Chemistry

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Abstract

Full Text

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Slow Dissociation of Associates of Alkoxy and Alkyl Derivatives of Metals in Solutions

In previous publications ([1,2]) we reported a phenomenon that we had observed —the slow decomposition of associates of alkoxy derivatives of titanium in dilute benzene solutions (at constant solution concentration and constant temperature).

We have now established that this phenomenon also occurs in solutions of organic compounds of other classes. It turned out that the degree of association in solutions of alkoxy derivatives of tin, zirconium, and aluminum, as shown by cryoscopic determinations, decreases with time and after several hours reaches unity.

Figure 1 presents curves for the change with time in the molecular-weight values of $(n\text{-}C_3H_7O)_4Sn$ in benzene solution at a concentration of 0.100 mole % (curve 1), and an analogous curve for $(n\text{-}C_4H_9O)_4Zr$ (benzene-solution concentration 0.161 mole %) (curve 2).

Tetra-*n*-propoxytin was obtained by the interaction ([3]) of tin tetrachloride with *n*-propyl alcohol in the presence of ammonia. The product was recrystallized from a mixture of hexane and benzene.

Found, %: C 39.73; 39.65; H 7.69; 7.74*
$Sn(OC_3H_7)_4$. Calculated, %: C 40.59; H 7.95

Tetra-*n*-propoxytin is a wax-like mass that decomposes ([4]) on distillation in a vacuum of 0.03 mm. Tetra-*n*-butoxyzirconium was obtained ([5]) by the action of *n*-butyl alcohol on zirconium tetraacetylacetonate. The product was purified by distillation at $1.5 \cdot 10^{-3}$ mm.

Found, %: C 49.81; 49.80; H 9.36; 9.29; Zr 23.91; 23.60
$(C_4H_9O)_4Zr$. Calculated, %: C 49.65; H 9.46; Zr 23.79

Figure 2 presents curves showing the change with time in the molecular-weight values of $(iso\text{-}C_4H_9)_2AlOC_2H_5$ in benzene solution at a concentration of 0.099 mole % (curve 1), and analogous curves for $(n\text{-}C_3H_7O)_3Al$ (benzene-solution concentration 0.112 mole %, curve 2) and for $(iso\text{-}C_4H_9O)_3Al$ (benzene-solution concentration 0.109 mole %, curve 3).

Fig. 1

Figure 1: Fig. 1

Diisobutylethoxyaluminum was obtained by the action of ethyl alcohol on triisobutylaluminum (^{6}).

Found, %: C 64.40; 64.49; H 12.40; 12.39; Al 14.42; 14.69
$(C_4H_9)_2AlOC_2H_5$. Calculated, %: C 64.48; H 12.45; Al 14.48

B.p. 125-126° at 2 mm. Literature data (^{7}): 110-114° at 1 mm.

Tri-*n*-propoxyaluminum was obtained by the action of aluminum on *n*-propyl alcohol.

Found, %: Al 13.30; 13.63
$(C_3H_7O)_3Al$. Calculated, %: Al 13.21

* The sample was kindly provided to us by R. Kh. Freidlina and E. M. Brainina.

M.p. 105-106°. Literature data (8): m.p. 106°.

Triisobutoxyaluminum was obtained by the action of aluminum on isobutyl alcohol.

Found, %:	C 58.05; 58.08;	H 10.94; 11.02;	Al 10.96; 11.35
$(C_4H_9O)_3Al$. Calculated, %:	C 58.51;	H 11.05;	Al 10.95

B.p. 247° at 12 mm. Literature data (8): b.p. 250° at 12 mm.

It is known that trimethylaluminum is dimeric (9–19) in vapors and solutions. The dimeric character of triethylaluminum (9,15,18,19) in solutions has also been shown. Dimeric molecules of trialkyl derivatives of gallium (18) and dialkyl derivatives of beryllium (18,20) are known. This dimerization, as established by a number of authors (11–14,16), is due to the alkyl-bridged three-center structure of these organometallic compounds. It is therefore very interesting that the slow decomposition of associates occurs not only in the case of alkoxy derivatives of metals, but also in the case of their alkyl derivatives, which we observed in the example of alkyl derivatives of aluminum. Indeed, the dimer of triethylaluminum slowly dissociates to the monomer stage in dilute benzene solutions at constant concentration and temperature of the solution.

Fig. 1

Figure 3 shows a curve illustrating the change with time in the molecular-weight values of $(C_2H_5)_3Al$ in a benzene solution of concentration 0.100 mol. %.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 2

The synthesis and determination of the molecular weight of triethylaluminum were carried out in an atmosphere of pure dry argon. The triethylaluminum was obtained by us by the act—

ethyl bromide with aluminum and then by symmetrizing the resulting sesquibromide with sodium [6].

Found, %:	C 63.56; 63.32;	H 13.57; 13.33;	Al 23.62; 23.46
$Al(C_2H_5)_3$. Calculated, %:	C 63.13;	H 13.24;	Al 23.63

B.p. 66—68°/0.5—1 mm.

Associates whose formation is due to hydrogen bonds, according to our observations, do not undergo slow dissociation in solutions. The value of the molecular weight of acetic acid (corresponding to the dimer) in a benzene solution of concentration 0.397 mole % remains unchanged during prolonged standing (23 hours). We observed the same in the case of phenol (concentration of the benzene solution 0.208 mole %).

Fig. 3

We also followed the course of dissociation of associated alkoxy derivatives of titanium in oxygen-containing solvents—dioxane and nitrobenzene—as well as in cyclohexane. It turned out that the slow decomposition of associates can be observed in these solvents as well, but, as was to be expected, dissociation in dioxane and nitrobenzene proceeds much faster than in benzene.

Fig. 4

Figure 4 gives curve 1 for the change with time of the molecular-weight values of $(n\text{-}C_4H_9O)_4Ti$ in nitrobenzene solution (concentration 0.107 mole %), curve 2, showing the change with time of the molecular-weight values of $(n\text{-}C_3H_7O)_4Ti$ in dioxane solution (concentration

Fig. 4

Figure 4: Fig. 4

0.254 mole % (we used a dioxane solution of $(n\text{-}C_3H_7O)_4Ti$ of this concentration, since at a concentration of 0.1 mole %, usually used by us, tetrapropoxytitanium, owing to the presence of the "dioxane effect," was not associated), and curve 3 for the change with time in the molecular-weight values of tetra-*n*-propoxytitanium in cyclohexane solution (concentration 0.105 mole %).

Tetra-*n*-butoxytitanium was obtained by the reaction of *n*-butyl alcohol with titanium tetrachloride in the presence of ammonia (^{21}). B.p. 161-162° at 2 mm, n_D^{20} 1.4910. Literature data: b.p. 160-162° at 2 mm (^{22}), n_D^{20} 1.4910 (^{23}).

Tetra-*n*-propoxytitanium was obtained by the same method (^{21}). B.p. 138° at 1.5 mm, n_D^{20} 1.4982. Literature data (^{23}): b.p. 135-136° at 1 mm, n_D^{20} 1.4979.

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