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Elementary Reactions of Metal Alkyl in Anionic Polymerization. VI.
The Synthesis and Reactivity of Calciumzinc Tetra-*n*-butyl

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According to the standard method proposed by Gilman,[1] calciumzinc tetraethyl ($CaZnEt_4$) is prepared in benzene by an interchange reaction between diethylzinc and metallic calcium. Diethyl ether cannot be used for the solvent, because it is too reactive, the calcium ate complex formed being decomposed by the ether.[2] Diethyl ether, on the other hand, has been found to be an appropriate solvent for the preparation of calciumzinc tetra-*n*-butyl ($CaZn(n\text{-}Bu)_4$).

Experimental

*Preparation and Analysis of Calciumzinc Tetra-*n*-butyl.* A mixture of 4.0g (0.10 atom) of calcium metal, 27 m*l* (0.155 mol) of $n\text{-}Bu_2Zn$, and 27 m*l* of diethyl ether was heated, under stirring, to 50—60°C (bath temperature), the temperature was maintained at that value for about 24hr. During the reaction a reddish suspension was produced. After 24hr, heating and stirring were stopped and the reaction mixture was allowed to stand at least one night. The supernatant layer was then taken out with a syringe and put into a 100-m*l* flask. Then the ether and the unreacted $n\text{-}Bu_2Zn$ were removed under reduced pressure. The yellow residue was washed with *n*-heptane several times and then freeze-dried from benzene. The residue was dissolved again into diethyl ether, and the calciumzinc tetra-*n*-butyl in the supernatant solution was analyzed by EDTA chelate titration, NMR, and vapor-phase chromatography (vpc). The tetrabutyl compound, unlike $CaZnEt_4$, cannot be prepared in benzene. The use of tetrahydrofuran as a solvent resulted in producing the ate compound in a lower yield. Dimethoxyethane and 1,4-dioxane could not be used as solvents because of their high reactivities toward the calcium compound.

*Analysis of Calciumzinc Tetra-*n*-butyl.* In EDTA chelate titration, the amount of zinc was determined by using xylenol orange (XO) as an indicator at pH 5.0—5.5 (CH_3COOH-CH_3COONa buffer solution).[3] The total amount of calcium plus zinc was determined by using Eriochrome Black T (EBT) as an indicator at pH 10.0 (NH_3-NH_4Cl buffer solution).[3] The results of the analyses are shown in Table 1. As is shown in Table 1, the ratio of calcium to zinc(1.05 ± 0.02), as well as that of *n*-butyl to metal (4.1 ± 0.1), is in accordance with the $CaZn(n\text{-}Bu)_4$ composition. A new triplet, observed in the vicinity of 9.8 τ in the NMR spectrum of Fig. 1, is assigned to the methylene signal of metal-CH_2- in the ate complex.

TABLE 1 EDTA AND VPC ANALYSES OF $CaZn(n\text{-}Bu)_4$

No	Ca/Zn	*n*-Butyl/Ca	*n*-Butyl/Zn
1	1.03	4.0	4.1
2	1.07	4.1	4.2

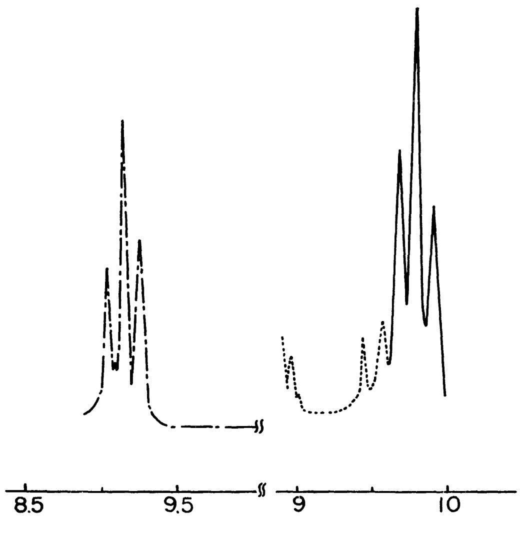

Fig. 1. NMR spectra of M-CH_2 in $Zn(n\text{-}Bu)_2$ and $CaZn(n\text{-}Bu)_4$. 60 MHz, room temperature.
Sample, 10 mol% of diethyl ether solution was used.
——$CaZn(n\text{-}Bu)_4$, ——$Zn(n\text{-}Bu)_2$, ----ether

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[1] H. Gilman and L. A. Woods, *J. Amer. Chem. Soc.*, **67**, 520 (1945).

[2] A. Isobe, H. Aoi, M. Ishimori, and T. Tsuruta, unpublished data.

[3] K. Ueno, "Chelate Titration," (in Japanese), Nankodo, Tokyo, (1960), p. 230, 241.

Table 2. Reaction of $CaZn(n\text{-}Bu)_4$ with CCl_4

Initial $CaZn(n\text{-}Bu)_4$	Recovered n-butane from supernatant (A)		Titrated metal in supernatant (A)		n-Butyl/Zn
	before drying-up	after drying-up	Zn	Ca	
0.390 mmol	0.787 mmol	0.784 mmol	0.389 mmol	0.0	2.0

Reaction with Carbon Tetrachloride. Di-n-butylzinc scarcely reacts with carbon tetrachloride. On the other hand, as is shown in Table 2, calciumzinc tetra-n-butyl, when reacted with exess CCl_4 to form white precipitates in diethyl ether, leaves di-n-butylzinc in the supernatant diethyl ether solution, (A), no calcium being detected by the EDTA chelate titration of the supernatant. Since n-butane corresponding to a half of the n-butyl groups of the $CaZn(n\text{-}Bu)_4$ used was recovered after the hydrolysis of the supernatant (A), the zinc alkyl component in $CaZn(n\text{-}Bu)_4$ was considered to survive in the supernatant without any reactions with carbon tetrachloride. This consideration was further supported by the following results: (i) The amount of the n-butane recovered by hydrolyzing the supernatant (A) after the "drying-up" procedure[4] was just the same as that of the n-butane recovered from (A) before the "drying-up" procedure.

(ii) The supernatant (A) polymerized methyl vinyl ketone (MVK) to give a stereoregular polymer. The behavior of (A) was in harmony with that of a zinc alkyl solution.[6]

(iii) Copolymerization between MVK and styrene initiated with (A) was shown to possess an anionic character in a way similar to the copolymerization initiated with zinc alkyl.

(iv) α,β-Unsaturated esters, *e.g.*, methyl methacrylate (MMA), were not polymerized by the supernatant (A). If the supernatant had contained a trace of calcium species, the unsaturated esters would have been polymerized anionically.

Judging from the data described above, $CaZn(n\text{-}Bu)_4$ seems to have an ate complex structure consisting of $Ca(n\text{-}Bu)_2$ and $Zn(n\text{-}Bu)_2$. Recently, a detailed report about the nature of the $MZnEt_4$, (in which M=Ca, Ba, and Sr) was published.[7] Another report concerning the structure of the ate complexes of the alkaline earth metals will be published elsewhere.[2]

Reaction with α,β-Unsaturated Ketones. The only elementary reaction of calciumzinc tetra-n-butyl with the saturated ketone or aldehyde is the hydrogen abstraction reaction. The calcium ate compound can virtually cause no carbonyl addition reaction, even with such a reactive carbonyl group as those of C_2H_5CHO, $C_2H_5COC_2H_5$, and CH_3COCH_3, as is shown in Table 3. The addition reaction would result in a decrease in the n-butane recovered before the "drying-up" procedure. When an α,β-unsaturated ketone was treated with $CaZn(n\text{-}Bu)_4$, no carbonyl addition products were detected, the elementary reactions between $CaZn(n\text{-}Bu)_4$ and α,β-unsaturated ketones presumably being conjugate addition and hydrogen abstraction reactions in the same way as is the case with $n\text{-}Bu_2Zn$.[5] When a diethyl ether solution of $CaZn(n\text{-}Bu)_4$ was added to MVK in diethyl ether (molar ratio 1 : 100), a rapid polymerization of MVK was observed, thus forming polymer precipitates. The supernatant (B) was found to contain neither MVK monomer nor any calcium compounds, the only species detected in (B) by EDTA chelate titration being zinc compound. When MVK was newly added to the supernatant (B), the polymerization of MVK was observed to take place, giving a stereoregular polymer.[6] MMA was not polymerized by the supernatant(B). The chemical behavior of the supernatant layer, (B), toward the α,β-unsaturated ketone and ester seems to coincide with the known chemical behavior of zinc alkyl. These observations showed that the calcium-alkyl part of $CaZn(n\text{-}Bu)_4$ reacted with MVK very rapidly, forming polymer precipitates, and that $n\text{-}Bu_2Zn$ was liberated in the supernatant layer, (B). The liberated $n\text{-}Bu_2Zn$ was reacted with MVK competitively with the calcium-alkyl part, though the reactivity of the former was much lower than that of the latter.

Table 3. Reaction of $CaZn(n\text{-}Bu)_4$ with carbonyl compounds[a]

Compound	Recovered n-butane from supernatant (B)	
	before drying-up[b] (%)	after drying-up[c] (%)
C_2H_5CHO	96	14
$C_2H_5COC_2H_5$	98	30
CH_3COCH_3	98	19
$CH_2{=}CHCOCH_3$	51	42
$CH_2{=}C(CH_3)COCH_3$	50	41[3]
$CH_3CH{=}CHCOCH_3$	75	5
$(CH_3)_2C{=}CHCOCH_3$	100	0

a) 30°C in Et_2O; $[CaZn(n\text{-}Bu)_4]$ 0.004 mol/l; [carbonyl compound] 0.40 mol/l; reaction time, 24 hr.

b) represents $100(1-\text{fraction of } n\text{-butyl group consumed in the addition reactions})$ %.

c) represents % of unreacted metal-n-butyl linkage.

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[4] By means of the "*drying-up*" procedure,[5] n-butane liberated from butylmetal is removed, while the unreacted butylmetal is left in the residue.

[6] T. Tsuruta, R. Fujio, and J. Furukawa, *Makromol. Chem.*, **80**, 172 (1964).

[7] F. Kaufmann, A. Geraudelle, B. Kaempf, F. Schue, A. Deluzarche, and A. Maillard, *J. Organometal. Chem.*, **24**, 13 (1970).

[5] Y.Kawakami, Y. Yasuda, and T. Tsuruta, *J. Macromol. Sci.-Chem.*, *A*3**(2)**, 205 (1969).