BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1694—1696 (1968)

Aluminum Silanolates Acid Strength and Polymerization Catalyst Activity

Takeo SAEGUSA, Takashi UESHIMA and Kunioki KATO

Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto

(Received January 24, 1968)

Two aluminum silanolates, diethyl(trimethylsiloxy)aluminum (I) and tris(trimethylsiloxy)-aluminum (II), were compared with the corresponding aluminum alcoholates in terms of their acid strength and in their catalyst behavior in the polymerizations of cyclic ethers and vinyl ether. The reference aluminum alcoholates were diethylaluminum *t*-butoxide (III) and aluminum *t*-butoxide (IV). The Lewis acid strength was examined by means of two methods, the Hammett indicator method and the shift of the IR carbonyl band ($\Delta\nu_{C=O}$) of *n*-butyraldehyde. Four aluminum compounds, I—IV, were weaker Lewis acids than triethylaluminum; *i. e.*, the replacement of the ethyl group of triethylaluminum with either a siloxy group or an alkoxy group brought about a decrease in the acid strength. The acid strength of I and II were demonstrated to be stronger than that of the reference alcoholates, III and IV. A difference in polymerization catalyst activity was also observed between aluminum silanolates and the reference alcoholates; it was reasonably explained by the difference in acid strength.

In a series of studies of metal alkyls and metal alcoholates as polymerization catalysts, we have reported that the triethylaluminum-trialkylsilanol system is an effective catalyst for the polymerizations of cyclic ethers such as tetrahydrofuran and epichlorohydrin, isobutyl vinyl ether and acetaldehyde.1)

The purpose of the present study is to examine the acid characters and the polymerization catalyst activities of two aluminum silanolates, diethyl-(trimethylsiloxy)aluminum (I) and tris(trimethylsiloxy)aluminum (II), in comparison with those of two reference aluminum alcoholates, diethylaluminum *t*-butoxide (III) and aluminum *t*-butoxide (IV).

A difference between II and IV in their catalytic behavior in the Tishchenko reaction has previously been reported.2)

Results and Discussion

Table 1 shows the results of the acid-strength measurements of aluminum silanolates and aluminum alcoholates as well as of triethylaluminum.

The acid strength was examined by two methods. The one was the Hammett indicator method,3,4) while the other was based upon the magnitude of the shift of the ir carbonyl band of *n*-butyraldehyde, which was adapted as the reference base. The indicator method showed that both aluminum silanolates and aluminum alcoholates were weaker Lewis acids than triethylaluminum. This acid-strength difference was also demonstrated by the ir technics; *i. e.*, triethylaluminum caused a shift of the ir carbonyl band of xanthone ($\Delta\nu_{C=O}$=83

---

1) T. Saegusa, T. Ueshima, T. Nakajima and J. Furukawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 2514 (1965).

2) T. Saegusa, S. Kitagawa and T. Ueshima, This Bulletin, **40**, 1960 (1967).

3) H. A. Benesi, *J. Am. Chem. Soc.*, **78**, 5490 (1956).

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

TABLE 1. ACID STRENGTH OF ALUMINUM SILANOLATES AND ALUMINUM ALCOHOLATES

	Indicators$^{a)}$ (pK_a value)						$\Delta\nu_{C=O}$(cm^{-1}) of n-butyraldehyde$^{b)}$
	I (+6.8)	II (+4.8)	III (+4.0)	IV (+3.3)	V (−3.0)	VI (−5.6)	
$Al(C_2H_5)_3$	—	A	A	A	A	B	
$(C_2H_5)_2AlOSi(CH_3)_3$ (I)	A	A	B	B	B	B	156
$(C_2H_5)_2AlOC(CH_3)_3$ (III)	A	A	B	B	B	B	147
$Al(OSi(CH_3)_3)_3$ (II)	A	A	B	B	B	B	147
$Al(OC(CH_3)_3)_3$ (IV)	B	B	B	B	B	B	140

a) Indicators: I = Neutral red; II = Methyl red; III = Phenylazonaphthylamine; IV = Butter yellow V = Dicinnamalacetone; VI = Benzalacetophenone. A; acidic color; B: basic color.

b) Error = ±3 cm^{-1}.

cm^{-1}), whereas two aluminum silanolates and two aluminum alcoholates did not. Thus, the replacement of the ethyl group of triethylaluminum by either a siloxy group or an alkoxy group decreased the acid strength. However, aluminum silanolates were stronger acids than the corresponding alcoholates. The magnitudes of the $\Delta\nu_{C=O}$ values of n-butyraldehyde caused by aluminum silanolates were higher than those caused by the reference aluminum alcoholates. This observation was partly supported by the indicator method; *i. e.,* II was acidic toward neutral red and methyl red, whereas IV was basic to these indicators. This acid-strength difference can not be explained by a simple consideration of electronegativity. From the electronegativities of carbon and silicon, the electron defınciency of aluminum alcoholates is considered to be higher than that of aluminum silanolates. Hence, the former might be expected to be stronger acids. However, the reverse is true in the present case. The stronger acid character of aluminum silanolates in comparison with the reference aluminum alcoholates may be due, at least in part, to the electron-withdrawing effect of the silicon atom through the d_π—p_π bond of the silicon-oxygen linkage.[5]

The catalyst activities of these aluminum compounds in the polymerizations of cyclic ethers and vinyl ether were interpreted in terms of their acid strength. The data of the ethylene oxide polymerization are summarized in Table 2, in which the polymer yield and the yield of the dioxane by-product, the cyclic dimer of ethylene oxide, are indicated. All four aluminum compounds induced the ethylene oxide polymerization. However, dioxane was formed only in the runs with aluminum silanolates catalysts. The dioxane formation is quite clear in the case of I, which implies the mechanism of cationic polymerization. In our mechanistic study[6] of the catalyst behavior of organoaluminum compound systems, we have established that the formation of dioxane as a by-product in the ethylene oxide polymerization is an indication of cationic polymerization.

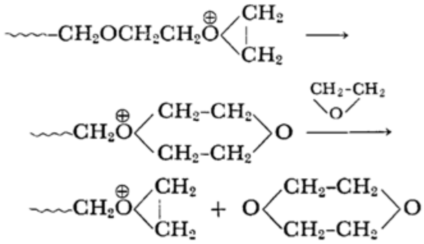

TABLE 2. POLYMERIZATION OF ETHYLENE OXIDE
(Monomer, 0.1 mol; catalyst, 2 mol%; bulk polymerization, at 55°C for 24 hr)

Catalyst	Polymer yield (%)	[η]$^{a)}$	Yield of dioxane (%)
$(C_2H_5)AlOSi(CH_3)_3$ (I)	13	0.62	5.8
$(C_2H_5)_2AlOC(CH_3)_3$ (III)	7	0.53	0
$Al(OSi(CH_3)_3)_3$ (II)	98	0.08	0.6
$Al(OC(CH_3)_3)_3$ (IV)	40	0.96	0

a) Measured in benzene at 30°C.

b) The limit of detection was 0.02%.

TABLE 3. POLYMERIZATIONS OF 3,3-BIS(CHLOROMETHYL)-OXACYCLOBUTANE (BCMO), TETRAHYDROFURAN (THF) AND ISOBUTYL VINYL ETHER (IBVE)
(Monomer, 0.1 mol; catalyst, 2 mol%; bulk polymerization, at 0°C for 24 hr)

Catalyst	Polymer yield		
	BCMO$^{a)}$	THF$^{a)}$	IBVE$^{b)}$
$(C_2H_5)_2AlOSi(CH_3)_3$ (I)	87	10	2
$(C_2H_5)_2AlOC(CH_3)_3$ (III)	2	0	0
$Al(OSi(CH_3)_3)_3$ (II)	—	3(7)$^{c)}$	77
$Al(OC(CH_3)_3)_3$ (IV)	—	0(0)	0

Cocatalyst: epichlorohydrin (2 mol%) for a)
$(CH_3)_3CCl$ (2 mol%) for b)

c) 40°C, 24 hr

---

[5] R. West and R. H. Baney, *J. Am. Chem. Soc.,* **81**, 1645 (1959).

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

Aluminum silanolates caused the polymerization of some cationically-polymerizable monomers, whereas the corresponding aluminum alcoholates did not do so (Table 3).

These cationic catalyst activities of aluminum silanolates correspond to their stronger Lewis-acid characters.

Experimental

All the experiments were conducted under a nitrogen atmosphere.

Reagents. *Monomers, Solvents and Cocatalysts.* All the reagents were carefully purified by the usual procedures.

Catalysts. I was prepared by a reaction between triethylaluminum and trimethylsilanol and was purified by fractional distillation; bp 103°C at 1.1 mmHg. II was synthesized according to the method reported in the literature.[7] III was prepared by the reaction of triethylaluminum with *t*-butanol which was sublimed at 90°C under reduced pressure (0.1 mmHg). IV was synthesized from *t*-butanol and aluminum foil and was purified, just prior to use, by being recrystallized from benzene five times. In the present study, it has been found that IV is not so stable and that it decomposed even at room temperature. The decomposition product, which was insoluble in hot benzene, was a stronger acid than IV. Therefore, it was necessary to purify IV by recrystallization just before use. Otherwise reliable results could not be obtained.

Others. Dioxane, methanol, and benzene were commercial reagents of a high purity and were used without further purification.

Acid-strength Measurements. The Hammett method was performed as has been described before.[4] The shifts of the carbonyl-stretching vibration of *n*-butyraldehyde were measured in Nujol.

Polymerization. Polymerization was performed in a sealed tube. The after-treatments of BCMO,[8] THF,[9] and IBVE[10] polymerization systems were the same as those described before.

In the ethylene oxide polymerization, the volatile matter was first evaporated from the reaction mixture at 80°C under reduced pressure (below 0.5 mmHg), and then analyzed by vpc for dioxane. A reference experiment showed that dioxane, if it was present in the polymerization mixture, could be detected and quantitatively analyzed by the above procedure. The evaporation residue was treated with a mixture of benzene and ammonia water and dried up. The polymer was then dissolved again in benzene. The catalyst precipitate was removed, and the polymer was recovered from the filtrate.

---

7) H. Schmidbaur, *Chem. Ber.*, **96**, 2696 (1963).

8) T. Saegusa, H. Imai and J. Furukawa, *Makromol. Chem.*, **65**, 224 (1963).

9) H. Imai, T. Saegusa, S. Matsumoto, T. Tadasa and J. Furukawa, *Makromol. Chem.*, **102**, 222 (1967).

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