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Preparation and Properties of Aluminum and Zinc Haloalcoholates

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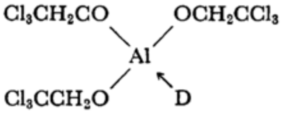
Seven haloalcoholates of aluminum and zinc were prepared by the reactions of haloalcohols with metal alkyls in ethyl ether, and their properties were examined. The following differences have been observed between these haloalcoholates and the usual alcoholates, those with no halogen in the alkyl groups. (1) The metal haloalcoholates are unstable to heat and decompose at 90—220°C. Except for $Al(OCH_2CF_3)_3$, they are neither distilled nor sublimed even *in vacuo*. The usual aluminum alcoholates, such as ethoxide and isopropoxide, are easily distilled under reduced pressures. (2) The haloalcoholates are stronger Lewis acids than the usual alcoholates. The acid strength of some aluminum haloalcoholates is even higher than triethylaluminum. The strong acid nature of the aluminum haloalcoholate can be ascribed to the electron-withdrawing effect of halogen. (3) As expected from their strong acid strength, the haloalcoholates induce the cationic polymerizations of vinyl monomers and cyclic ethers, such as styrene, α-methylstyrene, isobutyl vinyl ether, 3,3-bis-(chloromethyl)oxacyclobutane, and tetrahydrofuran. The usual metal alcoholates are weaker acids and do not cause the polymerizations of these monomers. In the ethylene oxide polymerization, both the haloalcoholates and the usual alcoholates showed catalytic activity. However, these two types of alcoholates differ from each other in the catalysis mechanism. For the polymerization of ethylene oxide by the haloalcoholate catalyst, a cationic polymerization mechanism was assumed on the basis of the formation of dioxane as a by-product. The polymerization by the usual alcoholate catalysts is assumed to be of a coordinate anionic mechanism.

In the course of studies upon the polymerization catalyst behavior of metal alkyls and alcoholates, we have shown that aluminum and zinc alcoholates of unsubstituted alcohols are weak Lewis acids which do not induce the cationic polymerizations of vinyl monomers and cyclic ethers, but which do cause the coordinate anionic polymerizations of alkylene oxides and acetaldehyde.[1,2] Recently, we reported the preparation of aluminum trichloroethoxide, $Al(OCH_2CCl_3)_3$, and showed its peculiar properties as compared with those of the usual aluminum alcoholates, such as aluminum isopropoxide and *t*-butoxide.[3] The dissociation of $Al(OCH_2CCl_3)_3$ to the monomeric form (I) in the presence of donor molecules (for example, dioxane, tetrahydrofuran, and pyridine) has been observed; this is in sharp contrast to the strong association tendency of the usual aluminum alcoholates even in the presence of the above donors.



(I) (D: donor molecule)

It has also been found, from the results of the acid-strength measurements by the IR method[4,5] using xanthone as the reference base, that $Al(OCH_2CCl_3)_3$ is a fairly strong acid; it is as strong as $AlEt_3$ and much stronger than the usual aluminum alcoholates. In the present experiments, several haloalcoholates of aluminum and zinc have been prepared and their properties, especially as polymerization catalysts, have been examined.

Experimental

Reagents. Commercially-available materials were purified carefully by the usual procedures. 1,1,1-Trifluoroethanol,[6] 1,1,1-trichloroethanol,[7] 1,1,1-tribromoethanol,[7] and 1,1-dichloroethanol[8] were prepared by the procedures described in the literatures and were purified by distillation. Tribromoethanol was further purified by recrystallization from a mixture of *n*-pentane and ethyl ether.

Preparation of Haloalcoholates. A typical procedure was as follows. $AlEt_3$ (0.1 mol) in ethyl ether (20 m*l*) was added, drop by drop, with vigorous stirring into a mixture of a haloalcohol (0.3 mol) and ethyl ether (60 m*l*) at −78°C. After the addition was complete, the reaction system was allowed to warm gradually to room temperature and finally heated to reflux for 2 hr. In the cases of $Al(OCH_2CCl_3)_3$ and $Al(OCH_2CBr_3)_3$, products separated from the reaction solutions; these

TABLE 1. PREPARATIONS AND DECOMPOSITION TEMPERATURES OF HALOALCOHOLATES

Alcoholate	Methods of purification	Decomposition temperature[f)]	Analysis: Al or Zn (%)		Analysis: RO/Al[b)] or RO/Zn[c)] (mol ratio)
			Calcd	Found	
$Al(OCH_2CF_3)_3$[a)]	Sublimation[a)] (80°C/0.18 mmHg)	110	8.33	9.05	3.09
$Al(OCH_2CCl_3)_3$	Recrystallization from benzene	145	5.74	5.71	2.97
$Al(OCH_2CBr_3)_3$	Washing with ethyl ether[e)]	155	3.09	3.07	2.98
$Al(OCH_2CHCl_2)_3$	Recrystallization from ethyl ether	180	7.32	7.45	3.02
$Al[OCH(CH_2Cl)_2]_3$	Recrystallization from ethyl ether	130	6.57	6.50	3.00
$Al(OCH_2CH_2Cl)_3$	Reprecipitation from *n*-heptane	220 (mp 180°C)	10.16	10.23	3.14
$Zn(OCH_2CCl_3)_2$	Reprecipitation from a mixture of *n*-heptane and pyridine	115	18.02	18.08	1.94[c)]
$EtZnOCH_2CCl_3$	Washing with ethyl ether[e)]	90	26.92	26.38	1.00[c,d)]

a) Very hygroscopic.
b) The calculated value for each aluminum alcoholate is 3.00, relative error=±5%.
c) Cl_3CCH_2O/Zn (mol ratio).
d) Et/Zn ratio was found to be 1.01 by gasometry.
e) Further purification was not possible, because no suitable solvent for recrystallization was found.
f) Decomposition temperature was measured under reduced pressure.
Metal haloalcoholates except $Al(OCH_2CF_3)_3$ and $Al(OH_2CH_2Cl)_3$ were decomposed without melting and subliming.

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1) H. Imai, T. Saegusa and J. Furukawa, *Makromol. Chem.*, **81**, 92 (1965).

2) J. Furukawa, T. Saegusa and H. Fujii, *ibid.*, **44/46**, 398 (1960).

3) T. Saegusa and T. Ueshima, *Inorg. Chem.*, **6**, 1679 (1967).

4) D. Cook, *Can. J. Chem.*, **41**, 526 (1963).

5) T. Saegusa, S. Matsumoto and H. Imai, *J. Polymer Sci.*, **A-1**, in press.

6) K. N. Campbell, J. O. Knoblock and B. K. Campbell, *J. Am. Chem. Soc.*, **72**, 4380 (1950).

7) H. Meerwein, G. Hinz and H. Majert, *J. Prakt. Chem.*, **147**, 236 (1936).

8) C. E. Sroog, C. M. Chih, F. A. Short and H. M. Woodburn, *J. Am. Chem. Soc.*, **71**, 1710 (1949).

products were isolated, washed with cold ethyl ether, and dried *in vacuo*. In other cases ethyl ether was removed from the reaction mixture under reduced pressure to give a white solid. The haloalcoholates were isolated and purified by the procedures presented in Table 1.

The products were usually analyzed as follows: a weighed sample was decomposed by excess 1 N hydrochloric acid. The alcohol thus produced was then extracted with ethyl ether and analyzed by vapor-phase chromatography (v.p.c.). In the case of $Al(OCH_2CF_3)_3$, a sample was treated with excess acetic acid, while CF_3CH_2OH was analyzed directly by v.p.c. without the procedure of extraction. The results of the analyses are also shown in Table 1.

$EtZnOCH_2CCl_3$ and $Zn(OCH_2CCl_3)_2$ were prepared by the same procedure, using diethylzinc.

Polymerization Procedures and After-treatments. Ethylene oxide and a catalyst were placed in a sealed tube, and the tube was heated for 24 hr. Then the reaction mixture was poured into a large amount of *n*-pentane in order to isolate the product polymer as a white precipitate, which was then dried and extracted with benzene to remove the catalyst residue. In the pentane layer, dioxane, the dimer of ethylene oxide, was searched for and its quantity, if it was present, was determined by v.p.c.

The other polymerization procedures and after-treatments were performed as described before.[2,9,10]

Spectroscopic Measurements. All the samples were prepared under a nitrogen atmosphere. The NMR spectra were measured at room temperature with a Varian A-60 spectrometer, with tetramethylsilane used as the internal standard. The infrared spectra measurements were carried out with a model 402G (Japan Spectroscopic Company), using a KBr liquid cell.

Results and Discussion

Aluminum and zinc haloalcoholates were first prepared in our series of studies by means of the reactions of metal alkyls with halogen-substituted alcohols carried out in ethyl ether. It is important to employ ethyl ether as the reaction solvent in order to suppress the side reactions between the halogen-carbon bond and metal alkyls. The product of a metal haloalcoholate is sometimes insoluble in ether and separates from the reaction mixture. The reaction in ethyl ether is thus recommended.

The following differences have been observed between haloalcoholates and the usual alcoholates:

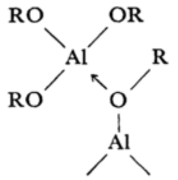
(1) Heat-stability. The usual aluminum alcoholates, such as aluminum ethoxide, isopropoxide, and amyloxides, are known to be distillable under reduced pressure at considerably high temperatures (160°C—250°C). Even unstable aluminum *t*-butoxide can be sublimed *in vacuo*. On the contrary, most aluminum haloalcoholates decompose without melting. Most of them can not be sublimed even under reduced pressures, as is shown in Table 1. Only $Al(OCH_2CF_3)_3$ can be sublimed at 80°C (0.18 mmHg). $Al(OCH_2CH_2Cl)_3$, which carries the minimum number of chlorine atoms, melts at 180°C, however, it is not distilled without decomposition.

(2) Acid Strength (Interaction with Donor Molecules). Acid-strength measurements of various haloalcoholates as well as of the usual alcoholates were done using infrared techniques and an indicator method.[1] From the magnitude of the $\Delta\nu_{C=N}$ of pyridine (the shift to a higher wavelength) and the $\Delta\nu_{C=O}$ of xanthone (the shift to a lower wavelength) caused by the coordination of these donor molecules to aluminum alcoholates, the following order of acid strength (acceptor powers of metal atoms) was found; $Al(OCH\langle{}^{CH_2Cl}_{CH_2Cl})_3 > Al(OCH_2CF_3)_3 \gtrsim Al(OCH_2CCl_3)_3 \gtrsim Al(OCH_2CBr_3)_3 > Al(OCH_2CHCl_2)_3 > Zn(OCH_2CCl_3)_2 > EtZnOCH_2CCl_3 > Al(OCH_2CH_2Cl)_3$, $Al(OR)_3$ (R: Et, *i*-Pr, *t*-Bu, *etc.*), EtZnOEt, and $Zn(OEt)_2$. The usual alcoholates and $Al(OCH_2CH_2Cl)_3$ did not cause any shift of $\nu_{C=N}$ and $\nu_{C=O}$ at all.

The weak acid strength of usual aluminum alcoholates has been explained in two ways. First, because of the contribution of the resonance structure (II), the electron-acceptor power of aluminum is lower than that to be expected from the electronegativities of aluminum and oxygen in the $\overset{\delta+}{Al}–\overset{\delta-}{O}$ bond. Secondly, the electron-acceptor power (strong acidic nature) of aluminum is neutralized by

$$\rangle Al\text{-}OR \longleftrightarrow \rangle\overset{\ominus}{Al}=\overset{\oplus}{O}R \quad (II)$$

the coordination of the oxygen atom of the neighboring aluminum-alkoxy linkage to make the coordination number of aluminum four or more than four (III); therefore, aluminum alcoholates do not act as strong electron acceptors.


(III)

The examination of highly acidic aluminum haloalcoholates in the present study has an important bearing on this problem. The first explanation leads to the assumption that the electron-withdrawing effect of halogen is extended to aluminum through oxygen, thus increasing the acceptor power of the aluminum atom. In this case, a donor molecule coordinates to aluminum with an expansion of the coordination number of aluminum, as is illustrated by structure IV. According to the alternative explanation, the electron-withdrawing effect of a halogen atom decreases the basic strength of the oxygen of an alkoxy group. The association of the aluminum haloalcoholates is easily broken by a donor molecule, thus forming the acid-base complex of a

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[9] T. Saegusa, H. Imai and J. Furukawa, *Makromol. Chem.*, **65**, 60 (1963).

[10] T. Saegusa, H. Imai and J. Furukawa, *ibid.*, **79**, 221 (1964).

TABLE 2. RELATION BETWEEN ACID STRENGTH AND NMR SPECTRA OF VARIOUS ALCOHOLATES

Alcoholate	$\Delta\nu_{C=N}$ of pyridine (cm^{-1})	$\Delta\nu_{C=O}$ of xanthone (cm^{-1})	NMR spectra[a]		
			A	B	C
$Al(OCH_2CF_3)_3$	31	91	—	A quartet centered at 5.77 (in CH_2Cl_2)	—
$Al(OCH_2CCl_3)_3$	30	90	Two singlets: 5.68(a) 5.28(b). Integration ratio a/b=2.0 (in CH_2Cl_2)	A singlet at 5.75 (in CH_2Cl_2)	A singlet at 5.70 (in CH_2Cl_2)
$Al(OCH_2CBr_3)_3$	29	89	Insoluble	A singlet at 5.52 (in benzene)	A singlet at 5.70[b] (in benzene)
$Al[OCH(CH_2Cl)_2]_3$	39	91	Complexed (in benzene)	A doublet at 6.40(c) and a multiplet at 5.94(d) ratio c/d=4 (in benzene)	A doublet at 6.27(c′) and a multiplet at 5.78(d′) (in benzene)
$Al(OCH_2CHCl_2)_3$	26	0	Two doublets at 6.18(e) and 5.49(f), two triplets at 4.71(g) and 3.90(h). e/f/g/h=4.0/2.0/2.0/1.0 (in benzene)	A doblet at 6.10(i), a triplet at 4.26(j) ratio i/j=2 (in benzene)	Essentially the same as A with slight broadening of peaks. e 6.15, f 5.42 g 4.66, h 3.88 (in benzene)
$Al(OCH_2CH_2Cl)_3$	0	0	Complexed. Signals appeared at the region of 6.9—5.5 (in benzene)	Complexed. Very broad singlet in the region of 6.9—5.5 (in benzene)[c]	Essentially the same as A with slight broadening of peaks. (in benzene)
$Al(OR)_3$ (R: *i*-Pr, *t*-Bu)	0	0	Two singlets at 8.80(k) and 8.55(l) (in CH_2Cl_2)[d]	The same as A 8.59 (k′) 8.50(l′) (in benzene)[d]	The same as A k″=8.80, l″=8.55 (in CH_2Cl_2)[d]
$Zn(OCH_2CCl_3)_2$	24	0			
$EtZnOCH_2CCl_3$	20	0	—	—	—
EtZnOEt $Zn(OEt)_2$	0	0			

[a] Chemical shifts are expressed in τ-value. A: NMR spectra in a non-donating solvent, B: in the presence of excess pyridine, C: in the presence of excess xanthone.

[b] A small broad singlet was observed at 5.18 ppm and its peak area increased when the ratio (xanthone/$Al(OCH_2CBr_3)_3$) was decreased. In this case, some dissociation may occur. ($Al(OCH_2CBr_3)_3$ xanthone $\rightleftarrows$ $Al(OCH_2CBr_3)_3$ + xanthone).

[c] From this NMR spectrum, considerable interaction between $Al(OCH_2CH_2Cl)_3$ and pyridine may be assumed although no shift of $\nu_{C=N}$ is observed.

[d] NMR spectra of $Al(OC(CH_3)_3)_3$.

TABLE 3. ACID STRENGTH MEASUREMENT BY INDICATOR METHOD[a]

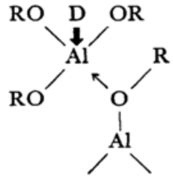
Alcoholate	Indicators		
	Neutral red (+6.8)[b]	Methyl red (+4.8)[b]	Benzeneazonaphtylamine (+4.0)[b]
$Al(OCH_2CH_2Cl)_3$	A	A	B
$Al(OR)_3$ (R: Et, *i*-Pr and *t*-Bu)	B	B	B

A: acidic color B: basic color

[a] Measurements were carried out as described before.[1]

[b] pK_a values of indicators.

monomeric structure (I), where the coordination number of aluminum is four.



(IV)

As has been described in our previous paper[8)] and in V. J. Shiner's work,[11)] associated aluminum alcoholates carry more than two kinds of alkoxy groups, which are indicated by signals at different positions in the NMR spectra. In the NMR spectrum of the monomeric aluminum alcoholate - donor complex (structure I), only one type of alkoxy group is observed. In view of these considerations, the NMR spectra of the aluminum haloalcoholates were examined (see Table 2), and the following results obtained: (1) When a shift of the $\nu_{C=O}$ of xanthone or the $\nu_{C=N}$ of pyridine is observed, the three alkoxy groups in the NMR spectra are always equivalent in the donor-acceptor complexes. (2) When the IR shift is not caused by the alcoholate, the three alkoxy groups in the NMR spectrum are not equivalent in the alcoholate-donor mixture, as has been observed in such non-donating solvents as benzene.[*1] From these findings, the strong acid nature of some aluminum haloalcoholates may be ascribed to the weak association tendency, which facilitates the formation of the monomeric donor-acceptor complex (structure I). The dissociation tendency is attributable to the decrease in the nucleophilicity of the oxygen atom in the alkoxy group by the electron-withdrawing effect of halogens.

It has also been realized, by comparing the magnitudes of $\Delta\nu_{C=N}$ and $\Delta\nu_{C=O}$, that the accepting power of aluminum alcoholates in the complexes (I) is affected to some extent by the kind and number of halogens in the haloalkoxy group. Thus, it is obvious that the electron-withdrawing effect of halogens directly influences the acceptor power of aluminum. The order of acid strength is as expected from the number and the electronegativities of halogen atoms, with the exception of $Al(OCH\langle{}^{CH_2Cl}_{CH_2Cl})_3$, whose alkoxy group has a structure very different from those of others. Although the acceptor powers of the aluminum haloalcoholates in the associated form were not measured by the above method, their order was supposed to be the same as that of the dissociated aluminum alcoholates if the coordination number of aluminum atoms is the same, which seems likely.

No difference in acid strength between $Al(OCH_2CH_2Cl)_3$ and the usual aluminum alcoholates was observed by the IR procedures. However, the indicator method[1)] revealed that $Al(OCH_2CH_2Cl)_3$ was a stronger acid (see Table 3).

Nearly the same discussion is applicable to zinc haloalcoholates. Detailed studies of zinc haloalcoholates will be published elsewhere.[12)]

TABLE 4. POLYMERIZATION OF TETRAHYDROFURAN BY ALUMINUM HALOALCOHOLATES*
Monomer 0.1 mol; catalyst and epichlorohydrin, each 0.00125 mol; CH_2Cl_2 2.5 m*l*; polymerizations, 48 hr, 0°C

Catalyst	Yield (%)	[η]
$Al(OCH_2CF_3)_3$	75.3	0.330
$Al(OCH_2CCl_3)_3$	29.5	0.360
$Al(OCH_2CBr_3)_3$	29.8	0.115
$Al[OCH(CH_2Cl)_2]_3$	70.5	0.440
$Al(OCH_2CHCl_2)_3$	73.9	0.260
$Al(OCH_2CH_2Cl)_3$	20.8	0.300
$Al[OCH(CH_3)_2]_3$, $Al[OC(CH_3)_3]_3$	0	—
$Al[OCH(CH_2Cl)_2]_3$	16.6[a)]	1.37
	88.3 (3.183 g)[b)]	0.356
	37.7 (3.974 g)[c)]	0.445

* $EtZnOCH_2CCl_3$ and $Zn(OCH_2CCl_3)_2$ did not produce any polymer.
a) Bulk polymerization, catalyst and epichlorohydrin 0.1 mol% for monomer, 7 days, 0°C.
b) Monomer, 0.1 mol; catalyst and epichlorohydrin each 0.001 mol; CH_2Cl_2, 1 m*l*; 2 days, 0°C.
c) After two days' polymerization (condition (b)), 0.2 mol of tetrahydrofuran was added and polymerization was continued for 5 days.

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11) V. J. Shiner, Jr., D. Whittaker and V. J. Fernandez, *J. Am. Chem. Soc.*, **85**, 2318 (1963).

[*1] $Al(OCH_2CH_2Cl)_3$ is the only exception. There the shift of $\Delta\nu_{C=N}$ is not observed. However, in the NMR spectrum of $Al(OCH_2CH_2Cl)_3$-pyridine the signals due to the $ClCH_2CH_2O$-group are not the same as those in benzene.

12) T. Saegusa and T. Ueshima, This Bulletin, in press.

TABLE 5. CATIONIC POLYMERIZATION BY HALOALCOHOLATES
Monomer 0.1 mol, haloalcoholate and CH_3OCH_2Cl, each 2.5 mol% for monomer

Catalyst	Yield (%)	[η][b]
CH_2=CHO-*i*-Bu[a] (in toluene, 30 m*l*; at −78°C, 24 hr)		
$Al(OCH_2CF_3)_3$	12.6	0.10
$Al(OCH_2CCl_3)_3$	71.1	0.10
$Al(OCH_2CBr_3)_3$	trace	—
$Al(OCH_2CHCl_2)_3$	16.9	0.12
$Al[OCH(CH_2Cl)_2]_3$	42.1	0.21
$Al(OCH_2CH_2Cl)_3$	0	—
$Zn(OCH_2CCl_3)_3$	3.0	0.09
$EtZnOCH_2CCl_3$	43.2	0.35
$Al(OR)_3$ (R: Et or *i*-Pr) EtZnOEt, $Zn(OEt)_2$	0	—
α-Methylstyrene (in CH_2Cl_2, 20 m*l*; at 0°C for 48 hr)		
$Al(OCH_2CCl_3)_3$	89.7	white powder
3,3-Bis(chloromethyl)oxacyclobutane[c] (in CH_2Cl_2, 20 m*l*; at 0°C for 72 hr)		
$Al(OCH_2CCl_3)_3$	34.9	white powder

a) All the polymers were amorphous (soluble in methyl ethyl ketone).
b) In benzene at 30°C.
c) Epichlorohydrin was used as a promoter.

TABLE 6. POLYMERIZATION OF ALKYLENE OXIDES
Monomer 0.1 mol

Catalyst	Yield of polymer (%)	[η][f]	Yield of dioxane (%)
Ethylene oxide (catalyst 1.25 mol%; in 2.5 m*l* CH_2Cl_2; at 50°C for 24 hr)			
$Al(OCH_2CF_3)_3$	32.1[b]	0.425	3.0
$Al(OCH_2CCl_3)_3$	15.9[c]	0.031	2.4
$Al(OCH_2CBr_3)_3$	29.2[d]	—	3.3
$Al(OCH_2CHCl_2)_3$	21.8[d]	—	1.3
$Al[OCH(CH_2Cl)_2]_3$	23.4[c]	0.037	5.9
$Al(OCH_2CH_2Cl)_3$	9.6[d]	—	1.6
$Al[OCH(CH_3)_2]_3$	9.6[e]	0.345	0
$Al(OCH_2CH_3)_3$[a]	0.8[e]	—	0
$EtZnOCH_2CCl_3$	15.9[d]	—	1.2
$Zn(OCH_2CCl_3)_2$	100[b]	0.037	0
$EtZnOCH_2CH_3$	34.5[e]	0.638	0
$Zn(OCH_2CH_3)_2$	100[e]	0.380	0
Propylene oxide (2.5 mol% of catalyst; in 10 m*l* CH_2Cl_2, at 50—60°C for 8 hr)			
$Al(OCH_2CCl_3)_3$	59.7	—	—
Epichlorohydrin (2.5 mol% of catalyst; in 10 m*l* CH_2Cl_2, at 0°C for 72 hr)			
$Al(OCH_2CCl_3)_3$	46.2	—	—

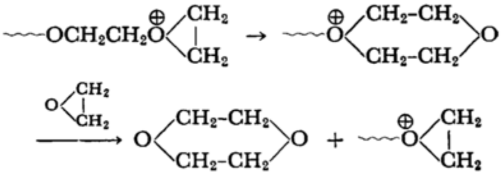
a) time, 12 hr b) waxy c) tacky semi-solid d) oily
e) resineous solid f) in benzene 30°C

(3) **Behavior as Polymerization Catalysts.** It has already been established that the usual alcoholates of aluminum and zinc do not cause the cationic polymerizations of vinyl monomers and cyclic ethers, such as isobutyl vinyl ether, styrene, α-methylstyrene, 3,3-bis(chloromethyl)oxacyclobutane, and tetrahydrofuran.[1] On the contrary, the haloalcoholates in the present study induced the

cationic polymerizations of the above monomers, as was expected from the stronger Lewis acid character of the haloalcoholates. The polymerizations by haloalcoholate catalysts are illustrated in Tables 4 and 5. In the tetrahydrofuran polymerization, solid polymers with quite high molecular weights were produced in high yields by the catalysts of all aluminum haloalcoholates. Polytetrahydrofuran with $[\eta]$ values above 1 could be prepared at low catalyst concentrations. When a new tetrahydrofuran monomer was added to a system in which polymerization had proceeded nearly completely, the yield as well as the intrinsic viscosity of the polymer were increased (compare b and c in Table 4). In the second stage, however, the polymerization did not proceed beyond 10% of the added monomer, even after 5 days' reaction. This observation suggests slow termination.

Heterogeneous polymerization of isobutyl vinyl ether with haloalcoholate catalysts in toluene produced only amorphous polymers (Table 5).

The results of the polymerizations of alkylene oxides are summarized in Table 6. Polymerizations of these monomers by the usual alcoholates are known to proceed through the coordinate anionic mechanism. The polymerizations by haloalcoholates are different in some respects from those by the usual alcoholates: (1) The ethylene oxide polymerization is caused both by haloalcoholates and the usual alcoholates. However, only in the polymerization by the haloalcoholates, dioxane, a dimer of ethylene oxide, is formed as a by-product. Our previous work13) has shown that dioxane is formed only by a cationic mechanism (Eq. (1)), not by a so-called coordinate anionic mechanism.



(1)

Therefore, it may be assumed that the haloalcoholates induce the cationic polymerization of ethylene oxide, whereas the usual alcoholates induce the coordinate anionic polymerization. (2) This assumption is consistent with the molecular weight of the product polymer. Polymers prepared using the haloalcoholates are oily or waxy (low molecular weights), whereas those prepared using the usual alcoholates were solid polymers with higher molecular weights. In the polymerizations of propylene oxide and epichlorohydrin, a similar tendency was observed.

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13) T. Saegusa, T. Ueshima and S. Tomita, *Makromol. Chem.*, **107**, 131 (1967).