBr). On the other hand, the λ_{max} values of alkoxysilane solutions were at 474—500 nm (I_2) or 425—455 nm (IBr), indicating blue shifts, and new peaks were also observed in the ultraviolet region. These results prove the formation of CT-complexes between iodine or iodine monobromide and alkoxysilanes.

Table 2. Wavelength of Absorption Peaks Observed on the Solutions of Iodine or Iodine Monobromide in Alkoxysilanes (λ_{max}/nm in ultraviolet and visible regions)

Alkoxysilane	λ_{max}/nm (I_2 solution)		λ_{max}/nm (IBr solution)	
	UV	Visible	UV	Visible
$Me_2Si(OEt)_2$	228	474	229	428
$Me_2Si(OEt)(Opr^n)$	243	474	244	428
$Me_2Si(OPr^n)_2$	233	478	238	428
$Me_2Si(OEt)(OBu^n)$	228	475	234	428
$Me_2Si(OBu^n)_2$	225	475	225	430
$Me_2Si(OEt)(OBu^s)$	230	482	223	430
$Me_2Si(OBu^s)_2$	237	492	218	436
$Me_2Si(OEt)(OBu^i)$	238	482	229	429
$Me_2Si(OBu^i)_2$	240	475	230	435
Et_3SiOEt	238	475	228	425
Et_3SiOPr^n	238	490	226	450
Et_3SiOBu^n	229	495	224	425
Et_3SiOBu^s	233	498	225	445
Et_3SiOBu^i	238	490	233	455

The observed absorption maxima are given in Table 2.

In general, the peaks in the visible region are gently sloping, and some peaks are shifted a little with change of concentration.

Formation Constants of Iodine-Ethoxytriethylsilane and Iodine-Diethoxydimethylsilane Complexes. As iodine-alkoxysilane complexes have absorption maxima at about 262 nm in carbon tetrachloride solutions, as shown in Fig. 1 and 2, the absorbances were measured at several wavelengths around the λ_{max} at about 22 °C.

Formation constants K_f were evaluated by employing the approximate equation developed by Ketelaar et al.[25]

$$C_I/(A-A_0)=1/\{(\varepsilon_C-\varepsilon_I)K_f\cdot C_D\}+1/(\varepsilon_C-\varepsilon_I)$$

where

A : Observed absorbance of the sample solution.

A_0 : Absorbance of I_2-CCl_4 solution.

C_I : Initial concentration of iodine.

C_D: Initial concentration of the alkoxysilane.

ε_C : Molar extinction coefficient of the complex.

ε_I : Molar extinction coefficient of iodine.

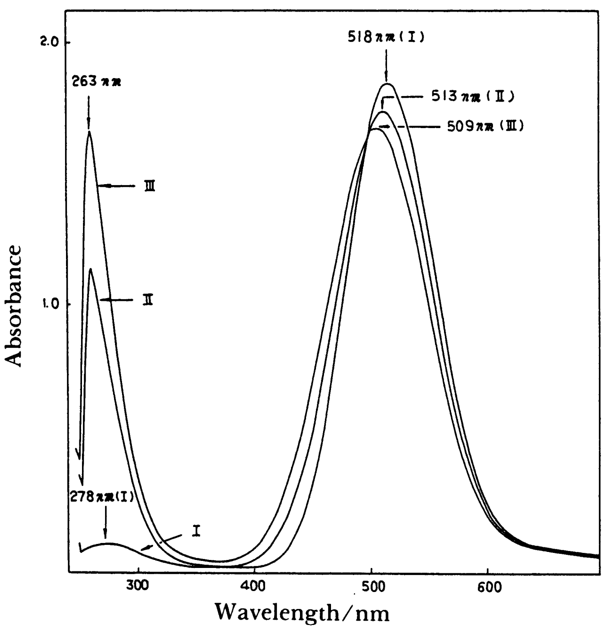


Fig. 1. The absorption spectra of the solutions I, II, III. I: iodine in carbon tetrachloride, II, III: ethoxytriethylsilane and iodine in carbon tetrachloride, $[I_2]=2\times10^{-3}$ mol dm^{-3}, $[Et_3SiOEt]=0.57$ (II), 1.01 (III) mol dm^{-3}.

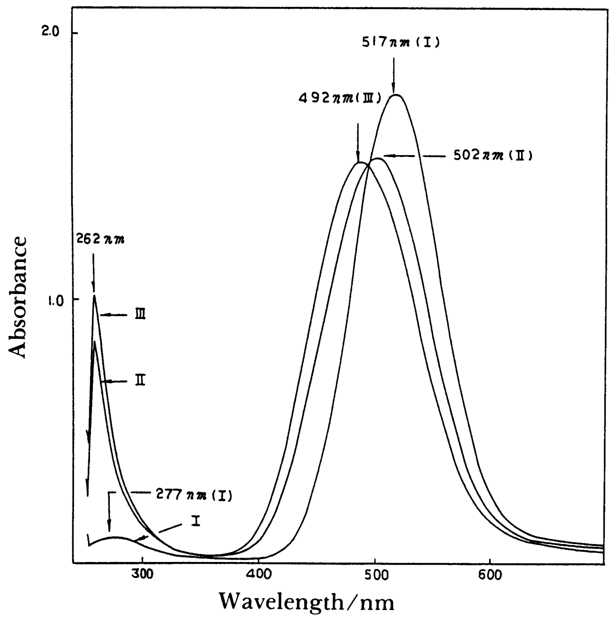


Fig. 2. The absorption spectra of the solutions I, II, III. I: iodine in carbon tetrachloride, II, III: diethoxydimethylsilane and iodine in carbon tetrachloride, $[I_2]=2\times10^{-3}$ mol dm^{-3}, $[Me_2Si(OEt)_2]=$ 1.13 (II), 2.10 (III) mol dm^{-3}.

This equation is derived with the approximation $C_D - C_C \fallingdotseq C_D$, as the complex concentration in which C_C is negligibly small compared to C_D under the operating conditions of $C_D \gg C_I$. The conditions of the present experiments satisfy the above approximation, because C_D/C_I is 50—200 (I_2-Et_3SiOEt-CCl_4 solutions) or 80—200 (I_2-$Me_2Si(OEt)_2$-CCl_4 solutions).

Typical examples of the results are illustrated in Fig. 3, and the formation constant of each complex was evaluated as follows.

$K_f = 0.55 \pm 0.01$

(I_2-Et_3SiOEt complex in CCl_4 solutions).

$K_f = 0.61 \pm 0.02$

(I_2-$Me_2Si(OEt)_2$ complex in CCl_4 solutions).

These are intermediate values between $K_f = 0.92$ (20 °C) of iodine-ethanol complex in heptane solution[6] and $K_f = 0.176$ (25 °C) of iodine-benzene complex in carbon tetrachloride solution.[26]

An alkoxysilane acts as a n-donor toward iodine, but the stability of this CT-complex seems to be lower than the iodine-ethanol complex, because of the smaller polarity of alkoxysilane than that of ethanol. This complex appears to be more stable than the iodine complex of benzene which is a π-donor. Consequently, the formation constants observed here may be regarded as reasonable.

Reconsideration of the Reaction Mechanism

The catalytic action of iodine or iodine monobromide was interpreted by a mechanism which involves a four-centered transition state containing a catalyst-alkoxysilane or alcohol CT-complex as an intermediate, as previously proposed.[1,2]

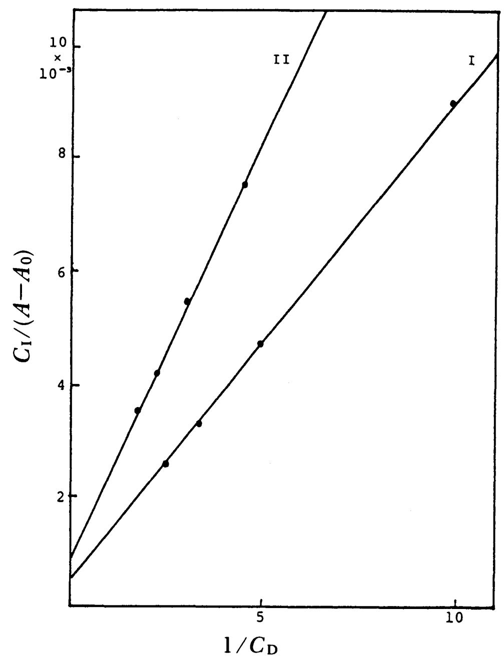


Fig. 3. Application to the Ketelaar's equation. Typical examples of plots of $C_I/(A-A_0)$ vs. $1/C_D$. I: I_2-Et_3SiOEt complex $K_f = 0.55$, II: I_2-$Me_2Si(OEt)_2$ complex $K_f = 0.61$.

Based on the results of the present spectroscopic work and the previously reported kinetic study on the alcoholysis,[7] together with the extensive work on the alkoxy-alkoxy exchange equilibria,[1,2] this mechanism is considered afresh.

Iodine and iodine monobromide promote both the alcoholysis and redistribution reaction of alkoxysilanes, with the latter catalyst being the more active. Therefore, it is proposed that in such a mechanism iodine and iodine monobromide promote both reactions in a similar manner, unlike the conventional mechanisms of base- or acid-catalyzed alcoholyses which can not apply to the redistribution reactions.

The mechanism should also satisfy the following requirements together with the above essential need.

(a) Iodine monobromide is more active than iodine.

(b) Alcoholyses proceed more rapidly than redistribution reactions in the presence of these catalysts.

(c) The reaction would be a bimolecular process, because the reaction is first order in both components at a constant catalyst concentration.

(d) The mechanism must proceed by a pathway via the transition state containing a catalyst molecule, as the reaction rate is first order with respect to the catalyst.

(e) The transition state should be of ionic character, because the rate constants of the alcoholysis increase with increasing alcohol contents, that is, with increasing polarity of the reaction mixture.

(f) The polarized transition state is also inferred from the large lowering of the activation entropy.

(g) Since alcohols as well as alkoxysilanes can form CT-complexes with iodine or iodine monobromide, such complexes should be used to form the transition state.

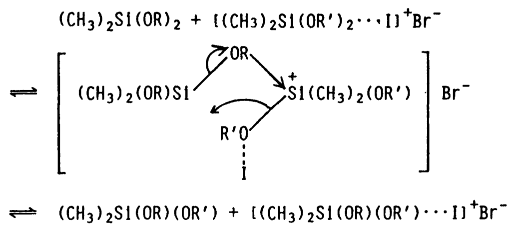
In regard to redistribution reactions among alkoxysilanes, no mechanism has been reported, but some mechanisms concerning the reactions with alkylsilanes or halosilanes or the like are reported in the literature. A mechanism involving a four-centered transition state has been proposed by Russell for the disproportionation of ethyltrimethylsilane catalyzed by aluminum bromide.[27] He concluded such a transition state with ionic character to be most favorable, based on arguments against other proposals. The present alcoholyses and redistribution reactions seem to be favorably interpreted by a mechanism analogous to this.

Iodine and iodine monobromide form charge-transfer complexes with alkoxysilanes as described above. A CT-complex is usually represented as a resonance hybrid of a no-bond form and a dative bond form. The dative bond forms of iodine or iodine monobromide-alkoxysilanes are regarded as $[(C_2H_5)_3SiOR\cdots I]^+I^-$ and $[(CH_3)_2Si(OR)_2\cdots I]^+ Br^-$, etc.

Since these CT-complexes are apparently of ionic character, and the silicon-alkoxy bond is considerably polar compared with the silicon-alkyl bond, the reaction systems involving alkoxysilanes can be shifted more smoothly.

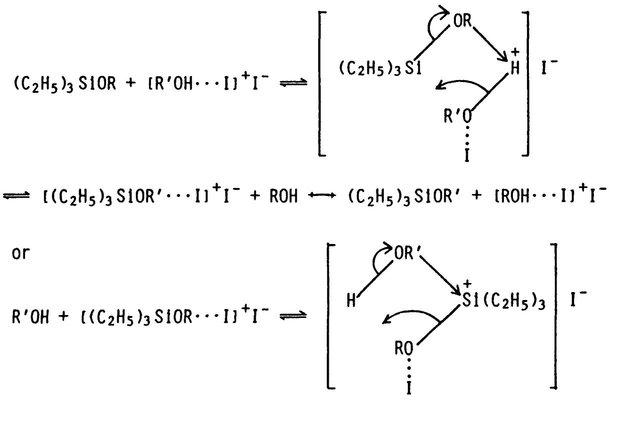
The formation of such transition states will be followed by cleavage of a Si-O bond and not of a C-O bond, in a similar manner to the case of the acid-catalyzed redistribution between optically active di-*s*-butoxydimethylsilane and diethoxydimethylsilane.[9]

The following reaction mechanism may be satisfactorily assumed for the iodine monobromide-catalyzed redistribution reactions among dialkoxydimethylsilanes.



Iodine appears to form a complex with ethanol more readily than with alkoxysilanes, since the formation constants K_f of the iodine-ethanol complex in heptane solution is 0.92 (24 °C),[6] while the observed K_f values of iodine-ethoxytriethylsilane and -diethoxydimethylsilane complexes are 0.55 and 0.61, respectively. In addition, alkoxysilane-alcohol complexing has also been suggested.[28]

Consequently, the four-centered transition state can be more favorably realized in the alcoholysis of alkoxysilanes than in the redistribution reaction. Thus the reaction mechanism of the alcoholysis of alkoxytriethylsilane can be proposed as follows.



The redistribution reaction as well as the alcoholysis can be satisfactorily interpreted by an identical reaction mechanism involving a four-centered transition state, which meets the requirements as described above.

Experimental

Reagents. Ethoxytriethylsilane, diethoxydiethylsilane, triethoxyethylsilane, and ethoxytrimethylsilane were prepared by the reactions of tetraethoxysilane with ethyl- or methylmagnesium bromide.

Diethoxydimethylsilane was prepared by the reaction of octamethylcyclotetrasiloxane with tetraethoxysilane in the presence of potassium hydroxide.[29]

Other alkoxytriethylsilanes, dialkoxydiethylsilanes and dialkoxydimethylsilanes were prepared by iodine-catalyzed alcoholysis of the above ethoxysilanes.

Four disiloxanes used for the spectroscopic work were synthesized by condensation of the corresponding trialkylethoxysilanes.

The crude products were purified by repeated fractional distillation at atmospheric or reduced pressure.

Alcohols, iodine and iodine monobromide were purified by methods similar to those previously reported.[1,2]

Analysis. Analyses of the reaction mixtures were performed by GLC using a Shimadzu model GC-4B gas chromatograph with a thermal conductivity detector. The stationary phases of the packings used in these GLC analyses were PEG 1000 (Reaction No. 1, Table 1), PEG 4000 (Nos. 2 and 3), PEG 6000 (No. 4) and Shinchrom E-71 (No. 5). PEG 6000 was also employed in examining the catalytic actions of the conventional catalysts.

General Procedure. The equilibrium constants of the various exchange reactions were determined by methods similar to those previously reported.[1,2] The compositions of the reaction mixtures were as follows.

Nos. 1, 2 [Alkoxysilane]: [Alcohol]≒1 : 3—6; $[I_2]$<0.1 mol%
No. 3 $[Me_2Si(OEt)_2]$: $[Me_2Si(OPr^n)_2]$: $[C_6H_{14}]$≒1 : 1 : 16;
$[Me_2Si(OEt)(OPr^n)]$: $[C_6H_{14}]$≒2 : 16;
[IBr]=0.03—0.4 mol%
Nos. 4, 5 [dialkoxydialkylsilane]: [Alkoxytriethylsilane]
≒1 : 1 or 1 : 2; [IBr]=0.3—1 mol%

The compositions of the reaction mixtures used in examining the catalytic actions of the conventional catalysts were approximately as follows. Et_3SiOBu: 0.013 mol; BuOH: 0.05 mol; Na: 0.01 mol, or acids: 10^{-3}—10^{-4} mol.

Spectrophotometric Measurements. The absorption spectra were measured with a Shimadzu model UV-200 double-beam spectrophotometer, using stoppered silica cells with a path length of 10 mm at 20—22 °C.

The compositions of the sample solutions for determining the formation constants of CT-complexes were as follows.

I_2-Et_3SiOEt-CCl_4 solutions
C_I (Iodine concentration)≒2×10^{-3} mol dm^{-3}
C_D (Alkoxysilane concentration)≒0.1, 0.2, 0.3, 0.4 mol dm^{-3}
I_2-$Me_2Si(OEt)_2$-CCl_4 solutions
C_I≒2.8×10^{-3} mol dm^{-3}
C_D≒0.22, 0.34, 0.45, 0.56 mol dm^{-3}

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