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Reactions of Tris(acetylacetonato)manganese(III) and -cobalt(III) with 1,10-Phenanthroline and α-Methylstyrene

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Synopsis. Lower-valence-state compounds, bis(acetylacetonato)manganese(II) and bis(acetylacetonato)(1,10-phenanthroline)manganese(II), were prepared from tris(acetylacetonato)manganese(III). ESR spectra of manganese(II) compounds were shown. Bis(acetylacetonato)(1,10-phenanthroline)Co(II) was also prepared. The results were compared with activity for the initiation of radical polymerization.

In the course of studying the initiation reaction of radical polymerization by tris(acetylacetonato)manganese(III), Mn(acac)$_3$, and tris(acetylacetonato)cobalt(III), Co(acac)$_3$, the present author has found that these chelates react with α-methylstyrene and 1,10-phenanthroline to give anhydrous crystalline bis(acetylacetonato)manganese(II), Mn(acac)$_2$, bis(acetylacetonato) (1,10-phenanthroline)manganese(II), Mn(acac)$_2$-phen, and bis(acetylacetonato)(1,10-phenanthroline)-cobalt(II), Co(acac)$_2$phen.

The kinetic data of the polymerization can be explained by assuming that Mn(acac)$_3$ dissociats into Mn(acac)$_2$ and an acetylacetonyl radical on heating, and that Mn(acac)$_2$ and the acetylacetonyl radical recombine in the absence of a radical scavenger such as a vinyl monomer.[1] Bamford and Ferrar found that Mn(acac)$_3$/amine systes were much more active than Mn(acac)$_3$ and proposed a ligand-exchange mechanism.[2] In fact, Nishikawa, Nakanuma, and Kawaguchi obtained heterochelates of Mn(acac)$_2$ with primary amines from Mn(acac)$_3$ and Mn(acac)$_2$(H$_2$O)$_2$.[3] It was reported in previous papers that 1,10-phenanthroline accelerated the elimination of the acetylacetonyl radical from Mn(acac)$_3$.[4,5] In the present investigation, the effects of α-methylstyrene and 1,10-phenanthroline have been examined and discussed in connection with the activity of the initiation of radical polymerization.

A concentrated Mn(acac)$_3$ solution was heated in the presence of a radical scavenger, α-methylstyrene, which was not polymerized to a high polymer above room temperature. Crystalline Mn(acac)$_2$ was thus obtained in a high yield. This crystal remained anhydrous over a month under atmospheric conditions. Figure 1 shows its unique ESR spectrum. Its solution in pyridine gives a spectrum of six lines, as is shown in Fig. 2, although their separations are insufficient. They agree with the nuclear spin of Mn 5/2. These spectra may rise from the paramagnetic Mn(II) ion, which has a long relaxation time. Crystalline Mn(acac)$_2$ was also obtained in the presence of cyclohexanone. The Mn(acac)$_2$ gives the same ESR spectra as those shown in Figs. 1 and 2.

The reaction of Mn(acac)$_3$ with 1,10-phenanthroline resulted in the formation of heterochelate, Mn(acac)$_2$-phen, in a high yield. The chelate gives a symmetrical ESR spectrum, as is shown in Fig. 3. Its solution in pyridine gives the same spectrum as that shown in Fig. 2.

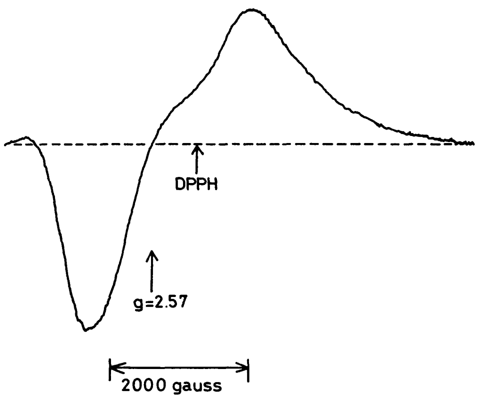

Fig. 1. ESR spectrum of Mn(acac)$_2$.

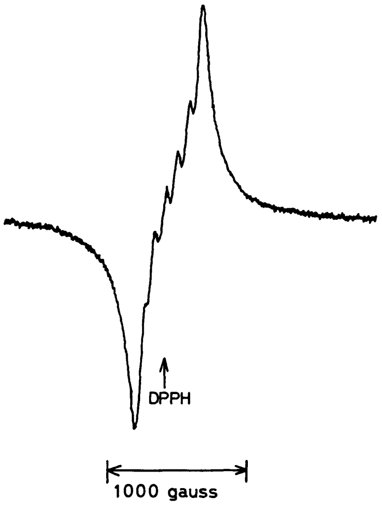

Fig. 2. ESR spectrum of Mn(acac)$_2$ solution in pyridine.
$g = 2.0$

When a benzene solution of Mn(acac)$_3$ was heated without any such additives as α-methylstyrene, cyclohexanone, and 1,10-phenanthroline, no evidence of Mn(acac)$_2$ was obtained.

Co(acac)$_2$ could not be prepared from Co(acac)$_3$ in the presence of α-methylstyrene, but Co(acac)$_2$phen was obtained after the long heating of Co(acac)$_3$ in the presence of both α-methylstyrene and 1,10-phenanthroline. Although chromium and iron have the same two oxidation states as manganese and cobalt, it was impossible to get lower-valence-state chelates from their higher homologs.

Mn(acac)$_3$ is the most active for the initiation of radical polymerization, Co(acac)$_3$ is the second most

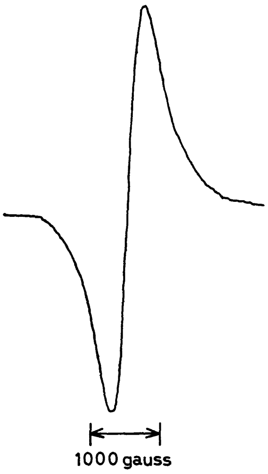

Fig. 3. ESR spectrum of 1,10-phenanthroline Mn(acac)$_2$. $g = 2.0$

active, and Fe(acac)$_3$ and Cr(acac)$_3$ are inactive.[5] The same order of activity is observed in the present preparation of lower-valence-state compounds.

Experimental

A solution of 750 mg of Mn(acac)$_3$ in 5 ml of benzene and 5 ml of α-methylstyrene was heated for 40 hr at 70 °C under a high vacuum in a sealed tube. A yellow precipitate was thus separated. The solution was cooled to room temperature, and then the precipitate was collected on a sintered glass filter, washed with a small portion of benzene, and dried. Yield, 452 mg (84%). Found: C, 47.35; H, 5.35%. Calcd for $MnC_{10}H_{14}O_4$: C, 47.44; H, 5.57%.

Instead of α-methylstyrene, a 5 ml portion of cyclohexanone was used. The same procedure as that described above gave a yield of 231 mg (43%). Found: C, 48.34; H, 5.34%.

In 10 ml of benzene were heated 750 mg of Mn(acac)$_3$ (2.13×10^{-3} mol) and 422 mg of 1,10-phenanthroline (2.13×10^{-3} mol) for 22 hr at 70 °C. A yellow precipitate was thus obtained. Yield, 848 mg (92%). Found: C, 61.89; H, 4.68; N, 6.18%. Calcd for $MnC_{10}H_{14}O_4\cdot C_{12}H_8N_2$: C, 60.97; H, 5.11; N, 6.47%.

A solution of 1.0 g of Co(acac)$_3$ and 587 mg of 1,10-phenanthroline in 5 ml of benzene and 5 ml of α-methylstyrene was heated for 5 days at 70 °C. Co(acac)$_2$ phen was thus precipitated from the solution. Yield, 717 mg (58.4%). Found: C, 60.53; H, 4.75; N, 6.85%. Calcd for $CoC_{10}H_{14}O_4\cdot C_{12}H_8N_2$: C, 60.42; H, 5.07; N, 6.41%.

ESR measurements were made on samples in a capillary by using the JES-3BS-X apparatus of the Japan Electron Optics Laboratory. The frequency of the microwave was around 9450 Mc.

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