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Reaction of Organoaluminum Coordination Compound with Carbon Dioxide

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The reaction of trialkylaluminum with carbon dioxide was suppressed by the presence of *N,N,N′,N′*-tetramethylethylenediamine, 2,2′-dipyridyl, *N*-methylimidazole (MIm), and diethyl ether. On the other hand, the insertion reaction of carbon dioxide into the Al–N bond of diethylaluminum diethylamide was accelerated by the presence of MIm, *N*-methylbenzimidazole, and pyridine. The complexing agents are considered to play two different roles, *i. e.*, affecting the nucleophilicity of Al–C or Al–N bond and the ability of aluminum atom to accomodate carbon dioxide.

We have studied the reaction of organozinc coordination compound with secondary amines,[1,2] acidic hydrocarbons,[3] and carbon dioxide.[4] In these reactions, the complexes of dialkylzinc with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), 2,2′-dipyridyl (Dipy), and *N*-methylimidazole (MIm) exhibit much enhanced reactivity when compared with dialkylzinc itself. The remarkable effect of MIm in the reaction with carbon dioxide was discussed in relation to the action of carbonic anhydrase, a zinc enzyme.[4]

Differently from dialkylzinc, trialkylaluminum is known to react readily with carbon dioxide at ordinary temperature and pressure.[5] In the present paper is reported the effect of the complex formation of organoaluminum compound with the above-mentioned complexing agents in the reaction toward carbon dioxide.

Results and Discussions

Reaction of Trialkylaluminum and Carbon Dioxide. The reaction of triisobutylaluminum with an atmos-

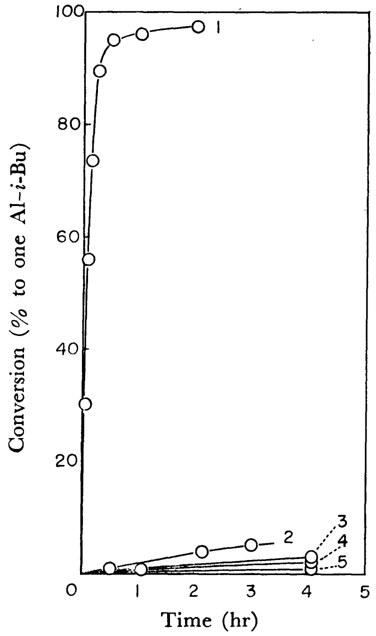

Fig. 1. Reaction of triisobutylaluminum and carbon dioxide, in toluene at 0°C.
[i-Bu$_3$Al]$_0$, 0.5 M; CO$_2$, 1 atm; complexing agent (molar ratio to Al):
1: none, 2: Dipy(1), 3: MIm(1), 4: TMEDA(1), 5: diethyl ether.

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[1] S. Inoue and T. Yamada, *J. Organometal. Chem.*, **25**, 1 (1970).

[2] S. Inoue and Y. Imanaka, *ibid.*, **35**, 1 (1972).

[3] S. Inoue and K. Furukawa, *ibid.*, **37**, 25 (1972).

[4] S. Inoue and Y. Yokoo, *ibid.*, **39**, 11 (1972).

[5] K. Ziegler, F. Krupp, K. Weyer, and W. Larbig, *Ann. Chem.*, **629**, 251 (1960); H. Lehmkuhl, *Angew. Chem.*, **76**, 817 (1964).

pheric pressure of carbon dioxide was examined at 0°C in toluene. As seen in Fig. 1, one of the isobutyl-aluminum linkages reacted rapidly and quantitatively with carbon dioxide, as determined by the absorption of carbon dioxide as well as by the formation of isovaleric acid. In the presence of an equimolar amount to triisobutylaluminum of TMEDA, Dipy, and MIm, the reaction was much suppressed, in contrast to the case of dialkylzinc. Even diethyl ether, which shows no effect on the reactivity of dialkylzinc, behaved similarly to TMEDA, etc. in the reaction of triisobutylaluminum.

When the reaction of triethylaluminum with carbon dioxide was carried out at 20°C, the absorption of carbon dioxide stopped at a quantity corresponding to 66% conversion of one ethyl-aluminum bond, and as the reaction products triethylcarbinol was detected together with propionic acid, indicating the fact that reaction (1) is accompanied by reactions (2) and (3).[5]

$$R_3Al + CO_2 \rightarrow RCOOAlR_2 \quad (1)$$

$$RCOOAlR_2 + R_3Al \rightarrow R_2CO + R_2AlOAlR_2 \quad (2)$$

$$R_2CO + R_3Al \rightarrow R_3COAlR_2 \quad (3)$$

In this case also, the absorption of carbon dioxide was much supperssed by the presence of TMEDA, MIm, diethyl ether; Dipy showed less suppressing effect.

Reaction of Diethylaluminum Diethylamide and Carbon Dioxide. As shown in Fig. 2, diethylaluminum diethylamide exhibited very low reactivity towards carbon dioxide even at 60°C. In the presence of some complexing agents, however, the absorption of carbon dioxide was accelerated, in contrast to the case of trialkylaluminum. In the infrared spectrum of the reaction mixture of diethylaluminum diethylamide–MIm (1 : 2) system with carbon dioxide, strong and broad IR bands were observed around 1490—1580 cm^{-1}, while diethylaluminum propionate shows corresponding band at 1550—1630 cm^{-1}. Upon acid hydrolysis of the reaction mixture, no propionic acid was detected. These facts indicate the formation of aluminum carbamate group, *i. e.*, the insertion of carbon dioxide to Al–N, but not to Al–C bond.

$$Et_2N\text{-}AlEt_2 + CO_2 \xrightarrow{\text{Complexing Agent}} Et_2N\text{-}COO\text{-}AlEt_2 \quad (4)$$

As seen in Fig. 2, aromatic monodentate complexing agents such as MIm, *N*-methylbenzimidazole, and pyridine were effective. Dipy exhibited only slight accelerating effect. The effect of MIm was very remarkable and the reaction took place readily even at 20°C. Furthermore, Al–N bond of diethylaluminum diethylamide reacted quantitatively with carbon dioxide even in the presence of a half mole ratio of MIm to the aluminum compound, indicating that MIm was effective as a catalyst (curve No. 9 of Fig. 2).

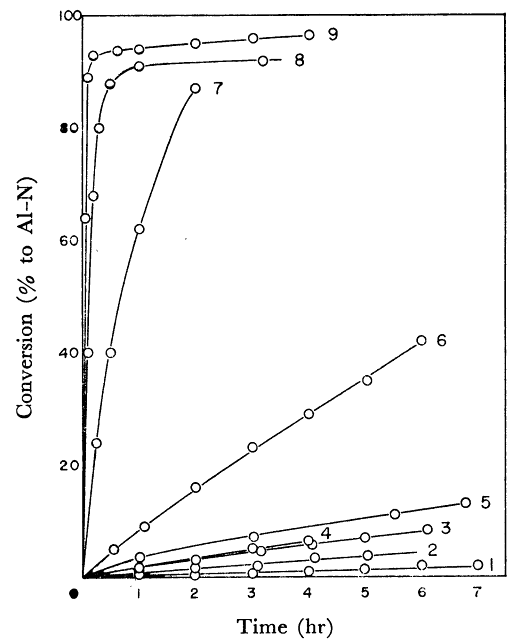

Fig. 2. Reaction of diethylaluminum diethylamide and carbon dioxide, in *p*-xylene at 60°C.
$[Et_2AlNEt_2]_0$, 0.5 M; CO_2, 1 atm; complexing agent (molar ratio to Al): 1: none, 2: tetrahydrofuran(2), 3: Dipy(1), 4: triethylamine(2), 5: TMEDA(1), 6: pyridine(2), 7: *N*-methylbenzimidazole(2), 8: MIm(2), 9: MIm(0.5).

Factors affecting the reactivity. Triethylaluminum is dimeric with Al–C bridges[6] while triisobutylaluminum is monomeric, and triethylaluminum is known to form complexes such as $Et_3Al \cdot Dipy$ (1 : 1),[7] $Et_3Al \cdot TMEDA$ (2 : 1),[7] and $Et_3Al \cdot O(C_2H_5)_2$ (1 : 1). Triisobutylaluminum probably forms similar complexes. Then the decrease in the reactivity of trialkylaluminum towards carbon dioxide in the presence of the complexing agents may be ascribed to low reactivity of such complexes. Although the nucleophilicity of C–Al linkage will be increased by the coordination with Lewis base, the coordination of the reacting carbon dioxide to the aluminum atom is considered to be hindered by the complex formation of trialkylaluminum. The reactivity is thus much lowered.

In this respect, apparently reverse effect of the complexing agents on the reactivity of diethylaluminum diethylamide is interesting. Diethylaluminum diethylamide exists in a dimeric form with Al–N bridges.[8] In the presence of some of the complexing agents, it will probably become monomeric by the complex formation. In this monomeric complex the nucleophilicity of Al–N bond, freed from the bridge, is further enhanced by the coordination with Lewis base. But, as in the case of trialkylaluminum, the coordination of the reacting carbon dioxide to the aluminum atom is considered unfavorable in the complex. However, the nuclophilicity of Al–N is much higher than Al–C bond, as exemplified by the fact that the reaction of diethylaluminum diethylamide with carbon dioxide took place at Al–N but not at Al–C linkage. Therefore, the nucleophilicity of Al–N bond is considered so much enhanced by the complex formation that the coordination of the reacting carbon dioxide is not important

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[6] K. S. Pitzer and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **68**, 2204 (1946).

[7] W. Brüser, K. H. Thiele, and H. K. Müller, *Z. Chem.* **2**, 342 (1962); G. E. Coates and K. Wade, "Organometallic Compounds," Vol. 1, Methuen, London (1967), p. 295.

[8] W. P. Neumann, *Ann. Chem.*, **667**, 1 (1963).

for the reactivity of diethylaluminum diethylamide in the presence of the complexing agent.

Thus, by the present study we may conclude that the complexing agents studied here play two different roles, *i. e.*, affecting the nucleophilicity of Al–C or Al–N bond and affecting the ability of Al atom to accommodate carbon dioxide. It should be noted here that the observed reactivity is also dependent on the stability of the complex, *i. e.*, the effective concentration of the complex.

The reverse effect of the complexing agents on the reactivity of trialkylaluminum and of dialkylzinc[4)] might be understood by different contribution of the above-mentioned factors in the Al and the Zn compounds. The contribution of *d*-orbitals (filled in Zn, but not in Al) might also be considered, but no conclusion may be made from the results so far obtained.

Experimental

Materials. Triethylaluminum was purified by distillation in a nitrogen atmosphere, bp 97°C/10 mmHg. Triisobutylaluminum was also purified by distillation, bp 86°C/10 mmHg. Diethylaluminum diethylamide[8)] was prepared by refluxing a *p*-xylene solution (200 m*l*) containing triethylaluminum (0.2 mol) and diethylamine (0.2 mol) for 6 hr. After the removal of *p*-xylene under reduced pressure, the product was obtained by distillation, bp 125°C/0.5 mmHg.

Carbon dioxide was purified by passing through a series of columns packed with cupric sulfate, potassium bicarbonate, reduced copper, phosphorus pentoxide, actived cupric oxide.

TMEDA was refluxed over calcium hydride and distilled, bp 121°C. Dipy was recrystallized from *n*-hexane, mp 69—70°C. MIm was prepared from imidazole, sodium and methyl iodide in liquid ammonia,[9)] bp 115°C/54 mmHg. *N*-methylbenzimidazole was prepared from benzimidazole (obtained by the reaction of *o*-phenylenediamine and formic acid[10)]) by the same method as MIm, mp 60°C. Pyridine and triethylamine were purified by distillation over barium oxide.

Benzene, toluene, *p*-xylene, diethyl ether, and tetrahydrofuran were purified by usual methods, refluxed over methallic sodium, and distilled.

Procedure. A mercury-sealed gas burette was connected with a 50 m*l* reaction flask by a three-way stopcock, the system was substituted by carbon dioxide, complexing agent and solvent was added, and the solution was saturated by carbon dioxide, The organoaluminum compound was added, and the absorption of carbon dioxide was followed by keeping the gas burette at the atmospheric pressure. The volume absorbed was corrected for temperature, atmospheric pressure and the partial pressure of the solvent. In order to determine carboxylic acid as the product, a definite amount of the reaction mixture was taken out, added by conc. hydrochloric acid, and subjected to gas chromatography using *p*-cymene as internal standard.

The authors wish to express their thanks to Professor Teiji Tsuruta for his valuable discussion.

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9) A. M. Roe, *J. Chem. Soc.*, **1963**, 2195.

10) E. C. Wagner and W. H. Millett, "Organic Syntheses", Coll. Vol. II, p. 65 (1955).