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The Effects of Additives on the Chemical Behavior of ^{60}Co Recoil Species in Neutron-irradiated Benzene Solutions of Tris(acetylacetonato)cobalt(III)

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In the course of our investigation of the behavior of recoil species in organic solutions of metal chelate complexes, we found that some metal salts could work as effective scavengers to suppress thermal reactions and thus minimize the apparent retention in the irradiated solutions as well as in solutions of the irradiated solids.[1–4] While the use of such metal salts as scavengers has proved to be a very useful technique for studying recoil reactions in solutions or solids, the detailed mechanism of the scavenging reactions has not yet been fully clarified. Accordingly, we have further investigated the effects of additives other than metal salts on the reactions of recoil species in irradiated organic solutions of metal complexes.

In the present article, a probable mechansim of the scavenging effect by metal salts is proposed on the basis of our recently obtained data concerning the change in the ^{60}Co retention with the time in irradiated Co(acac)$_3$ benzene solutions containing metal acetylacetonates as additives.

Experimental

The 0.2 M solutions of Co(acac)$_3$ in benzene containing 10% (by volume) of ethanol and small quantities of additives, such as metal acetylacetonates, metal chlorides and acetylacetone, were prepared by procedures similar to those described previously.[2] About 1-m*l* portions of Co(acac)$_3$ benzene solutions containing various additives were irradiated with slow neutrons for 5 min at room temperature in the rotary specimen rack of a TRIGA Mark II reactor at Rikkyo University (thermal neutron flux: 5×10^{11} n/cm^2·sec; γ dose: 7×10^4 R for 5 min). After the irradiated solutions had been kept standing for a desired length of time at room temperature, chemical separation was performed by means of a solvent-extraction method described previously.[2] The ^{60}Co retention, or the radiochemical yield of the parent chemical form, ^{60}Co(acac)$_3$, was obtained as the percentage of the total ^{60}Co activity found in the organic phase after the solvent extraction.

Results and Discussion

Figure 1 illustrates the change in the apparent ^{60}Co retention with the time after the irradiation of the Co(acac)$_3$ benzene solutions containing metal acetylacetonates and other additives. The ^{60}Co retention remains unchanged even after a solution has stood 7 days in the presence of ferric chloride as an additive, while it increases appreciably when the solution stands in the presence of magnesium chloride. It is worth mentioning that as additives both Ni(acac)$_2$·2H$_2$O and Mg(acac)$_2$ (3×10^{-3} M) enhance the increase in the ^{60}Co retention remarkably, as compared with the retention curve in the absence of an additive, whereas Fe(acac)$_3$ has practically no effect as an additive. It appears that the transfer of the ligand acetylacetonate ion from the less stable metal acetyl-

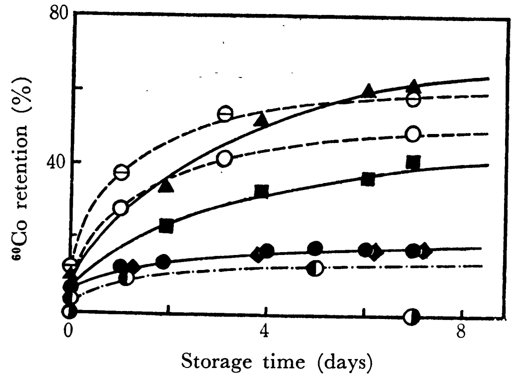

Fig. 1. ^{60}Co retention in the irradiated 0.2 M solutions of Co(acac)$_3$ in benzene containing 10% of ethanol and various additives.

—●—: No additive; —◑—: 2×10^{-3} M FeCl$_3$·6H$_2$O; ···◐···: 2×10^{-3} M MgCl$_2$·6H$_2$O; —◆—: 3×10^{-3} M Fe(acac)$_3$; —■—: 3×10^{-3} M Ni(acac)$_2$·2H$_2$O; —▲—: 3×10^{-3} M Mg(acac)$_2$; --⊖--: 10^{-2} M acetylacetone; --○--: 2×10^{-3} M acetylacetone.

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[1] T. Tominaga and K. Fujiwara, This Bulletin, **43**, 2279 (1970).

[2] T. Tominaga, T. Sakai, and K. Fujiwara, *ibid.*, **44**, 3036 (1971).

[3] T. Tominaga and Y. Nishi, *Radiochem. Radioanal. Lett.*, **8**, 151 (1971).

[4] T. Tominaga and T. Sakai, This Bulletin, **45**, 1237 (1972).

acetonates (*i. e.*, $Mg(acac)_2$ and $Ni(acac)_2 \cdot 2H_2O$) to the ligand-deficient ^{60}Co recoil species mainly contributes to the increase in the ^{60}Co retention in the presence of such metal acetylacetonates as additives. Similar effects were observed when the irradiated solid $Co(acac)_3$ was dissolved in benzene containing such additives and the mixture was then kept standing.

As is shown in Fig. 2, the scavenging power (percentage of the thermal reactions scavenged by an equal molar concentration of a scavenger) of metal salts measured within a few hours after irradiation[2] and after 7 days' standing apparently correlates well with the thermodynamic stability constants[5] of their acetylacetonates. Based on the present results, the mechanism of the overall phenomenon (apparent scavenger effect) may be explained in terms of the following reactions:

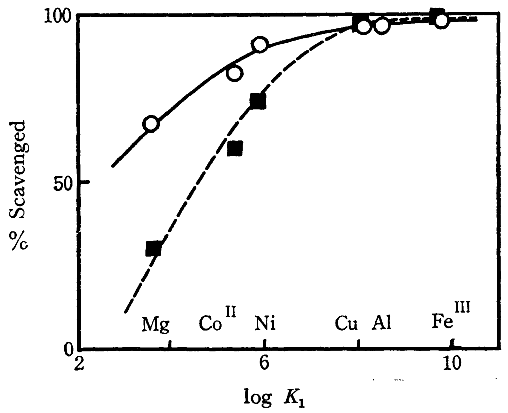

Fig. 2. Correlation of scavenging powers of various metal salts (2×10^{-3} M) with the thermodynamic stability constants of their acetylacetonates.
—○—: Separated within a few hours after irradiation;
--■--: Separated after 7 days.

(1) Recombination. $[^{60}Co(acac)_{3-x}] + acac^- \longrightarrow {}^{60}Co(acac)_3$

(2) Scavenging reaction. $MX_n + acac^- \longrightarrow M(acac)_n$

(3) Ligand transfer. $[^{60}Co(acac)_{3-x}] + M(acac)_n \longrightarrow {}^{60}Co(acac)_3 + M(acac)_m \quad (n > m)$

where $[^{60}Co(acac)_{3-x}]$ denotes the ligand-deficient ^{60}Co recoil species ($x = 1$, 2, or 3; cationic) and MX_n, scavenger salt. In the period immediately after irradiation, the competition between (1) and (2) is important, whereas the (3) reaction may still be relatively unimportant. The competition between (1) and (2) predominantly favors (2), and the correlation curve in Fig. 2 should closely approach the 100%-scavenged level for most of the metal salts investigated if the irradiation and storage periods become as brief as possible. If the (3) reaction gradually proceeds between the unreacted ligand-deficient ^{60}Co recoil species and $M(acac)_n$ remaining in the system,[6] the ^{60}Co retention increases, and the apparent scavenging power decreases, on standing. Hence, the corresponding plot-point on the correlation curve may be lowered from the 100%-scavenged level by a magnitude equivalent to the contribution of (3). Accordingly, the correlation between the apparent scavenging power and the stability constant may be explained by presuming that the extent of the (3) reaction reached after a solution has stood for a sufficiently long time depends mainly upon the stability of the metal acetylacetonate relative to $Co(acac)_3$. The present results on the effect of acetylacetonates of Fe, Ni, and Mg (Fig. 1) indicate that the extent of such a reaction actually increases with the decreasing stability of the acetylacetonates. Very similar results were obtained with irradiated $Cr(acac)_3$ benzene solutions.[7]

In conclusion, the scavenging effect of the salts of metals which can form more stable acetylacetonates may be ascribed mainly to the competition between the recombination (1) and the scavenging reactoin (2) to capture acetylacetone. For the salts of metals which form less stable acetylacetonates, however, the ligand transfer (3) may proceed appreciably on standing and may apparently diminish the overall scavenging effect.

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[5] R. M. Izatt, C. G. Haas, Jr., B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, **58**, 1133 (1954); R. M. Izatt, W. C. Fernelius, and R. P. Block, *ibid.*, **59**, 80 (1955); R. M. Izatt, W. C. Fernelius, C. G. Haas, Jr., and B. P. Block, *ibid.*, **59**, 170 (1955).

[6] Although the decomposition of the parent complex was spectrophotometrically found to be almost negligible even after standing, the irradiated solutions might contain very small amounts (10^{-4}—10^{-3} M) of free acetylacetone (as radiolytic product or impurity), from which resulted $M(acac)_n$.

[7] T. Tominaga and Y. Nishi, *Radiochem. Radioanal. Lett.*, in press.