over of the twist and wag frequencies has occurred. The spectrum of $SnCl_4 \cdot 2CH_2CHCN$ (3500–265 cm^{-1}) is shown in Figure 3.

This same splitting of the vinyl out-of-plane hydrogen deformations has been observed in the spectrum of acrylonitrile complexes of some transition metals,[14] and the reported frequencies are similar to those found for $SnCl_4 \cdot 2CH_2CHCN$. In light of the evidence presented above, it is likely that an analogous situation exists for the transition metal complexes.

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[14] R. J. Kern, *J. Inorg. Nucl. Chem.*, **25**, 5 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF SYNTHETIC CHEMISTRY,
KYOTO UNIVERSITY, KYOTO, JAPAN

Aluminum 2,2,2-Trichloroethoxide. Preparation and Properties

BY TAKEO SAEGUSA AND TAKASHI UESHIMA

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In the present study, aluminum 2,2,2-trichloroethoxide was prepared for the first time by the reaction of triethylaluminum with 2,2,2-trichloroethanol carried out in ethyl ether. The properties of aluminum 2,2,2-trichloroethoxide were studied in comparison with the usual aluminum alkoxides such as aluminum ethoxide, isopropoxide, and *t*-butoxide. By the determination of molecular weight in solution and nmr spectral studies, aluminum 2,2,2-trichloroethoxide has been shown to be monomeric in donor solvents such as dioxane and dimeric in methylene chloride and in benzene. Dissociation to monomer in donor solvents distinguishes aluminum 2,2,2-trichloroethoxide from the usual aluminum alkoxides which are in associated form even in donor solvents. A stronger accepting power of aluminum 2,2,2-trichloroethoxide as a Lewis acid has also been demonstrated by the infrared spectra of its donor–acceptor complexes with pyridine and xanthone. These two prominent characters of aluminum 2,2,2-trichloroethoxide have been ascribed, at least partly, to the electron-withdrawing effect of the three chlorine atoms of the trichloroethoxy group.

Introduction

For many years aluminum alkoxide has been studied in terms of physicochemical properties and structural features as well as the catalytic behavior in organic synthetic reactions and in the polymerization of aldehydes and alkylene oxides.

The present paper describes the studies on aluminum 2,2,2-trichloroethoxide, $Al(OCH_2CCl_3)_3$, which has not been prepared until the present study. $Al(OCH_2CCl_3)_3$ was prepared successfully by the reaction of triethylaluminum with 2,2,2-trichloroethanol. The properties of $Al(OCH_2CCl_3)_3$, particularly the degree of association in solution and the Lewis acid character, have been compared with those of the usual aluminum trialkoxides of unsubstituted alcohols.

Experimental Section

Materials.—Solvents, triethylaluminum ($Al(C_2H_5)_3$), and other reagents were carefully purified by the usual procedures. 2,2,2-Trichloroethanol, Cl_3CCH_2OH, was synthesized by the reduction of trichloroacetaldehyde (chloral) with $Al(C_2H_5)_3$ in ether solution according to the procedure given by Meerwein, *et al.*,[1] which was purified by repeated distillation, bp 66° (26 mm).

Synthesis of $Al(OCH_2CCl_3)_3$.—Under nitrogen atmosphere, 0.53 mole of Cl_3CCH_2OH was dissolved in 150 ml of ethyl ether at −78°, to which a solution of 0.17 mole of $Al(C_2H_5)_3$ in 50 ml of ethyl ether was added slowly with vigorous stirring and cooling during 1 hr. Then the reaction system was allowed to warm slowly to room temperature and was finally heated to reflux for 2 hr. From the reaction system a white powder precipitated, which was washed repeatedly with cold ethyl ether, dried *in vacuo*, and recrystallized three times from benzene. The yield of $Al(OCH_2CCl_3)_3$ (purified) was about 50%. *Anal.* Calcd for $C_6H_6Cl_9OAl$: Al, 5.71. Found: Al, 5.74. The trichloroethoxy group of the product was quantitatively analyzed by the determination of Cl_3CCH_2OH by vpc in the acid hydrolysis mixture of the product. The analyses of aluminum and the Cl_3CCH_2O group showed the Cl_3CCHO/Al ratio to be 2.97, supporting the formula $Al(OCH_2CCl_3)_3$. $Al(OCH_2CCl_3)_3$ decomposed without melting above 100°.

Isolation of Aluminum 2,2,2-Trichloroethoxide–Pyridine (1:1) Complex.—Under nitrogen atmosphere, 1.015 g (12.8 mmoles) of pyridine was added at room temperature to a solution of 2.19 g (4.65 mmoles) of $Al(OCH_2CCl_3)_3$ in 10 ml of benzene, and the mixture was stirred for 1 hr. Then the volatile materials were removed *in vacuo* (8×10^{-3} mm) at 50° for 10 hr. A white powdery matter was left, which was shown by nmr spectrum to be a 1:1 aluminum 2,2,2-trichloroethoxide–pyridine complex.

Nmr Measurements.—At room temperature, the nmr spectrum was measured by using a Varian 60-Mc (A-60) spectrometer. All samples were prepared under nitrogen atmosphere, and tetramethylsilane was used as the standard.

Results and Discussion

In the present study, $Al(OCH_2CCl_3)_3$ was prepared for the first time by means of the reaction of $Al(C_2H_5)_3$ with Cl_3CCH_2OH carried out in ether. The employment of ether as the reaction solvent is highly recom-

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

mended. First, awkward side reactions between the trichloromethyl group and $Al(C_2H_5)_3$ are suppressed conveniently, and, second, the isolation of the product $Al(OCH_2CCl_3)_3$ is facilitated because $Al(OCH_2CCl_3)_3$ precipitated in fine powder from the reaction system. The results of analysis of $Al(OCH_2CCl_3)_3$ were quite satisfactory as shown in the Experimental Section.

$Al(OCH_2CCl_3)_3$ is soluble in dioxane, pyridine, tetrahydrofuran, chloroform, methylene chloride, and hot aromatic hydrocarbons, slightly soluble in ether and cold aromatic hydrocarbons, and insoluble in heptane, cyclohexane, and carbon tetrachloride. It is to be mentioned that $Al(OCH_2CCl_3)_3$ is especially soluble in donor solvents.

$Al(OCH_2CCl_3)_3$ was not stable at higher temperatures. It decomposed above 100° without melting. A trial to sublime $Al(OCH_2CCl_3)_3$ at a pressure of 8×10^{-3} mm up to the temperature of decomposition was unsuccessful.

The molecular weight of $Al(OCH_2CCl_3)_3$ was measured in three solvents—dioxane, methylene chloride, and benzene—by cryoscopy or ebullioscopy. The results are shown in Table I. It is indicated that $Al(OCH_2CCl_3)_3$ is monomeric in dioxane and dimeric in methylene chloride and in benzene.

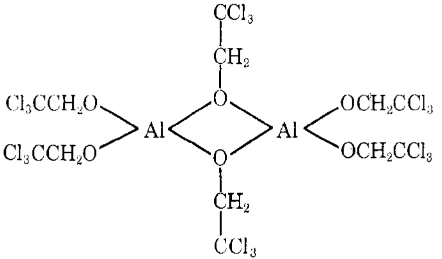
TABLE I

MOLECULAR WEIGHT DETERMINATION OF $Al(OCH_2CCl_3)_3$

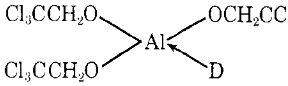
Solvent	Method	Mol wt[a]	Degree of assocn
Dioxane	Cryoscopy	473	1.00
Methylene chloride	Ebullioscopy	945	2.00
Benzene	Ebullioscopy	922	1.95

[a] Molecular weight calculated for $Al(OCH_2CCl_3)_3$ is 472.

The above observations have been supported by nmr spectral studies of $Al(OCH_2CCl_3)_3$ in solution. In dioxane, only one singlet was observed at 4.30 ppm, except the signals of the dioxane protons. This result indicates that all of the hydrogen atoms of $Al(OCH_2CCl_3)_3$ are equivalent, and hence, $Al(OCH_2CCl_3)_3$ is not associated. In methylene chloride, two singlets were observed at 4.32 ppm (a) and at 4.72 ppm (b). The integration ratio a/b is 2, which shows the association through alkoxy bridges; *i.e.*, the peak b is assigned to the protons of bridging trichloroethoxy groups and a to those of the terminal, nonbridging groups. Together with the results of molecular weight determination in methylene chloride, the following dimeric structure may be reasonably formulated.

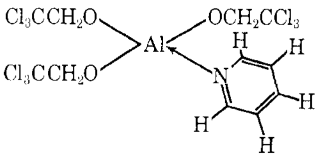


As will be discussed later, $Al(OCH_2CCl_3)_3$ is monomeric also in pyridine. The monomeric form of $Al(OCH_2CCl_3)_3$ in donor solvents of dioxane and pyridine is shown below where D is a donor solvent molecule.



These findings present a striking contrast with the association tendency of the usual aluminum alkoxides of unsubstituted alcohols. From molecular weight determination and nmr studies, Shiner, *et al.*,[2] found that usual aluminum alkoxides such as $Al[OCH(CH_3)_2]_3$ and $Al[OC(CH_3)_3]_3$ were in associated forms having the degrees of association of two and higher in various solvents including donor solvents such as dioxane. Reference experiments of the nmr spectrum in the present studies have also shown that $Al[OC(CH_3)_3]_3$ is associated in pyridine. The dissociation tendency of $Al(OCH_2CCl_3)_3$ may be due, at least partly, to the depressed nucleophilicity of the oxygen of the trichloroethoxy group caused by the three chlorine atoms having an electron-withdrawing effect, and thus oxygen does not compete successfully against the donor solvents.

An adduct of $Al(OCH_2CCl_3)_3$ and pyridine was isolated (see the Experimental Section), which was studied by nmr and infrared spectra. In the nmr spectrum a singlet (c) at 4.25 ppm and a set of multiplets (d) in the region of 7.5–9.0 ppm (protons of the pyridine ring) were observed. The integration ratio of c/d = 1.2 is consistent with the 1:1 complex



The formation of a donor–acceptor complex between $Al(OCH_2CCl_3)_3$ and pyridine has also been demonstrated by infrared spectral studies. In the infrared spectrum of a mixture of $Al(OCH_2CCl_3)_3$ and pyridine (1:1.5) in benzene (Figure 1), two absorptions at 1612 and 1580 cm^{-1} are observed, both of which can be assigned to $\nu_{C=N}$ of pyridine. $Al(OCH_2CCl_3)_3$ itself has no absorption in this region. The band at 1612 cm^{-1} may be assigned to $\nu_{C=N}$ of the complexed species of pyridine,[3] and the one at 1580 cm^{-1} to $\nu_{C=N}$ of free pyridine. The shift of $\nu_{C=N}$ of pyridine was not caused by the usual aluminum alkoxides of unsubstituted alcohols. These findings may be taken to indicate that $Al(OCH_2CCl_3)_3$ is a stronger Lewis acid in comparison with the usual aluminum alkoxides.

The acid strength of $Al(OCH_2CCl_3)_3$ was further examined by an infrared technique of Cook,[4] in which the shift of $\nu_{C=O}$ of xanthone caused by coordination to a Lewis acid was taken as a measure of acid strength (Table II). $Al(OCH_2CCl_3)_3$ is distinguished by the

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

[3] M. R. Basila, T. R. Kanter, and K. H. Rhee, *J. Phys. Chem.*, **68**, 3197 (1964).

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

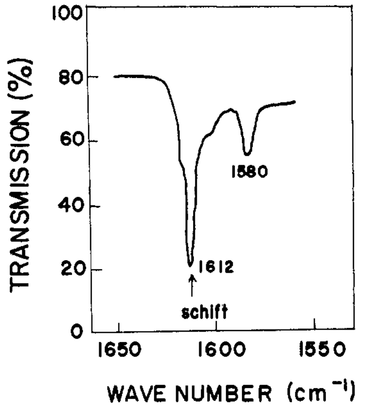

Figure 1.—Infrared spectrum of the aluminum 2,2,2-trichloroethoxide–pyridine (1:1.5) system in benzene.

TABLE II

ACID STRENGTHS OF VARIOUS ALUMINUM COMPOUNDS AND METAL HALIDES

Lewis acids	$\Delta\nu_{C-O}$ of xanthone, cm^{-1}
$Al(OCH_2CCl_3)_3$	90
$Al(OC_2H_5)_3$, $Al[OCH(CH_3)_2]_3$	0
$(C_2H_5)_2Al(OC_2H_5)$	0
$Al(C_2H_5)_3$	83[a]
$Al(C_2H_5)_2Cl$	104[a]
$Al(C_2H_5)Cl_2$	108[a]
$ZnCl_2$	57[b]
$FeCl_3$	141[b]
$SbCl_5$	253[b]

[a] From ref 5. [b] From ref 4.

magnitude of $\Delta\nu_{C=O}$ from the usual aluminum alkoxides $Al(OCH_2CH_3)_3$ and $Al[OCH(CH_3)_2]_3$. In Table II, the acid strength of $Al(OCH_2CCl_3)_3$ toward xanthone is also interestingly compared with the acid strength of $(C_2H_5)_2Al(OC_2H_5)$ and other alkylaluminum compounds[5] as well as metal halides.

This peculiar behavior of $Al(OCH_2CCl_3)_3$ as compared with that of the usual aluminum alkoxides may reasonably be explained as follows. The strong electron-withdrawing effect of trichloromethyl group decreases the basicity of the oxygen atom in the OCH_2CCl_3 group and enhances the accepting power of aluminum atom. The former effect of the trichloromethyl group facilitates the coordination of donor solvents to aluminum in preference to that of the oxygen in the OCH_2CCl_3 group of the neighboring $Al(OCH_2CCl_3)_3$ molecule. Therefore $Al(OCH_2CCl_3)_3$ dissociates in the presence of donor molecules, such as pyridine and dioxane, to the monomeric form. The increased Lewis acid strength of $Al(OCH_2CCl_3)_3$ over the usual aluminum alkoxides may be due to the latter effect of the trichloromethyl group. Coordination of reference bases such as xanthone and pyridine is thus realized by the dissociation of aluminum alkoxide and the increased Lewis acid strength of aluminum.

The strong Lewis acid character of $Al(OCH_2CCl_3)_3$ is linked with its catalytic feature for the polymerization of various monomers. Aluminum alkoxide has generally been known to be a coordinate anionic catalyst for the polymerization of aldehydes[6,7] and alkylene oxides.[8–10] Unlike the usual aluminum alkoxides, $Al(OCH_2CCl_3)_3$ induces the cationic polymerizations of vinyl ether, α-methylstyrene, tetrahydrofuran, 3,3-bis(chloromethyl)oxacyclobutane, and ethylene oxide.[11]

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(5) T. Saegusa, S. Matsumoto, and H. Imai, *Makromol. Chem.*, in press.

(6) J. Furukawa and T. Saegusa, "Polymerization of Aldehydes and Oxides," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 89–103.

(7) J. Furukawa, T. Saegusa, and H. Fujii, *Makromol. Chem.*, **44–46**, 398 (1961).

(8) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 690 (1956).

(9) M. Osgan and C. C. Price, *J. Polymer Sci.*, **34**, 153 (1959).

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

(11) T. Saegusa and T. Ueshima, to be presented at the 20th Annual Meeting of the Japan Chemical Society, Tokyo, 1967.