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NOVEL EFFECTS OF CROWN-ETHER COMPLEXATION ON THE HETEROGENEOUS GAS-PHASE REACTIONS OF ALKYL HALIDES OVER SILICA GEL-SUPPORTED METAL CHLORIDES

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Gas-phase reactions of alkyl halides over the complexes of KCl and $CaCl_2$ with dibenzo-18-crown-6 supported on silica gel exhibited high substitution to elimination ratio and relative reactivities of primary $>$ secondary and iodide $>$ bromide, in contrast to those over uncomplexed metal chlorides. These results together with stereochemistry and poisoning effect indicate that the complexation with crown ether enhances the nucleophilicity or basicity of metal chlorides.

Several examples of successful application of macrocyclic polyethers ("crown" ethers) to organic synthesis have been reported.1) However, these studies so far are limited to the reactions in liquid phase. We attempted to utilize these compounds in heterogeneous gas-phase reactions, and found that the metal chloride-crown ether complexes supported on silica gel showed peculiar behavior as compared with uncomplexed metal chlorides supported on silica gel for the reaction of alkyl halides.

Dibenzo-18-crown-6 (abbreviated as B-18) was commercially obtained from the Nisso Chemicals Co. Ltd. and used as received. The metal chloride—B-18 complexes were synthesized by mixing B-18 with metal chlorides in 1:1 molar ratio in an appropriate solvent ($CaCl_2$: 1-butanol at 90°C, KCl: methanol at room temperature). Supported catalysts were prepared by impregnating silica gel (Davison ID gel, 60—150 mesh, surface area: 250 m^2/g) in alcoholic solutions of crown ether complexes followed by the evaporation of the solvents. For comparison, uncomplexed metal chlorides supported on silica gel were prepared by using the same solvents. The amounts of metal chlorides supported were 0.3—0.4 mg-ion Cl^-/g-cat. Reactions were carried out by a pulse technique by using helium as a carrier gas (flow rate: 60 cm^3/min). Each catalyst (usually ca. 100 mg) was treated in a helium stream for 1 h at 200°C, prior to the reaction at 150°C. Reagents used and procedure of reaction were the same as described elsewhere.2,3)

Reactions over silica gel and uncomplexed B-18 supported on silica gel Considerable dehydrobromination was observed over silica gel itself (ca. 10% conversion of 2-bromobutane over 100 mg at 150°C), due to higher acidity of the present silica gel as compared with that employed previously.2) However, when uncomplexed B-18 was supported, the activity of silica gel decreased to less than one-tenth, indicating that B-18 is not active catalyst for this reaction. It is considered that uncomplexed B-18 is adsorbed on the acid sites of the silica gel and acts as a poison.

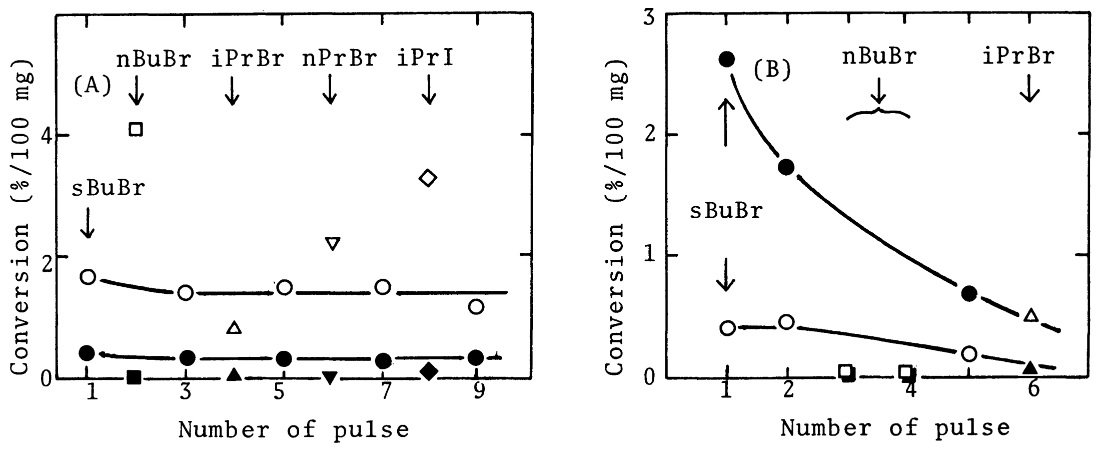
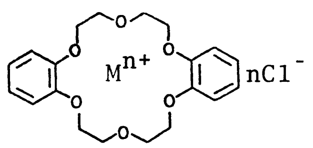


Fig. 1. Reactions of alkyl halides over KCl–B-18/SiO$_2$ (A) and KCl/SiO$_2$ (B) at 150°C
Open symbols: substitution, $RX + Cl^- \longrightarrow RCl + X^-$
Solid symbols: elimination, $RX \longrightarrow R' + HX$.

Reactions over silica gel-supported metal chlorides complexed and uncomplexed with B-18 Substitution and elimination reactions of alkyl halides (RX) took place over metal chloride–B-18 complexes.

RX ⟶ RCl (substitution) and olefin (elimination)



X = Br, I
M = K, Ca

In Fig. 1, the experimental results obtained for KCl–B-18 complex may be compared with those for uncomplexed KCl. In those experiments, several alkyl halides were pulsed one after another over both metal chlorides. The reactivity of s-butyl bromide pulsed occasionally was almost constant or changed monotonously, so that the relative reactivity of each alkyl halide may be determined by comparison with that of s-butyl bromide. First of all, it is noted in Fig. 1A and B that, by complexation, the activity of elimination to form butene decreased, while that of the substitution to 2-chlorobutane increased, so that the activity ratio of substitution to elimination increased from 0.15 to 4.5. In the case of CaCl$_2$, although the activities for both reactions were lower for CaCl$_2$–B-18, the activity ratio of substitution to elimination was similarly increased by complexation from 0.2 to almost 10. These results indicate that the chloride ion, the counter anion, become much more nucleophilic (or more labile) by the complex formation.

Table 1 summarizes the experimental results. It was noted in Fig. 1 and Table 1 that primary alkyl halides were more reactive than secondary alkyl halides in substitution reaction over metal chloride–B-18 complexes (n-butyl > s-butyl and n-propyl > isopropyl), in contrast with the results for metal chloride alone. Opposite reactivity order was also found in the effect of halogen on the substitution of alkyl halides (Table 1). These trend in reactivity for metal chloride–B-18 complexes are

Table 1. Comparison among Supported Metal Chlorides Complexed and Uncomplexed with Dibenzo-18-crown-6 (B-18)

	SiO_2-supported catalyst			
	KCl	KCl—B-18	$CaCl_2$	$CaCl_2$—B-18
Reaction of 2-bromobutane (1st pulse, %/100 mg)				
Elimination:	2.6	0.4	73.8	1.0
Substitution:	0.4	1.8	15.1	9.8
Reactivity for substitution of alkyl halides (RX)				
R:	1° < 2°	1° > 2°	1° < 2°	1° > 2°
X:	Br < I	Br < I	Br > I	Br < I
Effect of pyridine poisoning on activity			yes	no

Table 2. Dehydrobromination of 2-Bromobutane-3-d_1[a] over Supported $CaCl_2$ and $CaCl_2$—B-18

SiO_2-supported catalyst	Reaction temperature (°C)	Content of butene-d_1 (%)			%Anti	Isotope effect
		1-C_4'	cis-2-C_4'	trans-2-C_4'		
$CaCl_2$—B-18	200	88	64	43	72	1.7
$CaCl_2$	120	91	58	71	37	2.2

a) erythro : threo : d_0 = 70 : 19 : 11 for $CaCl_2$—B-18
77 : 17 : 6 for $CaCl_2$.

similar to those found for CsCl supported silica gel which showed basic character for this reaction.[4)] Therefore, $CaCl_2$ which showed acidic nature for the present reaction seems to become basic after complexation with B-18. In accordance with this idea, the preadsorbed pyridine did not reduce the activity of $CaCl_2$—B-18, while it had considerable poisoning effect on the activity of $CaCl_2$. In the case of KCl, the basicity was probably enhanced by the complexation. The relative reactivity of RI > RBr may also suggest that the complexation increases the "softness" of metal chlorides.

Stereochemistry of both reactions was investigated by the method described previously.[2,3)] As is shown in Table 2, dehydrobromination of 2-bromobutane-3-d_1 proceeded preferentially by anti mode over $CaCl_2$—B-18 while syn mode was favored over $CaCl_2$. This result also supports the idea that the acidic sites of $CaCl_2$ become basic after complexation with B-18, if the relationship observed between acid-base properties and steric course of reaction[2] is taken into account. The reaction of optically active 2-bromobutane revealed that racemization was rapid and the substitution to form 2-chlorobutane proceeded with partial inversion of configuration.

In summary, it was revealed by the present study that crown ether complexation of metal chlorides exhibits specific effects in some heterogeneous gas-phase reactions, by modifying the properties of metal salts such as nucleophilicity, basicity, and "softness". Further investigations of this complex may provide a good example of "well-defined" solid catalyst, with which the regio- and stereoselectivity of catalytic reactions can be controlled.

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